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Performance and Durability Assessment of Anode Oxygen Evolution Reaction (Co-)Catalysts for PEM Fuel Cells and PEM Water Electrolyzers

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Abstract

While oxygen evolution reaction (OER) catalysts play a key role in the development of proton exchange membrane water electrolyzers (PEMWEs), their application as anode co-catalysts to mitigate the damages caused by H₂-starvation in proton exchange membrane fuel cells (PEMFCs) has also attracted great attention. This PhD thesis aims to improve the assessment of anode OER (co-)catalysts with regards to their performance and durability in PEMFC and PEMWE applications.

The OER catalyst activity and stability measurements will be investigated using the rotating disk electrode (RDE) technique and membrane electrode assemblies (MEAs) in a single-cell PEMWE. While OER activity measurements by RDE result in comparable activity values to those measured in an MEA in a PEMWE, RDE measurements are not reliable for OER catalyst lifetime estimation, due to the artefact caused by the accumulation of microscopic oxygen bubbles in/on the catalyst layer.

Subsequently, the degradation mechanism of an IrO₂ anode co-catalyst under transient operation conditions of a PEMFC will be elaborated. It will be shown that the origin of this degradation is the chemical reduction of the OER co-catalysts by H₂ in the PEMFC anode environment, and that a reduction resistant catalyst would be required to prevent this degradation. The preparation of such irreducible OER catalysts is also subject of this thesis. Two unprecedented approaches to produce irreducible OER catalysts will be introduced: i) preparation of irreducible IrO₂ by a heat treatment approach; and ii) preparation of irreducible IrO₂- and RuO₂-based catalysts by a solid solution

approach. The advantages and limitations of these new types of OER catalysts will be discussed.

Kurzfassung

Katalysatoren für die Sauerstoffentwicklungsreaktion (OER) sind in der Protonenaustauschmembran-Wasserelektrolyse (PEMWE) unabdingbar, jedoch gewinnt auch deren Anwendung als anodenseitige (Co-)Katalysatoren in Protonenaustauschmembran-Brennstoffzellen (PEMFCs) an Bedeutung, wo sie zur Vermeidung von Schäden durch H_2 -Verarmung eingesetzt werden. In dieser Dissertation soll die anwendungsnahe Evaluierung solcher OER-Co-Katalysatoren im Hinblick auf deren Leistungsfähigkeit und Langlebigkeit in PEMFC und PEMWE verbessert werden.

Zunächst werden Aktivität und Stabilität der OER-Katalysatoren mittels rotierender Scheibenelektroden (RDE) Messungen sowie mittels Messungen an Membran-Elektroden-Einheiten (MEA) in PEMWE Einzellern untersucht. Während OER-Aktivitätsbestimmungen via RDE und MEA Messungen übereinstimmende Ergebnisse liefern, sind Abschätzungen der Lebensdauer von OER-Katalysatoren auf der Basis von RDE Messungen nicht verlässlich. Die Ansammlung von mikroskopischen Sauerstoffbläschen in der Katalysatorschicht und auf deren Oberfläche führt hier zu Messartefakten, die eine verkürzte Lebensdauer suggerieren.

Weiterhin werden die Degradationsmechanismen eines IrO_2 Co-Katalysators in einer PEMFC bei transienter Betriebsführung beleuchtet. Die Degradation wird dabei auf die chemische Reduktion des OER-Co-Katalysators durch H_2 in der Brennstoffzellen-Anode zurückgeführt. Zur Vermeidung dieser Degradation wäre folglich ein reduktionsbeständiger OER-Katalysators erforderlich. Die Herstellung solch nicht-reduzierbarer OER-Katalysatoren stellt ein weiteres Ziel

dieser Dissertation dar und wird mithilfe zweier neuartiger Synthesestrategien verfolgt: Dies ist zum einen die Herstellung von nicht-reduzierbarem IrO_2 durch gezielte Temperaturbehandlung, zum anderen die Synthese von IrO_2 - und RuO_2 -basierten Katalysatoren über einen Mischkristall-Ansatz. Vorzüge und Limitierungen dieser neuartigen Klasse von OER-Katalysatoren werden ausführlich diskutiert.

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List of Abbreviations

Abbreviation	Description
AEM	Adsorbate Evolution Mechanism
ATO	Antimony Doped Tin Oxide
BET	Brunauer-Emmet-Teller
BPP	Bipolar Plate
CCM	Catalyst Coated Membrane
CE	Counter Electrode
COR	Carbon Oxidation Reaction
CV	Cyclic Voltammetry
ECSA	Electrochemically Active Surface Area
EIS	Electrochemical Impedance Spectroscopy
FF	Flow Field
FTO	Fluorine Doped Tin Oxide
GDL	Gas Diffusion Layer
HDPE	High Density Polyethylene
HER	Hydrogen Evolution Reaction
HOR	Hydrogen Oxidation Reaction
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
IR	Infrared
ITO	Indium Tin Oxide
LOM	Lattice Oxygen Mechanism
MEA	Membrane Electrode Assembly
OCV	Open Circuit Voltage
OER	Oxygen Evolution Reaction
ORR	Oxygen Reduction Reaction

PEMFC	Proton Exchange Membrane Fuel Cell
PEMWE	Proton Exchange Membrane Water Electrolyzer
PFSA	Perfluorosulfonic Acid
PGM	Platinum Group Metal
PTFE	Polytetrafluoroethylene
PTL	Porous Transport Layer
R(R)DE	Rotating (Ring) Disk Electrode
RE	Reference Electrode
rf	Roughness Factor
RH	Relative Humidity
RHE	Reversible Hydrogen Electrode
RTA	Reversal Tolerant Anode
SFC	Scanning Flow Cell
SUSD	Start-Up/Shut-Down
TEM	Transmission Electron Microscopy
TGA	Thermogravimetric Analysis
WE	Working Electrode
XPD	X-ray Powder Diffraction
XPS	X-ray Photoelectron Spectroscopy

1 Introduction

After overcoming the COVID-19 pandemic between 2019-2022, the impact of greenhouse gas emissions on global warming remains again the topmost priority that humankind has to tackle with.¹ Since most of the global energy demand over the last decades has been met by burning fossil fuels, carbon dioxide (CO₂) emissions have increased accordingly.² As a consequence, the average global temperature has been substantially increasing since 1980, with last year (2023) being the warmest year since modern recordkeeping began in 1880.^{3, 4} As an effort to address these problems, the 2015 Paris Agreement set a goal to keep the global temperature rise below 2 °C within this century compared to its pre-industrial level, and to take efforts to even more strictly limit the temperature increase to 1.5 °C.⁵ Here, the necessity of a transition to carbon-neutral power production is undeniable, whereby hydrogen can play a central role to serve as a flexible and on-demand energy carrier, so that hydrogen can be considered as an alternative energy storage and supply medium for the long term.⁶ In this context, the main focus is the electrochemical production and conversion of hydrogen according to eq. 1.1. Water electrolyzers powered with renewable electricity produce CO₂ emission-free hydrogen (green hydrogen) while fuel cells convert the chemical energy stored in hydrogen to electricity for stationary applications or for the propulsion of fuel cell driven vehicles in the mobility sector.



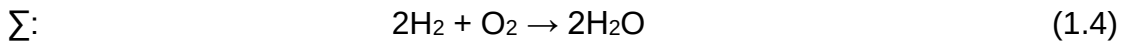
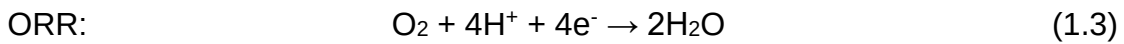
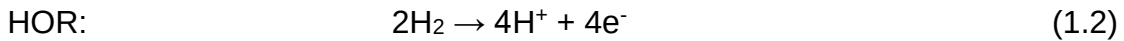
There are several types of fuel cell and electrolyzer technologies, and the choice between these technologies depends mainly on the targeted application and the operational conditions. Low temperature proton exchange membrane fuel cells

(PEMFCs) and proton exchange membrane water electrolyzers (PEMWEs) are promising technologies, which have attracted great attention in the last years. While PEMFCs have proven their market readiness for the production of fuel cell-powered passenger vehicles with a long driving range^{7, 8} (e.g., up to 650 km for the Toyota Mirai 2nd Generation⁹), PEMWEs have become suitable candidates to be integrated with renewable energy sources (solar and wind) due to their high power density, compact size, and flexible operation range.¹⁰ The benefit of operating at low pH are the fast kinetics for the hydrogen oxidation reaction (HOR) and the hydrogen evolution reaction (HER) with platinum group metal (PGM) catalysts.¹¹ Although the sluggish kinetics for the oxygen reduction reaction (ORR) and the oxygen evolution reaction (OER) require larger amounts of PGM catalysts, there are several practical approaches to design new catalyst concepts to overcome this challenge.¹²⁻¹⁴

In the following, a short overview of the working principle of PEMFCs and PEMWEs, and the electrochemical cell components of each system with a specific focus on the catalyst materials will be given. Several degradation phenomena of PEMFCs and PEMWEs with regards to the performance deterioration related to the OER (co-)catalyst will be introduced, and the desired OER (co-)catalyst properties to mitigate those degradation phenomena will be provided. Finally, an overview of the state-of-the-art OER catalysts from the literature and the current challenges regarding OER catalyst development with a specific focus on the durability testing will be given.

1.1 Proton Exchange Membrane Fuel Cell (PEMFC)

Proton exchange membrane fuel cells (PEMFCs) are energy conversion devices where the chemical energy stored in hydrogen (H_2) and oxygen (O_2) is converted to electrical energy and heat, whereby the hydrogen oxidation reaction (HOR, eq. 1.2) and the oxygen reduction reaction (ORR, eq. 1.3) are locally separated, summing up to the production of water (H_2O) according to eq. 1.4.



In a PEMFC, hydrogen oxidation occurs at the anode electrode and the produced protons travel through a proton exchange membrane to the cathode electrode while the produced electrons travel an external path, producing electrical power. At the cathode electrode, oxygen from air and the protons and electrons produced at the anode react to form water maintaining charge neutrality.

In the following, the major components of a fuel cell are shortly reviewed. The structural components of a fuel cell mainly include the endplates, sealing materials, and bipolar plates (BPPs). The endplates are in contact with the outermost cells of a series of cells which are stacked in a so-called fuel cell and provide the mechanical integrity of the stack, while, as the name suggests, the sealing materials are used to make the system gas tight. The BPPs typically have specific flow field (FF) patterns machined into their surface to allow for gas distribution over the entire active area of the anode and cathode electrodes, coolant channels are placed between the anode and cathode flow fields of the BPPs to provide cooling for each individual cell. The heart of the fuel cell is the electrochemical unit which is composed of the anode electrode, the proton conducting membrane, and the cathode electrode, which is commonly referred to as catalyst coated membrane (CCM) or 3-layer membrane electrode assembly (MEA). The CCM is sandwiched between two gas diffusion layers (GDLs) to form

a 5-layer MEA. Since the focus of this thesis is the performance deterioration of PEMFCs with regards to the catalyst materials, the following sections will focus on the materials and degradation mechanisms of the 3-layer MEA components in a PEMFC.

1.1.1 3-Layer Membrane Electrode Assembly (MEA)

The 3-layer MEA is built up symmetrically, with the membrane in the center and the catalyst layers (anode and cathode) on each side, as schematically shown in fig. 1.1. The membrane, which acts as an electrical insulator between the anode and cathode electrodes, is composed of a perfluorinated polymer with ionic groups. The perfluorinated polymer is based on polytetrafluoroethylene (PTFE) and the ionic side chains are commonly perfluorosulfonic acid (PFSA) groups.¹⁵ The sulfonic acid groups dissociate in the presence of water (produced by the electrochemical reactions within the MEA or introduced to it with the reactant gasses) and create a highly acidic medium that enables facile proton transport through the well-known Grotthuss mechanism. In state-of-the-art PEMFCs, membranes are as thin as ~8-15 μm to minimize the ohmic loss associated with the ionic resistance, and to maintain the mechanical integrity of such thin membranes, reinforcement layers such as expanded PTFE are typically employed within the membranes.¹⁵⁻¹⁷

The anode and cathode electrodes in an MEA are typically composed of platinum (or platinum alloy) nanoparticles supported on a high surface area carbon black (Pt/C), and a PFSA ionomer (similar to the membrane material) acting as a proton conductivity medium within the electrode. Since the electrochemical reactions take place on the surface of the catalyst, the size of the Pt nanoparticles is typically in the range of 2-5 nm in order to achieve a high surface area to mass ratio, i.e., a high electrochemical surface area (ECSA). The electronic conductivity of the electrodes is provided by the high electrical conductivity of the carbon black support material. Furthermore, the poor packing density of the employed carbon support materials provides a high void volume inside the electrode, enabling an efficient transport of the reactant gasses and

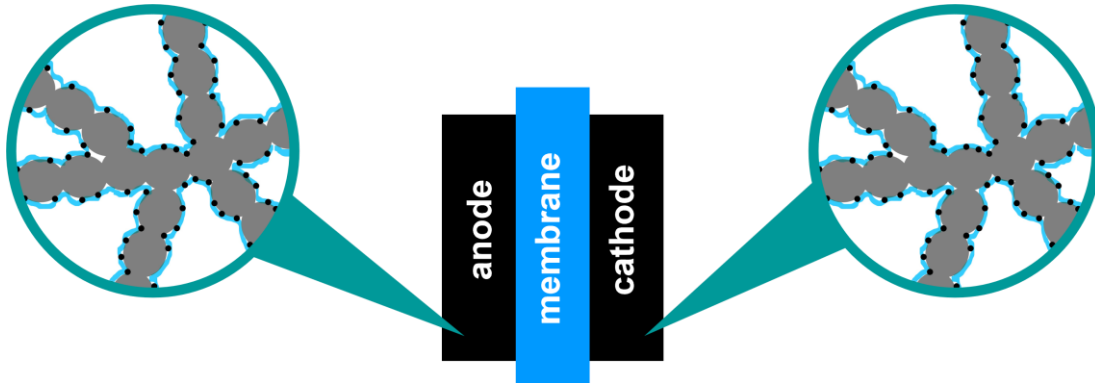


Figure 1.1. Schematic representation of a 3-layer MEA (or CCM), with the membrane sandwiched between the anode and cathode electrodes. The insets are the schematic representations of the anode and cathode electrode components, including platinum nanoparticles (black dots) supported on a high surface area carbon black (gray spheres) and a well-connected network of a proton-conducting ionomer coating (blue film).

the product water.^{18, 19} In order to achieve a continuous network of ionomer for a good proton conduction throughout the electrode, a sufficient amount of ionomer is used by adjusting an appropriate ionomer to carbon mass ratio (I/C) during the MEA fabrication process. Although the ionomer used in the electrodes is generally the same as that used in the ~ 8-15 μm thick membrane, where gas transport from one side to the other side must be minimized, O_2 and H_2 supply to the Pt active sites is possible because the ionomer film that covers the Pt nanoparticles is very thin ($< 10 \text{ nm}$).²⁰⁻²²

1.1.2 MEA Performance and Durability

This section provides a short overview of the parameters that determine the performance of a freshly made MEA, followed by a description of two common degradation phenomena in automotive PEMFCs.

The thermodynamic equilibrium potential of the fuel cell reaction (eq. 1.4) can be determined based on the general Nernst equation (eq. 1.5) for the two half-cell reactions (eq. 1.2 and 1.3) and considering the 4-electron transfer for the reaction shown in eq. 1.4:

$$E_{\text{rev}} = E_0^{\text{OER/ORR}} - E_0^{\text{HOR/HER}} + \frac{R \cdot T}{4F} \cdot \ln \left(\frac{(p_{\text{O}_2}/p^0) \cdot (p_{\text{H}_2}/p^0)^2}{\left(\frac{p_{\text{H}_2\text{O}}}{p_{\text{H}_2\text{O}}^{\text{sat}}}\right)^2} \right) \quad (1.5)$$

where E_{rev} is the reversible cell potential at the fuel cell operating conditions, E_0 is the equilibrium potential of the individual half-cell reactions at standard conditions (25 °C, 101.3 kPa gas partial pressure, and liquid H₂O), R is the ideal gas constant (8.314 J mol⁻¹ K⁻¹), T is the temperature (in K), F is the Faraday constant (96485 A s mol⁻¹), p_{H_2}/p^0 and p_{O_2}/p^0 are the partial pressure of the respective gases divided by the reference gas pressure at standard conditions ($p^0 = 101.3$ kPa), and $p_{\text{H}_2\text{O}}/p_{\text{H}_2\text{O}}^{\text{sat}}$ is the partial pressure of H₂O divided by the water saturation pressure at the respective temperature, which corresponds to the relative humidity (RH).

While the thermodynamic equilibrium potential is constant for a specific operation condition (temperature and gas partial pressure), the cell potential can be lowered by so-called overpotentials and by parasitic currents. The individual components of each phenomenon and their significance are well described in the PhD thesis of G. S. Harzer.²³ However, the changes in kinetic overpotentials for the oxygen reduction reaction (η_{ORR}) and the hydrogen oxidation reaction (η_{HOR}) are the major focus in MEA performance monitoring in this thesis and are explained shortly in the following.

The kinetic overpotential of a half-cell reactions is generally described by the Butler-Volmer equation (eq. 1.6):

$$i = i_0 \cdot r_f \cdot \left(e^{\frac{\alpha_a \cdot F}{R \cdot T} \cdot \eta} - e^{-\frac{\alpha_c \cdot F}{R \cdot T} \cdot \eta} \right) \quad (1.6)$$

where i is the current density (in units of A cm⁻²_{MEA}), i_0 is the exchange current density (in units of A cm⁻²_{Pt}), r_f is the roughness factor of the electrode (active surface area of the catalyst, normalized to the geometric area of the electrode, typically given in cm²_{Pt} cm⁻²_{MEA}), α_a and α_c are the anodic and cathodic transfer

coefficients, and η is the kinetic overpotential of a given half-cell reaction. Equation 1.6 considers the reaction in both anodic (e.g., OER) and cathodic (e.g., ORR) directions, and the contribution of each reaction to the overall current is determined by the applied overpotential and the transfer coefficient. Based on eq. 1.6, small kinetic overpotentials at a certain current density can be achieved by using a high catalytically active surface area in a given electrode (high r_f) or by having a reaction with a high i_0 , i.e., a fast reaction. The extremely fast HOR kinetics on Pt catalysts enables the use of very low Pt loadings on the anode electrode ($\leq 0.05 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}_{\text{MEA}}$), since even in this case the contribution of the anode overpotentials to the overall overpotential is almost negligible under most operating conditions.²⁴ On the other hand, owing to the sluggish ORR kinetics, the ORR overpotential contributes significantly to the overall overpotential, so that even though advanced catalysts are used for state-of-the-art cathodes, higher cathode Pt loadings ($\geq 0.1 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}_{\text{MEA}}$) are still required.^{25, 26}

Long-term durability of MEAs is affected by many factors. In the following, two common degradation phenomena which result in the severe corrosion of the carbon support in Pt/C catalysts will be introduced.

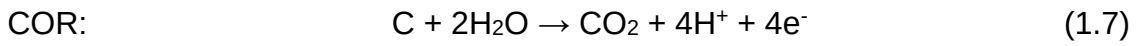
1.1.2.1 Start-Up/Shut-Down (SUSD)

During start-up/shut-down (SUSD) events, a H_2 /air-front passes through the anode flow field due to the replacement of the H_2 gas by air during shut-down and vice versa during start-up.²⁷ After the initial explanation of the SUSD mechanism,²⁷ the effect of various operating conditions and of different catalyst materials have been subject to many studies. It has been shown that SUSD invokes oxidative currents in the cathode electrode, which leads to carbon corrosion and structural collapse of the cathode catalyst layer, as well as loss of catalyst ECSA due to the detachment of Pt nanoparticles from the carbon support.^{28, 29}

SUSD also leads to an anode potential transient between ~0 and ~1 V vs. the reversible hydrogen electrode potential (V_{RHE}) upon the passage of a H_2 /air-front through the anode flow field.³⁰ While the kinetics of the carbon oxidation reaction (COR) are very sluggish and the exposure of carbon to ~1 V_{RHE} does not noticeably corrode the support material,³¹⁻³³ these voltage cycles lead to a significant Pt ECSA loss at the anode during SUSD events.³⁰ The stability of anode catalysts upon voltage transients induced by SUSD events is one of the focal points of this thesis and it will be further investigated in the results chapter.

1.1.2.2 Cell Reversal

The cell (voltage) reversal in a PEMFC occurs on account of a short under-supply of H_2 (hydrogen starvation) to one or several cells in a fuel cell stack.³⁴⁻³⁷ During cell reversal, the anode potential rises far above 1 V_{RHE} , causing a continuous corrosion of the carbon support through the carbon oxidation reaction (COR):



Although the COR according to eq. 1.7 is thermodynamically favorable at potentials $> 0.2 V_{RHE}$, considerable carbon corrosion rates are only observed at potentials $> 0.9 V_{RHE}$ due to its sluggish kinetics.^{31-33, 38} Such high anode potentials occur during cell reversal and lead to the substantial degradation of anode catalysts and anode electrodes. This damage is substantial even if the cell reversal only occurs over time scales of tens of milliseconds, since the catalyst layer collapse occurs already after less than 10% of the carbon mass have been corroded.³⁹ Therefore, there is a need to mitigate the damages caused by cell reversal by the following three main strategies: i) replacing the conventional high surface area carbon support materials by corrosion resistant support materials such as graphitized carbons and metal oxides;^{37, 40, 41} ii) application of system mitigation strategies;^{42, 43} and, iii) addition of an anode co-catalyst which catalyzes the non-damaging OER over the COR.^{34, 36, 37, 44-47} While graphitized carbons are currently used as support materials for the Pt/C anode catalysts in PEMFC stacks,³⁷ there are still several challenges for the

application of non-carbon support materials such as their low electrical conductivity, their low stability at the fuel cell operating conditions, the risk of cationic contamination and/or degradation of the ionomer and membrane, and cost issues.⁴⁸⁻⁵⁰ System mitigation strategies would add complexity and cost to the PEMFC system: as mentioned above, the damages caused by cell reversal can be substantial even over time scales of tens of milliseconds, which would require the control system to be able to detect cell reversals on this time scale and to respond very quickly to prevent MEA damage. The addition of an OER co-catalyst to the anode electrode would be the most straightforward strategy to mitigate cell reversal damages, and it is the mitigation strategy that is the focus of this thesis.

Anode OER co-catalysts are mostly based on iridium (Ir), ruthenium (Ru), or their respective heat-treated oxides (i.e., IrO₂ and RuO₂) owing to the higher OER activity of these materials compared to platinum.^{37, 51-54} Typically, the anode co-catalyst is added to the Pt/C anode catalyst during the MEA fabrication process, and the anode electrode containing the OER co-catalyst is occasionally referred to as reversal tolerant anode (RTA).^{46, 54, 55} Fig. 1.2 shows a schematic representation of the reactions occurring in an MEA with and without an RTA under regular and cell reversal (hydrogen starvation) conditions. Due to the low OER activity of platinum in a Pt/C anode catalyst, the carbon corrosion rate in the anode electrode of an MEA is rather high during cell reversal in the absence of an anode co-catalyst, while on the other hand, in the presence of an anode co-catalyst, its high OER activity renders water electrolysis rather than the COR to be the dominating reaction during cell reversal. That being said, the OER activity of an anode co-catalyst reliably correlates with its effectiveness for mitigating cell reversal degradation in a PEMFC, so that it is a major selection criterion for benchmarking anode OER co-catalysts in the literature.^{46, 51-53}

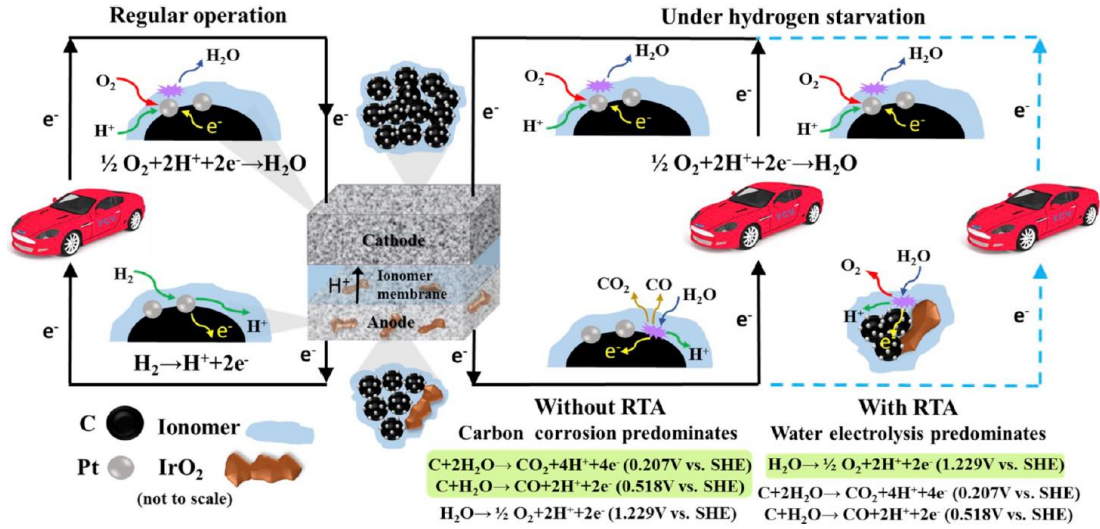


Figure 1.2. Schematic representation of the addition of an IrO₂ anode co-catalyst to the MEA to mitigate cell reversal (hydrogen starvation) damages. The electrochemical reactions during the regular operating conditions are not expected to be altered by adding an IrO₂ anode co-catalyst. However, due to the low OER activity of platinum, the rate of the damaging carbon corrosion reaction in the anode is very high in the MEA without reversal tolerant anode (RTA) during hydrogen starvation. On the other hand, the non-damaging water electrolysis is the dominating anode reaction in the MEA with RTA during hydrogen starvation, due to the high OER activity of an IrO₂ anode co-catalyst. Reprinted from Y. Wang et al., J. Power Sources, 449, 227542, Copyright (2024), with permission from Elsevier.⁵⁵

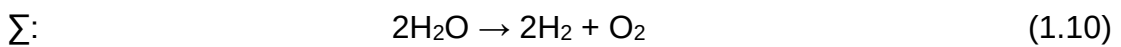
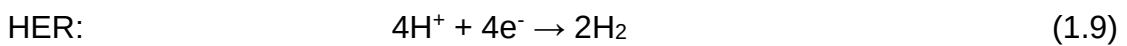
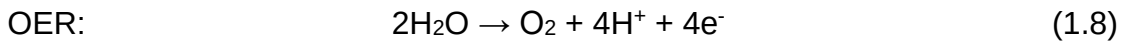
Another requirement that an OER co-catalyst needs to fulfil is that it should be stable under the normal and transient operating conditions of a PEMFC anode. When a heat-treated oxide-based OER co-catalyst (like IrO₂) is used in the PEMFC anode, the near surface layers of this catalyst can be reduced to metallic Ir by H₂ during the normal operation of the fuel cell,⁵⁶ a phenomenon that is not commonly considered when benchmarking OER anode co-catalysts for PEMFC applications. Such alternation of the catalyst surface could ultimately affect its stability during repetitive SUSD events, where the anode potential cycles between $\sim 0 \text{ V}_{\text{RHE}}$ and $\sim 1 \text{ V}_{\text{RHE}}$.³⁰ Voltage cycling of ruthenium and iridium-based OER catalysts in this potential range can trigger the dissolution of the catalyst surface through the so-called transient dissolution mechanism, with the dissolution rate of metallic surfaces being ~ 100 times higher than those of the heat treated oxide surfaces.^{57, 58} The continuous dissolution of an anode OER co-catalyst during repetitive SUSD cycles could ultimately result in its

degradation and in a loss of MEA performance. This phenomenon is the subject of one of the studies in the Results chapter of this thesis (section 3.3).⁵⁶

As the OER activity of a co-catalyst and its stability during transient operating conditions of a fuel cell anode are set as the two major criteria in benchmarking anode co-catalysts in this thesis, a literature overview of the currently available OER catalysts with respect to these criteria will be provided in section 1.3.

1.2 Proton Exchange Membrane Water Electrolyzer (PEMWE)

Proton exchange membrane water electrolyzers (PEMWEs) offer an efficient way to produce hydrogen via the electrochemical splitting of water. During operation, liquid water is supplied to the anode electrode where it is oxidized to protons, electrons, and O₂ via the OER (eq. 1.8). Driven by the electric field, protons move through the membrane to the cathode electrode where they are reduced to H₂ via the HER (eq. 1.9). The anodic and cathodic reactions are locally separated, summing up to the water electrolysis reaction according to eq. 1.10.



The major components of a water electrolyzer are very similar in terms of functionality to the ones described for a fuel cell in section 1.1, with the endplates, sealing materials, and BPPs constituting the structural components and with the CCM or the 3-layer MEA constituting the electrochemical reaction unit. The CCM is sandwiched between two porous transport layers (PTLs) to form a 5-layer MEA. The cathode PTL is typically similar to a carbon fiber-based fuel cell GDL; however, at the anode side the application of carbon fiber-based PTLs is not possible due to the rapid carbon oxidation at the high anode electrode potentials

(> 1 V_{RHE}). Therefore, anode PTLs are typically made of a corrosion resistant material such as titanium.⁵⁹ Since the focus of this thesis is the performance and durability of PEMWEs with regards to the catalyst materials, the following sections will provide a short overview on the catalysts and the durability of a 3-layer MEA in a PEMWE.

1.2.1 3-Layer Membrane Electrode Assembly (MEA)

The 3-layer MEA for a PEMWE is composed of the membrane sandwiched by the catalyst layers (anode and cathode), similar to the schematic shown in fig. 1.1 for a 3-layer MEA for a PEMFC. Similar to PEMFCs, PFSA-based ionomers and membranes are used in state-of-the-art PEMWEs. However, unlike PEMFCs, relatively thick PFSA membranes (Nafion® 115 or 117 with thicknesses of ~125 or ~175 µm, respectively) are used in PEMWEs in order to provide better mechanical robustness and low gas permeability for the operation at high gas pressures. Knowledge and experience gained over several decades of PEMFC R&D in the development of Pt/C catalysts applied in a CCM at low Pt loadings could be transferred efficiently to PEMWE development, and Pt/C has become the standard HER catalyst for PEMWE cathodes. On the anode electrode, unsupported Ir or IrO₂ based catalysts are used in state-of-the-art PEMWEs, resulting in high Ir loadings of ~2 mg_{Ir} cm⁻²_{MEA}.

1.2.2 MEA Performance and Durability

Since the electrochemical half-cell reactions of a PEMWE are similar to the of a PEMFC, just in the opposite direction, the thermodynamic equilibrium potential and the kinetic overpotentials in PEMWE are derived similarly through eq. 1.5 and 1.6. Due to the extremely fast HER kinetics on Pt catalysts, cathode overpotentials are relatively small and a significant reduction of the Pt loading is possible without affecting the overall performance.⁶⁰ On the other hand, the kinetic losses due to the sluggish OER kinetics are one of the major sources of the overall overpotential even at high anode Ir loadings of ~2 mg_{Ir} cm⁻²_{MEA}.⁶⁰

Therefore, the research focus has been directed towards the development of anode catalysts with high intrinsic OER activity and a reduction of the PGM loading of the anode electrode. Among several PGMs, the highest OER activity in acidic media is obtained for Ir and Ru,⁶¹ however, the rate of dissolution and corrosion of Ru is very high at the high electrochemical potentials of the anode ($> 1.4 V_{RHE}$),⁶² making Ir a more suitable OER catalyst for PEMWEs. There are several challenges regarding the strategies to reduce the anode catalyst loading by improving the mass activity (i.e., the activity normalized by the mass of noble metal), which will be investigated in section 1.3.

The long-term durability of MEAs can be affected by the degradation of either the anode and/or the cathode catalyst layers. The degradation of the Pt/C cathode catalyst is mainly triggered by the dissolution and agglomeration of the small Pt nanoparticles or by the corrosion of the carbon support. However, these degradation mechanisms mainly happen at high potentials or during potential cycling events.^{28, 63, 64} Since the cathode potential in a PEMWE is usually close to the HOR/HER reversible potential (i.e., $\sim 0 V_{RHE}$) during operation, a severe degradation of the Pt/C cathode catalyst is not expected. However, the degradation of anode catalyst layer can occur where times of operation and idle periods alternate, which might, e.g., occur when a PEMWE is coupled with renewable energy sources. Due to the fluctuating power supply of the latter, the current density supplied to the PEMWE fluctuates between low and high voltages, resulting in anode potential cycles in the potential region of $> 1 V_{RHE}$.⁶⁵ However, during idle periods, i.e., when no current is supplied and the cell is left at open circuit voltage (OCV), it has been shown that H_2 can permeate through the membrane from the cathode electrode to the anode electrode. The enrichment of such permeated H_2 within the anode compartment ultimately leads to a drop of the anode potential to $\sim 0 V_{RHE}$ and to a reduction of the surface of oxide base OER catalysts to its metallic state, which in turn gets reoxidized during the subsequent normal operation period at the high anode potentials.^{65, 66} The repetitive cycling between reducing conditions during extended OCV periods and oxidizing conditions during operation were shown to cause the enhanced

dissolution of the anode catalyst, which may result in a significant loss of active material.⁶⁵ Therefore, besides the stability of an OER catalyst at highly oxidizing anode potentials during operation, its stability under the transient condition between the reducing potentials at idle periods and the oxidizing potentials during operation should be considered. The next section provides a literature overview of the currently available OER catalysts with respect to these criteria.

1.3 OER Catalyst Materials

This section provides a summary of the previous sections with regards to the requirements for an OER (co-)catalyst for the application in the anode electrode of PEMFCs and PEMWEs. Then, benchmarking of the state-of-the-art OER catalysts with regards to those requirements will be provided, followed by the current challenges of durability testing of OER catalysts.

1.3.1 Anode OER (Co-)Catalyst Requirements

Fig. 1.3 gives an overview of several operational modes in a PEMFC and a PEMWE, the anticipated anode electrode potential (E_{anode}) during these modes, and the desired OER catalyst property to fulfill the requirements for the operation under these conditions.

A high OER activity and corrosion stability at high anode electrode potentials of $E_{\text{anode}} \gg 1 V_{\text{RHE}}$ are the most basic requirements of an anode (co-)catalyst in order to serve its main function during cell reversal events in a PEMFC or under normal operation in a PEMWE. In other words, if a catalyst has a low OER activity or its OER performance quickly decays due to catalyst corrosion and a concomitant loss of its ECSA at $E_{\text{anode}} \gg 1 V_{\text{RHE}}$, it can clearly be ruled out as an anode (co-)catalyst.

OER co-catalysts in PEMFC anode		
Mode of operation	E_{anode}	Desired catalyst property
Cell reversal	$\gg 1 V_{\text{RHE}}$	High OER activity, corrosion stability
Normal operation	$\sim 0 V_{\text{RHE}}$	Reduction resistance (for oxides)
SUSD	Cycling between $\sim 0 V_{\text{RHE}}$ and $\sim 1 V_{\text{RHE}}$	Stability against transient dissolution
Normal operation + cell reversal	Cycling between $\sim 0 V_{\text{RHE}}$ and $\gg 1 V_{\text{RHE}}$	Stability against transient dissolution

OER catalysts in PEMWE anode		
Mode of operation	E_{anode}	Desired catalyst property
Normal operation	$\gg 1 V_{\text{RHE}}$	High OER activity, corrosion stability
Idle (OCV)	$\sim 0 V_{\text{RHE}}$	Reduction resistance (for oxides)
Normal operation + idle (OCV)	Cycling between $\sim 0 V_{\text{RHE}}$ and $\gg 1 V_{\text{RHE}}$	Stability against transient dissolution

Figure 1.3. An overview of several modes of operation in a PEMFC and a PEMWE, together with the predicted anode electrode potential (E_{anode}) during these operation modes, and the desired properties of an anode OER (co-)catalyst to fulfill the requirements for the operation under these conditions.

As introduced in the previous sections, the surface of a heat-treated noble metal oxide catalyst can be completely reduced to a metallic surface upon exposure to H_2 , a condition that occurs under the normal operation of a PEMFC anode (cf. section 1.1.2.2) or under extended idle (OCV) periods of a PEMWE anode (cf. section 1.2.2). The significance of such an alteration of the catalyst surface is revealed during specific anode potential transients in a PEMFC (i.e., during SUSD-cycles or sequences of normal operation + cell reversal) and in a PEMWE (i.e., during sequences of normal operation + idle (OCV) periods). Under such conditions, the anode potential cycles between reducing ($E_{\text{anode}} \approx 0 V_{\text{RHE}}$) and oxidizing ($E_{\text{anode}} \geq 1 V_{\text{RHE}}$) potentials, leading to the dissolution of PGM-based catalysts through a mechanism called transient dissolution.^{61, 67-69} As will be shown in the following sections, the stability of the common OER catalysts against transient dissolution strongly depends on their surface chemical nature, with metallic catalyst surfaces having substantially higher transient dissolution rates compared to heat-treated oxide surfaces. Therefore, if a high stability against transient dissolution is required for an anode (co-)catalyst, it is necessary to pick a heat-treated oxide catalyst which has a high reduction resistance in a H_2 -containing atmosphere.

The following sections provide an overview of the state-of-the-art OER catalysts with a specific focus on their OER activity, their corrosion stability at high potentials, and their stability against transient dissolution.

1.3.2 State-of-the-art OER Catalysts

As mentioned in section 1.2.2, the acidic OER according to eq. 1.8 has a very slow reaction kinetics and requires high overpotentials to take place; therefore, substantial research efforts have been dedicated for the design and development of OER catalysts. Understanding the underlying OER mechanism on the atomic level can help to design and synthesize catalysts with high OER activity and sufficient stability.^{70, 71} In terms of the origin of the oxygen atoms involved in the reaction, the proposed OER mechanisms can be divided into two main categories:^{72, 73} the adsorbate evolution mechanism (AEM) and the lattice oxygen oxidation mechanism (LOM). In case of the AEM, the oxygen atoms involved in the OER come from surface adsorbates ($\text{H}_2\text{O}/\text{OH}^-$), while for the LOM all or part of the oxygen atoms involved in the OER originate from the lattice oxygen atoms in the catalyst structure. While the created lattice oxygen vacancies could be beneficial for OER following the LOM pathway, these vacancies may not be refilled by oxygen atoms in the subsequent catalytic cycle, which could decrease the stability of the catalyst and lead to a severe metal cation leaching.^{72, 74, 75} Therefore, the underlying OER mechanism plays a role in determining the stability and activity of a catalyst.

A variety of OER catalysts have been reported in the literature. Although Ir- and Ru-based materials are the most commonly used OER catalysts, other types of catalysts such as PGM-free materials and Ru or Ir single-atom catalysts have also recently attracted attention. Fig. 1.4 shows the classification of these catalysts and the link between activity/stability with the underlying OER mechanism. PGM-free OER catalysts are typically based on transition metal oxides (MnO_x , CoO_x , FeO_x , etc.)⁷⁶⁻⁸⁸ or carbon based electrocatalysts.⁸⁹⁻⁹⁴ However, these PGM-free catalysts would suffer from severe loss of ECSA due to the instability and dissolution of the transition metals or from severe carbon

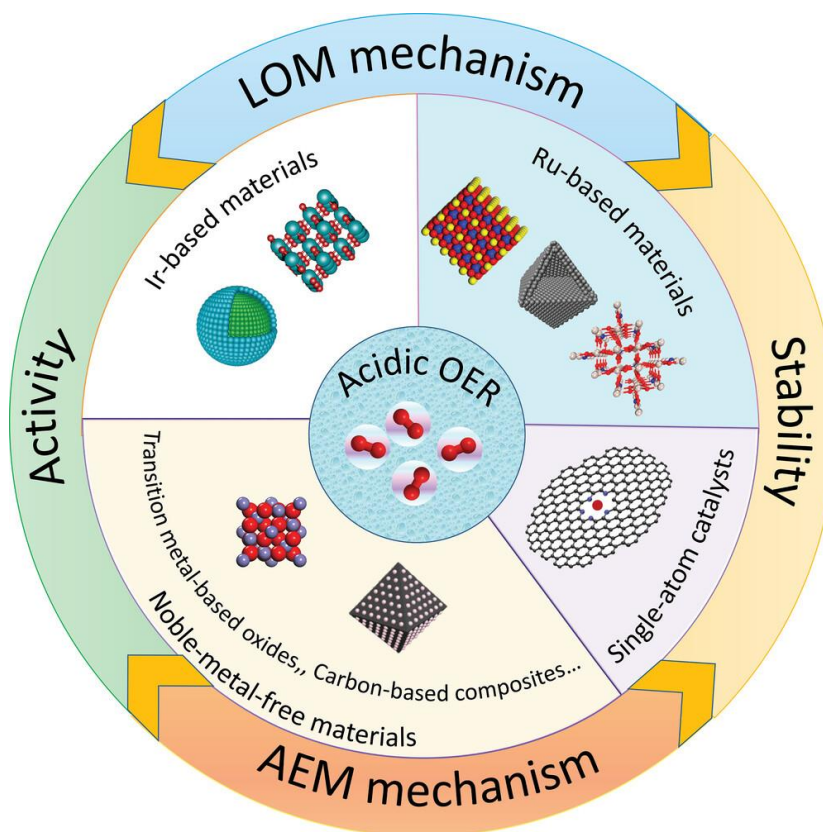


Figure 1.4. A general classification of the commonly used catalysts for acidic OER and the link between activity/stability with the underlying OER mechanism. Reprinted from Y. Lin et al., *Advanced Materials*, 35, 2210565, Copyright (2024), with permission from JOHN WILEY AND SONS.⁷²

corrosion at the highly oxidative potential during OER ($E \gg 1 \text{ V}_{\text{RHE}}$).^{31, 33, 72} Since Ru or Ir single-atom catalysts are often prepared by doping PGM-free materials (transition metals, carbon, ...) by Ru or Ir,⁹⁵ they would also suffer from severe degradation during OER. Therefore, most of the research focus in the field of acidic OER has been on the development of more promising Ir and Ru-based OER catalysts due to their higher stability, and the following sections will provide overviews of these types of catalysts.

1.3.2.1 Iridium-based Catalysts

Due to the corrosion stability of iridium at high potentials ($> 1 \text{ V}_{\text{RHE}}$) according to the Pourbaix diagram,⁹⁶ iridium-based materials are the most promising types of OER catalysts in acidic media. Nevertheless, the chemical nature of the catalyst

surface plays a critical role in determining its OER activity and its durability. In general, Ir-based catalysts can be categorized into metallic Ir, iridium oxide ($\text{IrO}_x/\text{IrO}_2$), and Ir-based alloys.^{72, 73} The product of the electrochemical oxidation of metallic Ir is a highly porous and hydrated iridium oxy-hydroxide phase referred to as e- IrO_x .^{69, 97-99} This phase is usually formed when a metallic Ir surface is exposed to the high potentials during OER for an extended time, or when it undergoes an extensive potential cycling between reducing ($\sim 0 \text{ V}_{\text{RHE}}$) and oxidizing potentials ($\sim 1 \text{ V}_{\text{RHE}}$). An interesting phenomenon that occurs during the extensive electrochemical oxidation of metallic Ir surfaces is the further oxidation of sub-surface metallic Ir and the formation of a thicker, porous e- IrO_x layer on the catalyst surface.^{69, 99} This phenomenon can result in a so-called three-dimensional electrocatalysis,⁹⁸ which describes the inclusion of sub-surface atoms/moieties into the electrochemical processes as active sites, which in turn can lead to an improved OER activity of the catalyst.

Another type of iridium oxide-based catalysts is heat-treated IrO_2 , which is typically obtained by a thermal treatment of an Ir precursor (typically a hydrated iridium oxy-hydroxide) in an O_2 -containing atmosphere.^{46, 100-103} Depending on the heat treatment temperature, the thermal oxidation product can be either an amorphous iridium oxide (a- IrO_x), a highly crystalline rutile-type iridium oxide (c- IrO_2), or a combination of both. The a- IrO_x is typically the dominating product when the heat treatment is done at $T < 400 \text{ }^\circ\text{C}$, while the crystallization of the thermal decomposition products to form a rutile-type IrO_2 starts to take place at $T \approx 400 \text{ }^\circ\text{C}$.¹⁰⁰ Therefore, if a sample is heat-treated at a temperature around $400 \text{ }^\circ\text{C}$, the resulting product might be a mixture of a- IrO_x and c- IrO_2 . Due to the presence of a hydrous-amorphous $\text{IrO}(\text{OH})_x$ species on an a- IrO_x surface, a- IrO_x has a higher intrinsic OER activity than c- IrO_2 ; therefore, higher OER activities are observed for catalysts having a higher a- IrO_x content, i.e., being heat-treated at a lower temperature.^{46, 100, 103} However, the OER activity of heat-treated iridium oxide catalysts is lower than that of metallic Ir,⁶¹ and if the OER activity of the catalyst is the only criterion for catalyst selection, metallic Ir catalysts would be

the material of choice. Heat treatment of iridium oxide is the subject of one of the studies in this thesis and it will be investigated in detail in section 3.4.

The third type of Ir-based catalysts are the alloys of Ir with transition metals such as Ni, Co, Cu, etc.¹⁰⁴⁻¹¹⁰ Although a better specific OER activity can be achieved by alloying Ir with transition metals, the transition metal stability under the operating conditions of an MEA is still a remaining challenge which needs to be addressed. Such stability issue has previously been shown for PtCo alloy ORR catalysts in PEMFC cathodes, where Co leaching under the transient operating conditions of PEMFCs leads to the cationic Co contamination of the ionomer in electrode and membrane and a concomitant loss of PEMFC performance.¹¹¹

Besides the approach of seeking to increase the intrinsic OER activity of an Ir-based catalyst (i.e., its specific OER activity) in order to reduce the OER overpotential and thereby enable lower iridium loadings of the electrode, another practical approach to reduce the iridium loadings is to improve the OER mass activity of an OER catalyst (i.e., the activity normalized by the mass of iridium). This is typically done by supporting small nanoparticles or nm-thin films of metallic iridium or iridium oxide on high surface area support materials, thereby maximizing the iridium dispersion (defined as the fraction of iridium surface atoms with respect to the total number of iridium atoms). However, the high anode potential of $E_{\text{anode}} \gg 1 \text{ V}_{\text{RHE}}$ in a PEMWE prevents the usage of carbon support materials, since they would be oxidized under these conditions.^{31, 33} Alternative conductive support materials such as indium tin oxide (ITO), fluorine doped tin oxide (FTO), and antimony doped tin oxide (ATO) have also been developed for application in a PEMWE anode electrode.¹¹²⁻¹¹⁴ Unfortunately, the potential-dependent dissolution of the doping elements and the resulting electrical conductivity loss of these support materials limit their practical application.^{113, 115} Therefore, the need for a suitable support material led to the investigation of metal oxides (MO_x) which are stable, commercially available, and inexpensive, such as titanium dioxide (TiO_2).^{116, 117} However, since TiO_2 itself is not an electrically conductive material, an alternative catalyst design concept had

been developed, where the electrical conductivity is provided through a contiguous network of IrO₂ nanoparticles covering the surface of a TiO₂ support material in a sort of IrO₂/TiO₂ shell/core catalyst.^{14, 118} Contrary to the high Ir loadings of ~1-2 mg cm⁻² which are typically required for unsupported Ir or IrO_x based catalysts in PEMWE anodes,¹⁰ low Ir loadings of ~0.3 mg cm⁻² can be achieved by an advanced IrO_x/TiO₂ catalyst concept, where the Ir packing density in the electrode can be effectively controlled by controlling the surface area of TiO₂ support material.¹⁴ This way, even for low iridium loadings, reasonably thick electrodes (~3-5 μm) are obtained, which can be coated reliably and which have a sufficiently low in-plane electrical resistance. The upper panel in fig. 1.5 schematically compares this advanced catalyst design concept to a conventional unsupported IrO₂ catalyst concept for PEMWE anode applications.

On the other hand, an anode OER co-catalyst for a PEMFC is typically prepared in form of, e.g., IrO₂ powder, which is physically mixed with a Pt/C anode HOR catalyst during the MEA fabrication process.⁴⁶ As physically mixing the catalysts during the MEA fabrication process might not be efficient enough to break up the IrO₂ catalyst agglomerates, the IrO₂ utilization is likely compromised. As an alternative to this conventionally used method, IrO₂ nanoparticles can be deposited directly onto the anode catalyst carbon support or onto the Pt/C anode catalyst, which would lead to a better dispersion of IrO₂ nanoparticles and to a better OER co-catalyst performance.^{51, 52, 119} The lower panel in fig. 1.5 compares such an advanced anode catalyst design to the conventional anode catalyst design for PEMFC applications.

In addition to the OER activity of the Ir-based catalysts, their stability under specific transient operating conditions during which the electrode potential cycles between reducing and oxidizing potentials (c.f. section 1.3.1) is also affected by the chemical nature of the catalyst surface. These potential cycles are well known to lead to the dissolution of Ir-based catalysts (via the formation of Irⁿ⁺ ions) through the so-called transient dissolution mechanism. Experiments to quantitatively evaluate the transient dissolution rates of a given catalyst are

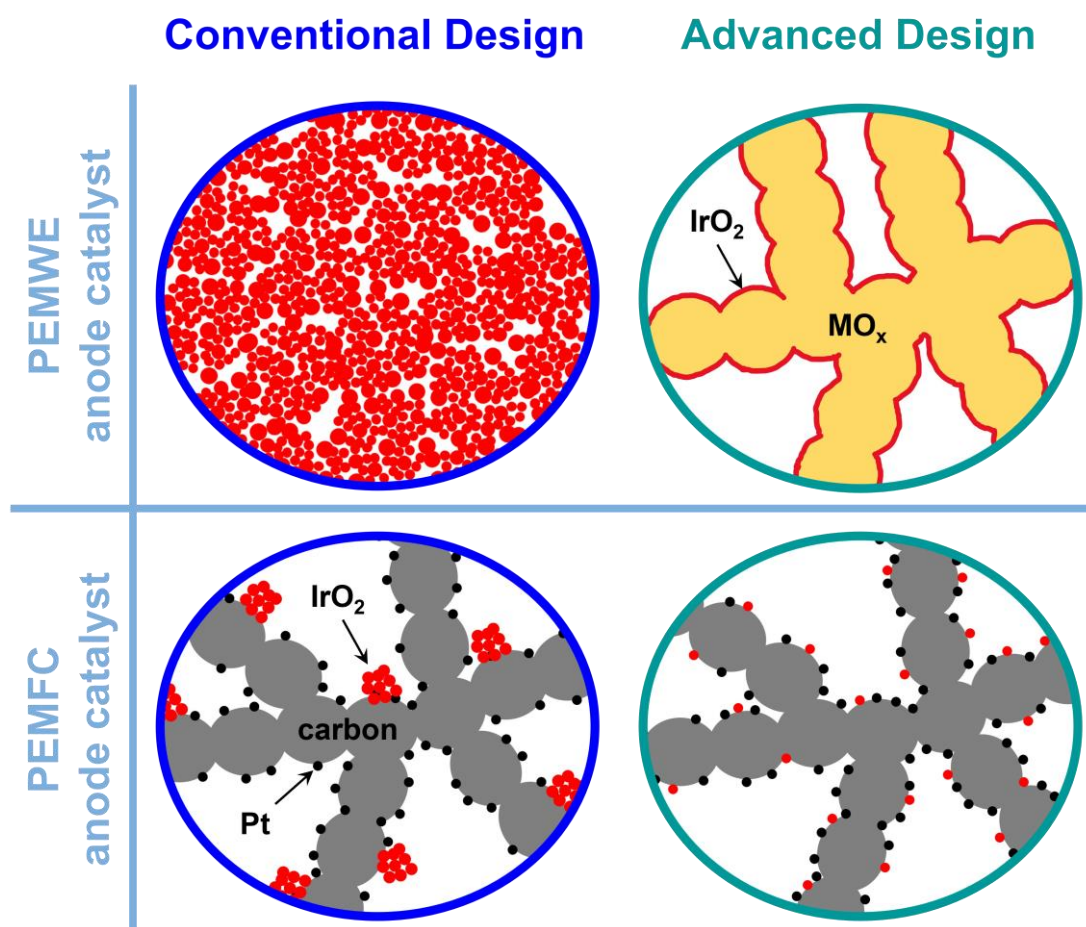


Figure 1.5. Design of anode catalysts for PEMWE (upper panel) and PEMFC (lower panel) applications. Unsupported IrO_2 catalysts are conventionally used in a PEMWE anode (upper left image), while a continuous IrO_2 film or a contiguous layer of nm-sized IrO_2 particles is formed on a high surface area metal oxide (MO_x) support material in the advanced catalyst design concepts (upper right image). For PEMFC anodes, an IrO_2 co-catalyst powder is conventionally mixed with a Pt/C anode HOR catalyst during the MEA fabrication process (lower left image), while IrO_2 is directly precipitated onto the Pt/C anode catalyst during the IrO_2 synthesis process in the advanced design (lower right image).

typically performed in liquid cells, where a scanning flow-cell (SFC) in combination with inductively coupled plasma mass spectrometry (ICP-MS) is used to measure the iridium dissolution rate during a linear sweep voltammetry (LSV) experiments between reducing and oxidizing potentials.^{61, 68, 69} It has been previously shown that transient dissolution rates are ~ 2 orders of magnitude higher for metallic Ir compared to heat-treated IrO_2 catalysts.⁵⁸ This would mean that heat-treated IrO_2 catalysts are the anode (co-)catalyst of choice if a

compromise between OER activity and stability against transient dissolution is the metric for catalyst screening. However, it will be shown in section 3.3 that the typically employed heat-treated IrO_2 catalysts are reduced to metallic Ir upon exposure to a H_2 -containing atmosphere, leading to their increased transient dissolution rate.⁵⁶ This would mean that a reduction resistant IrO_2 catalyst is required, and the strategies to produce such catalyst are the subject of sections 3.4 and 3.5 in this thesis.^{120, 121}

1.3.2.2 Ruthenium-based Catalysts

Ruthenium-based catalysts are also widely investigated in the literature due to their superior OER activity compared to Ir-based catalysts.⁶¹ Similar to Ir-based catalysts, the OER activity and the stability against transient dissolution for the Ru-based catalysts depend on the chemical nature of the catalyst surface, with metallic Ru catalysts having higher OER activities and significantly higher transient dissolution rates than heat-treated RuO_2 catalysts.^{57, 61} Nevertheless, due to the low thermodynamic stability of ruthenium at high potentials during OER, the rate of its dissolution and corrosion is unacceptably high, and Ru or RuO_2 is typically not considered to be a stable OER catalyst.^{62, 122} Therefore, Ru-based catalysts can be suitable OER catalysts only if their stability can be improved significantly. In this regard, mixed oxides of Ru and Ir ($\text{Ru}_x\text{Ir}_y\text{O}_2$) could be a way to find a compromise between the high OER activity of Ru and the good stability of Ir. Several groups have investigated $\text{Ru}_x\text{Ir}_y\text{O}_2$ OER catalysts and have found improved OER activity compared to pure IrO_2 .^{62, 123, 124} While the investigated $\text{Ru}_x\text{Ir}_y\text{O}_2$ anode catalysts were stable under a constant current operation in a PEMWE over a few hundred hours,^{62, 123} it remains unclear whether Ru in the structure is really stabilized over the extended time at the high potentials in a PEMWE and whether $\text{Ru}_x\text{Ir}_y\text{O}_2$ catalysts are indeed viable alternatives to IrO_2 .

In section 3.5, it will be shown that heat-treated RuO_2 catalysts are reduced to metallic Ru upon exposure to a H_2 -containing atmosphere.¹²¹ As the formation of metallic Ru would lead to an increased transient dissolution rate of the catalyst

during the intermittent operation of a device (c.f. section 1.3.1), a strategy to produce reduction resistant RuO₂ catalysts by forming solid-solution phases of RuO₂ with titanium oxide or niobium oxide will be introduced.¹²¹ To evaluate if the incorporation of TiO₂ to the lattice structure of RuO₂ will improve its stability at high potentials during the OER, the stability of the prepared solid-solution OER catalyst is compared to that of pure RuO₂ in an MEA under constant current operation of a single-cell PEMWE.¹²¹

1.3.3 OER Catalyst Activity and Stability Measurements

Fast screening of catalysts activity and stability is essential for the development of suitable anode OER (co-)catalysts. While testing the activity and stability of OER catalysts directly in the anode of a PEMWE is possible, this approach has several disadvantages: i) it requires the time-consuming preparation and optimization of electrodes and their integration in MEAs; ii) MEA preparation requires a considerable amount of catalyst (at least a few hundred milligrams), which often is a significant hurdle when exploring new catalysts and new synthesis methods; and iii) the electrochemical characterization methods to determine catalyst activity and stability in a PEMWE are often complex and time-consuming. As an alternative to the MEA measurements, screening tests based on half-cell measurements with a liquid electrolyte in, e.g., a rotating disk electrode (RDE) or a flow-channel configuration are commonly used to evaluate the activity and stability of OER catalysts.^{114, 125-129} RDE measurements are typically performed in a three-electrode cell using an RHE reference electrode, a high surface area gold (Au) or platinum (Pt) mesh as a counter electrode, and a disk working electrode which consists of a thin layer of catalyst deposited onto an electrically conductive non-porous substrate (e.g., a polycrystalline gold disk).¹³⁰ Most commonly, diluted sulfuric acid is used as a liquid electrolyte and, in contrast to MEA measurements, electrode coating optimization is less time consuming and only a few milligrams of catalyst are required for the activity and stability testing. Catalyst OER activity screening using the RDE technique is very well-established, and it will be shown in section 3.2 that the OER activities determined from RDE measurements are comparable to those obtained from

MEA measurements. Therefore, measuring the OER activity using the RDE technique is a quick and reasonably reliable approach to predict the performance of a new OER catalyst in a MEA evaluated in a PEMWE.

Other than measuring the OER activity of newly synthesized catalysts, estimating their long-term stability is crucially important for their implementation in a real device. OER catalysts stability measurements are based on either constant current (chronopotentiometry), constant potential (chronoamperometry), or potential cycling experiments,⁷⁰ but the estimated catalyst lifetimes in half-cell measurements with liquid electrolyte are orders of magnitude lower than those obtained in a PEMWE.^{13, 131} There are several hypotheses in the literature to explain this discrepancy. A first hypothesis is that the passivation of the electrode substrate surface and the associated formation of a high contact resistance at the catalyst layer/ substrate interface makes the catalyst no longer electrochemically accessible.¹³² Hence, it is recommended to use electrode substrate materials that are not passivated at the high OER potentials, such as Au or boron-doped diamond. A second hypothesis is that the continuous oxygen evolution at high potentials could transform the highly OER-active hydrous iridium oxy-hydroxide into the less OER-active anhydrous iridium oxide.¹³³ It should be mentioned that this hypothesis was proposed exclusively based on RDE measurements and that if such depletion of active sites takes place in a liquid electrolyte, it should similarly occur in MEA measurements, resulting in comparably short catalyst lifetimes, which have not been observed. A third hypothesis is that the actual acidity in the vicinity of the OER catalyst surface in an anode catalyst layer in an MEA is perhaps lower than the estimated acidity for an ionomer phase in an electrode, and that such lower acidity results in a lower iridium dissolution and longer catalyst lifetime in an MEA in a PEMWE.¹³⁴ Lastly, the fourth hypothesis is that the accumulation of microscopic oxygen gas bubbles at the surface of the RDE tip and/or within the pores of the catalyst layer might shield parts of the active surface area of the catalyst, resulting in very high specific current densities that might lead to accelerated catalyst degradation.

Assuming that this effect is enhanced in the RDE configuration, this would explain the lower catalyst durability in RDE vs. MEA measurements.^{13, 131, 135, 136}

With respect to these four hypotheses, there is strong evidence that the accumulation of microscopic oxygen gas bubbles is one of the major reasons for the discrepancy in catalyst lifetimes obtained from RDE and MEA measurements. In sections 3.1 and 3.2 of this thesis, a comprehensive study on this phenomenon will be presented, where it will be shown that the accumulation of oxygen bubbles occurs in all RDE-based stability tests, independent of whether these are conducted under galvanostatic, potentiostatic, or potential-cycling conditions. A possible way to mitigate the accumulation of gas bubbles in RDE-based measurements will be shown. Furthermore, it will be shown that the same phenomenon also occurs during the stability tests carried out using an MEA configuration in a PEMWE, but to a much lesser extent compared to that associated with the RDE technique.

2 Experimental Methods

This chapter provides an overview of the experimental procedures presented in the individual works in Chapter 3, and serves as a guide for the efficient planning, execution, and evaluation of physical/chemical and electrochemical experiments.

2.1 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) of the anode OER (co-)catalyst powder samples was performed by a Mettler Toledo TGA/DSC 1 instrument. For these, ~3-10 mg of a catalyst powder was weighed into a sapphire crucible (volume 70 μl), which then was closed with a perforated sapphire lid and directly inserted into the TGA furnace. All the gases used in the TGA experiments were 5.0-grade and supplied by Westfalen AG. Ar (at 20 ml min^{-1}) was used as the cell carrier gas in addition to the reactive gases during all TGA experiment steps. In general, two types of TGA experiments were performed in this thesis: i) experiments to investigate a sample's mass loss upon an oxidative heat treatment in an O_2 -containing atmosphere, and ii) TGA experiments to investigate the reduction resistance of the anode OER (co-)catalysts in a H_2 -containing atmosphere. Details on each type of experiments are provided in the following.

2.1.1 Study of the Oxidative Treatment of Metal Oxides

In order to investigate the mass loss behavior of a metal oxide precursor upon calcination in an oxidative atmosphere, TGA temperature ramp experiments were performed in an O_2 -containing atmosphere. During this type of experiment,

the temperature was ramped from 25 to 1150 °C with a heating rate of 2.5 K min⁻¹ while supplying synthetic air (20.5 vol.% O₂/N₂, 40 mL min⁻¹) to the TGA furnace. This step was followed by cooling to 25 °C (at ca. -20 K min⁻¹) with the same gas feed. It should be noted that during this experiment, the effective O₂ concentration was 13.7 vol.% O₂/(Ar+N₂) due to the additional cell carrier gas stream of Ar.

2.1.2 Study of the Reduction of Metal Oxides

TGA is a useful tool for quick and reliable benchmarking of metal oxide catalysts with respect to their reduction resistance in a H₂-containing atmosphere. The designed TGA experiments to investigate the reduction resistance of the anode OER (co-)catalysts were composed of two main steps: i) an initial in situ drying/cleaning step in oxidative atmosphere, and ii) a subsequent metal oxide reduction step in reductive atmosphere. Note that the TGA plots shown in this thesis only depict the reduction step, i.e., the second part of this sequence. Fig. 2.1 shows the temperature profile and the gas environment during these TGA experiments.

The in situ drying/cleaning step was used in order to desorb any adsorbed water and to oxidatively remove any organic impurities from the surface of the catalyst powder, so that the mass losses during the subsequent reduction step are only due to the reduction of the metal oxides. The procedure of the in situ drying/cleaning step was as follows: flushing the TGA furnace with Ar (100 ml min⁻¹) for 5 min at 25 °C, ramping the temperature from 25 to 200 °C (10 K min⁻¹) in O₂ (100 ml min⁻¹), holding the temperature at 200 °C for 10 min in O₂ (100 ml min⁻¹), cooling down the furnace from 200 to 25 °C (-10 K min⁻¹) in O₂ (100 ml min⁻¹), and finally purging the TGA furnace with Ar (100 ml min⁻¹) for 5 min at 25 °C. It should be mentioned that all the anode OER (co-)catalysts had already been heat-treated in air atmosphere at temperatures of ≥ 375 °C (c.f. sections 2.2 and 2.3), so that the drying/cleaning step at 200 °C in O₂ at the beginning of each TGA experiment will not have a significant influence on the

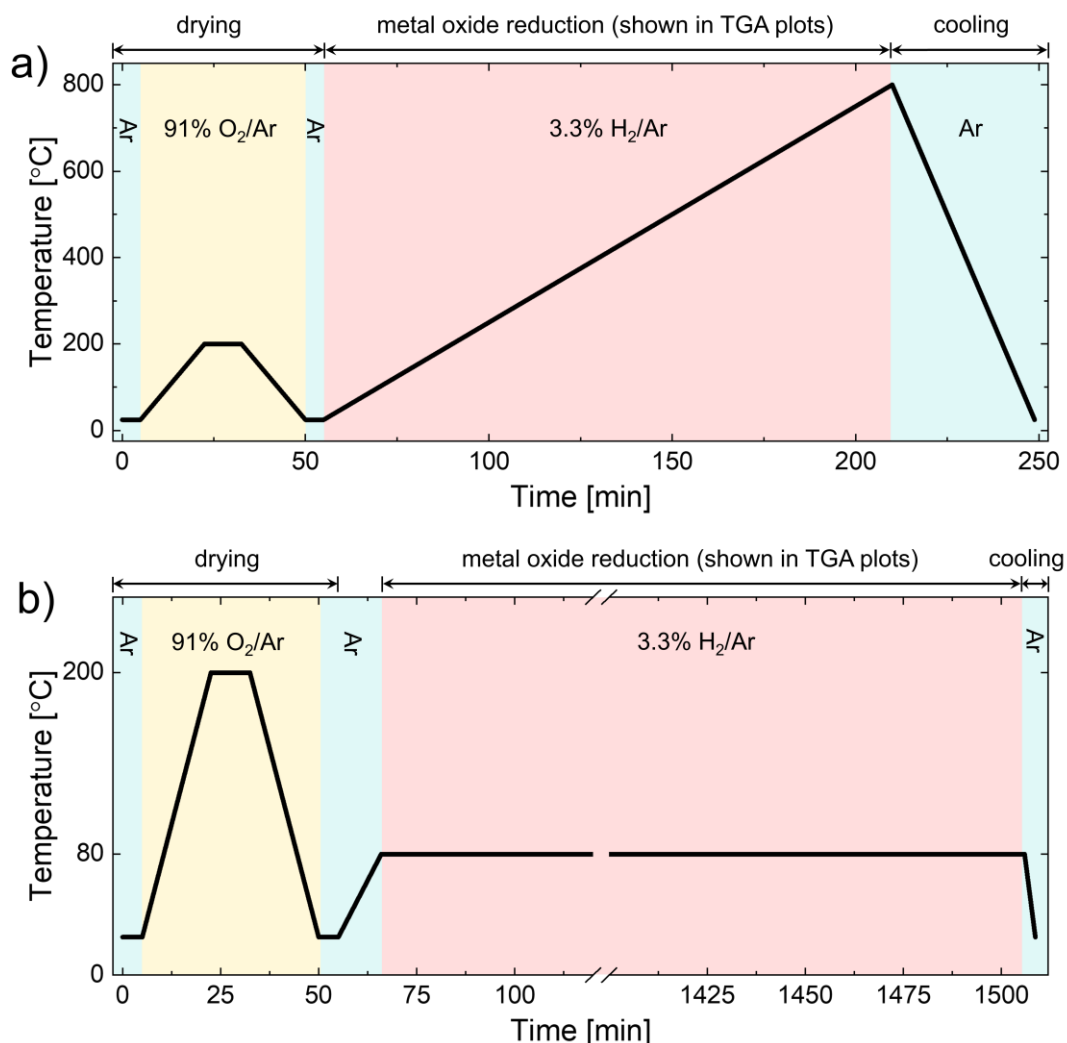


Figure 2.1. Temperature profile and gas environment of the TGA experiments to investigate the reduction resistance of the anode OER (co-)catalysts. The experiments were composed of two main steps: i) an initial in situ drying/cleaning step in oxidative atmosphere (91% O₂/Ar), highlighted in yellow, and ii) a subsequent metal oxide reduction step in reductive atmosphere (3.3% H₂/Ar), highlighted in red. Note that in the TGA plots shown in this thesis, the mass profiles of only the latter step are shown. The metal oxide reduction step was carried out in two different modes: a) a temperature ramp mode, where the temperature was ramped from 25 to 800 °C with a heating rate of 5 K min⁻¹, b) an isothermal mode, where the temperature was kept at 80 °C for 24 h. For further details refer to the text.

physical/chemical properties of the catalysts (surface area, particle size, oxidation state, etc.).

After the initial drying/cleaning step, the metal oxide reduction step was carried out in two different modes: i) a temperature ramp mode (fig. 2.1 a) and ii) an isothermal mode (fig. 2.1 b). During the temperature ramp experiment, the temperature was ramped from 25 to 800 °C (in some experiments only to 300 °C or 500 °C) with a heating rate of 5 K min⁻¹ (in some instances, additional experiments at 1, 2.5, or 10 K min⁻¹ were conducted) while supplying 5 vol.% H₂/Ar (40 ml min⁻¹), which was followed by cooling the furnace from 800 to 25 °C (-20 K min⁻¹) in Ar (100 ml min⁻¹). The isothermal reduction experiments were carried out by heating the TGA furnace from 25 to 80 °C (in some cases to 100, 120, 160, or 240 °C) at a heating rate of 5 K min⁻¹ in Ar (100 ml min⁻¹), followed by switching the gas supply from Ar to 5 vol.% H₂/Ar (40 ml min⁻¹) and keeping the furnace at this temperature for up to 24 h. After this, the furnace was cooled down to 25 °C (-20 K min⁻¹) in Ar (100 ml min⁻¹). It should be noted that during the drying/cleaning as well as during the metal oxide reduction steps, an extra 20 ml min⁻¹ flow of Ar as cell carrier gas was supplied in addition to the 40 ml min⁻¹ 5 vol.% H₂/Ar and 100 ml min⁻¹ O₂; therefore the effective reactive gas concentrations were 3.3 vol.% H₂/Ar and 91 vol.% O₂/Ar.

During the TGA experiments under diluted H₂ atmosphere, RuO₂ and IrO₂ can be reduced according to the following reaction:



Stoichiometric RuO₂ (ruthenium(IV) oxide) and IrO₂ (iridium(IV) oxide) contain 24 wt.% O and 14.3 wt.% O, respectively. Hence, the total mass loss of a RuO₂ or IrO₂ catalyst upon the complete reduction to the respective metals would be accompanied by a total mass loss of the RuO₂ and IrO₂ catalysts of 24 wt.% and 14.3 wt.%, respectively. These values will be used to quantify the reduction extent of a given oxide catalyst, corresponding to the fraction α of the metal oxide that had been reduced to the respective metal; this reduction extent α will be given in the later shown TGA data.

2.2 Stabilization of IrO₂ and RuO₂ by the Solid-Solution Approach

This section provides an overview of the stabilization of IrO₂ and RuO₂ catalysts by preparing reduction resistant IrO₂- or RuO₂-based solid-solution phase with metal oxides that have a high reduction resistance. A generalized preparation route for solid-solution phases based on IrO₂-TiO₂ (ssTi-IrO_x), RuO₂-TiO₂ (ssTi-RuO_x), and RuO₂-Nb₂O₅ (ssNb-RuO_x) is summarized here, with a special focus on aspects that require attention to ensure reproducible results but could not be discussed in detail in the respective publication. For details on the preparation of solid-solution catalysts (e.g., reactant quantities and temperature profiles), the reader is referred to section 3.5.

First, a desired amount of TiO₂ (rutile titanium(IV) oxide, 99.9 %; Alfa Aesar) or Nb₂O₅ (niobium(V) oxide, 99.95 %; Alfa Aesar) was weighed and added to the already weighed IrO₂ or RuO₂ (ruthenium(IV) oxide, anhydrous, 99.9 %; Alfa Aesar) in a mortar. Then, the resulting powder was hand-mixed with a disposable plastic spatula and was added to a 500 ml round-bottom flask containing 200 ml DI water (15 MΩ cm, E-POD, Merck Millipore KGaA); this mixture was dispersed by ultrasonication for 30 min. The resulting dispersion was stirred overnight at room temperature and then centrifuged and dried at 70 °C.

Based on the reported phase diagrams, the formation of IrO₂-TiO₂ and RuO₂-TiO₂ solid-solution phases were carried out at 1000 °C and 1300 °C, respectively.^{137, 138} The formation of RuO₂-Nb₂O₅ solid-solution phases was also attempted at 1300 °C, as we are not aware of any reported phase diagram for this system. The heat treatments were performed in synthetic air atmosphere (0.5-1 L min⁻¹) in a tube furnace, where a quartz glass tube and an alumina tube were used for the heat treatment at 1000 °C and 1300 °C, respectively. It is reported in the literature that volatile oxides of Ir or Ru begin to form when IrO₂ or RuO₂ is heated in air at temperatures > 800 °C based on the following reactions:¹³⁹⁻¹⁴¹



The evaporation and loss of IrO₂ and RuO₂ in the powder mixtures and from the resulting solid-solution phases upon extended heating at high temperatures would eventually result in a deviation between the targeted versus the obtained solid-solution phase composition, a problem that was noted for an IrO₂-TiO₂ powder mixture with a molar ratio of 20:80. This mixture was heat-treated for 2 h at either 800 or 1000 °C in the tube furnace and then the samples were analyzed using the TGA temperature ramp experiment in 3.3 vol.% H₂/Ar shown in fig. 2.2

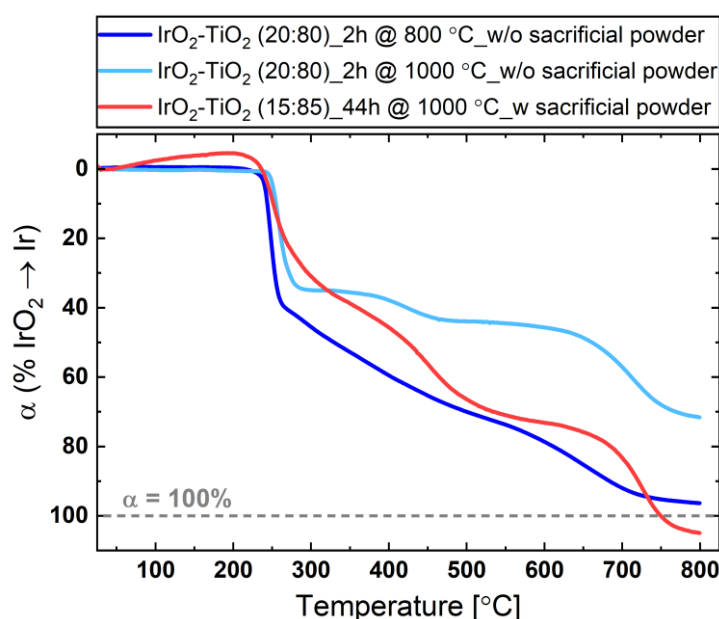


Figure 2.2. TGA (5 K min⁻¹) experiments under 3.3 vol.% H₂/Ar (following a drying/cleaning step; see section 2.1.2 for further details) with the heat-treated IrO₂-TiO₂ mixtures (20:80 and 15:85 molar ratios), showing the effect of sacrificial IrO₂ powder on preventing evaporation and loss of IrO₂ during the heat treatment of the mixtures at high temperature. The y-axis represents the fraction of the IrO₂ phase in the samples that is reduced to metallic Ir (α), with the gray horizontal dashed line marking the theoretical α = 100% value that would be expected for the full reduction of IrO₂ in the mixtures.

(dark and light blue curves). As TiO_2 is not reduced by H_2 in the here analyzed temperature range (25-800 °C),^{142, 143} the observed mass loss during the TGA experiment is attributed to the reduction of the IrO_2 phase of this mixture according to eq. 2.2, and the y-axis represents the fraction of the IrO_2 phase in this mixture that is reduced to metallic Ir (α). It can be seen that for the mixture heat treated at 800 °C, the α vs temperature curve is approaching the theoretical $\alpha = 100\%$ value that would be expected for the full reduction of IrO_2 in the IrO_2 - TiO_2 mixture. However, for the mixture heat-treated at 1000 °C, α does not reach the expected theoretical value of $\alpha = 100\%$, indicating a lower amount of IrO_2 in this sample. This means that IrO_2 loss occurred upon heat treatment of the IrO_2 - TiO_2 mixture at 1000 °C, presumably through the formation of gas phase IrO_3 according to eq. 2.3. Further evidence for this assumption was the formation of a black precipitate downstream of the heated zone of the quartz tube of the furnace when the heat treatment was performed at 1000 °C.

To suppress the evaporation of RuO_2 from RuO_2 - TiO_2 mixtures at high temperatures, it has been proposed in the literature to form a gas buffer zone around the samples during heat treatment. Such a gas buffer zone is created by burying RuO_2 - TiO_2 mixtures under a sacrificial RuO_2 powder layer, in which case most of the ruthenium loss during heat treatment occurs from the sacrificial powder layer, with no significant ruthenium loss from the sample.^{144, 145} In these studies, the samples are compressed into pellets for better handling and easier separation of the samples from the sacrificial powder. This sacrificial powder approach was tested for a IrO_2 - TiO_2 powder mixture with a molar ratio of 15:85. Pellets (11 mm diameter) were prepared by placing ~500 mg of the powder mixture into a pellet press die and compressing it at a pressure of ~100 MPa using a manual press. The resulting pellets were placed inside an alumina crucible and then buried under a layer of sacrificial IrO_2 powder, as schematically shown in fig. 2.3. Note that the direct contact between the pellets and the alumina crucible was prevented by a buffer layer of sacrificial IrO_2 powder. Due to the formation of an IrO_3 gas buffer zone around the pellet at high temperatures, there is no driving force for IrO_3 gas from the pellet into the surrounding buffer zone,

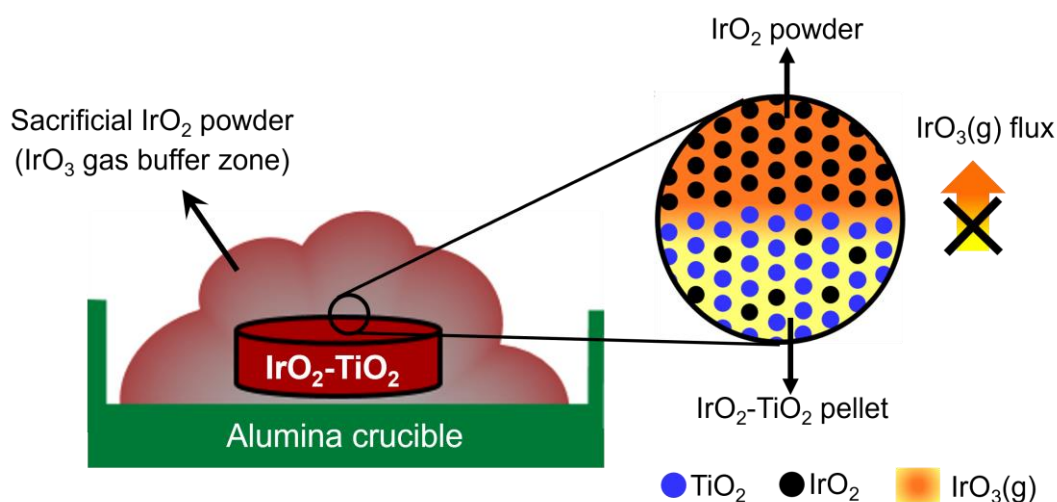


Figure 2.3. Schematic illustration of burying a pellet made of $\text{IrO}_2\text{-TiO}_2$ mixture under a layer of sacrificial IrO_2 powder during the high-temperature heat treatment step to form a solid-solution phase. At high temperatures, the sacrificial IrO_2 powder forms an IrO_3 gas buffer zone around the pelletized sample, which prevents any significant IrO_3 gas flux from the pellet into the surrounding buffer zone and this prevents the loss of iridium from the $\text{IrO}_2\text{-TiO}_2$ sample.

so that there is no significant evaporation and loss of iridium from the pellet. The $\text{IrO}_2\text{-TiO}_2$ pellet surrounded by a sacrificial IrO_2 powder was heat treated at $1000\text{ }^\circ\text{C}$ for 44 h. After heat treatment, the pellet was crashed and ground using a mortar and a pestle, and the resulting powder sample was analyzed by the TGA temperature ramp experiment (red curve in fig. 2.2). It can be seen that the α vs temperature curve is approaching the theoretical $\alpha = 100\%$ value that would be expected for the full reduction of the nominal, weighed-in amount of IrO_2 in this sample, meaning that the sacrificial powder approach was successful in preventing the evaporation and loss of IrO_2 at high temperature. Therefore, the sacrificial powder approach was utilized during the high temperature heat treatment step for the formation of $\text{IrO}_2\text{-}$ and $\text{RuO}_2\text{-}$ based solid solution phases.

The preparation of $\text{IrO}_2\text{-}$ and $\text{RuO}_2\text{-}$ based solid-solution catalysts is thus comprised of three steps: i) a high-temperature heat treatment for the formation of a solid-solution phase; ii) a subsequent ball milling to decrease the particle size and thus increase its specific surface area; and iii) a low-temperature heat treatment to recover the reduction stability of the samples. In step i, $\sim 12\text{ g}$ of the

pre-mixed oxide powders (mixing by ultrasonication and stirring in water as described above) were pressed into pellets and buried under the corresponding sacrificial PGM-oxide powder in an alumina crucible. Then, the sample-containing crucible was pushed into the hot zone of the already pre-heated tube furnace (1000 or 1300 °C for IrO₂- or RuO₂-based samples, respectively), and the heat-treated for 2 h in synthetic air atmosphere. Finally, the crucible was pulled out of the hot zone of the tube furnace to cool down to room temperature under ambient air. After cooling, the crucible was removed from the tube furnace and the pellets were crushed and ground using a mortar and a pestle and then thoroughly hand-mixed using a disposable plastic spatula. The process of making pellets, their heat treatment, and the grinding/hand mixing was repeated three times, resulting in an overall heat treatment duration of 6 h. The three obtained solid-solution samples are denoted as ssTi-IrO_x, ssTi-RuO_x, and ssNb-RuO_x.

In order to increase the specific surface area of the solid-solution samples, ball milling was performed in step ii, using ZrO₂ beads (1 mm diameter; FRITSCH GmbH, Germany) and a grinding bowl (a 20 ml ZrO₂ vessel, encased in stainless steel; FRITSCH GmbH, Germany) for an overall duration of 80 min at 1000 RPM. Water was added to the ball milling media for better efficiency of the ball milling process and to avoid material sticking to the walls of the grinding bowl. The ball milling process is described in great details in sections 3.4 and 3.5. After ball milling, the resulting slurry was washed through a sieve using DI water to separate it from the ZrO₂ beads; subsequently, the slurry was centrifuged at 10000 RPM to separate the sample from the water, and the resulting paste was dried in an oven at 70 °C for 12 h in ambient air atmosphere. After drying, the samples were ground with a mortar and pestle. The resulting powders were stored in glass vials and are denoted as ssTi-IrO_x-M, ssTi-RuO_x-M, and ssNb-RuO_x-M (M standing for 80 minutes of active ball milling according to step ii).

In step iii, a post-annealing was performed on the ball milled samples in order to largely recover their compromised reduction stability caused by the ball milling process. To do this, a certain amount of the ball milled sample was placed in an alumina crucible and pushed into the hot zone of a tube furnace pre-heated at 400 °C in an air atmosphere. After 15 minutes, the sample was pulled out of the furnace to cool down to room temperature in the ambient environment. Since the reduction stability of the samples was largely recovered after this post annealing step, it is referred to as “healing” step throughout this thesis, and the ball milled samples after the healing step are denoted as ssTi-IrO_x-MH, ssTi-RuO_x-MH, and ssNb-RuO_x-MH. After the healing step, the samples were thoroughly ground using mortar and pestle and stored in glass vials for further characterization.

2.3 Preparation of Reduction Resistant IrO₂ Catalysts

This section provides a short overview of the preparation of reduction resistant IrO₂ catalysts by a three-step synthesis procedure. For details on the preparation of this type of catalysts, the reader is referred to section 3.4.

A hydrated iridium oxy-hydroxide was used as a precursor for the following IrO₂-based catalysts. The synthesis procedure is comprised of three steps: i) a high temperature heat treatment; ii) a ball milling step; and iii) a low-temperature heat treatment to recover the reduction stability of the samples. In step i, ~ 12 g of the precursor were weighed into an alumina crucible and heat-treated for 2 h at different temperatures, namely at 650, 750, and 1000 °C (these temperatures were established at a heating rate of 10 K min⁻¹) in a synthetic air atmosphere to obtain the heat-treated samples denoted as IrO₂-T, (T standing for the heat treatment temperature of the sample in °C). In step ii, wet ball milling was performed using DI water, ZrO₂ beads (1 mm diameter; FRITSCH GmbH, Germany) and a grinding bowl (a 20 ml ZrO₂ vessel, encased in stainless steel; FRITSCH GmbH, Germany) for an overall duration of 80 min at 1000 RPM. After ball milling, the samples were denoted as IrO₂-T-M (T standing for the heat treatment temperature in step i and M for the 80-minute ball milling according to

step ii). In step iii, a short post-annealing at 400 °C (referred to as “healing”) was performed with the IrO₂-T-M samples in order to recover their compromised reduction resistance caused by ball milling. The IrO₂-T-M samples after the healing step are denoted as IrO₂-T-MH.

2.4 Rotating Disk Electrode (RDE) Measurements

As mentioned in section 1.3.3, rotating disk electrode (RDE) measurements are often used as a fast screening tool to characterize the activity and stability of new electrocatalyst materials. RDE measurements were carried out in a three-electrode cell using a static H₂ reference electrode (RE), consisting of a Pt wire sealed into one end of a glass tube that was drawn to a capillary and filled with electrolyte and a bubble of electrochemically evolved H₂ (all potentials given for RDE experiments in this thesis are quoted vs. the potential of this reversible hydrogen electrode (V_{RHE})). As counter electrode (CE), a high surface area Au was used, while the working electrode (WE) was a 5 mm diameter polycrystalline Au disk that was assembled in an interchangeable rotating ring-disk electrode (RRDE) shaft made of polyether ketone (Pine Research Instrumentation, USA) and was coated with a thin film of the catalyst under investigation. The reference electrode potential was calibrated in a H₂ saturated electrolyte prior to each experiment using the Pt ring of the RRDE. A 0.05 M H₂SO₄ aqueous solution was used as electrolyte, which was prepared by mixing high purity H₂SO₄ (Ultrapur, 96%, Merck Millipore KGaA, Germany) and ultra-pure water (18.2 MΩ cm at 20 °C, Merck Millipore KGaA, Germany). High purity Ar, H₂, and O₂ (6.0-grade, Westfalen AG) were used to purge the electrolyte.

Before each measurement, the Au disk working electrode was removed from the RRDE shaft and was polished with 0.3 μm alumina polishing suspension (Buhler AG) and then sonicated in ultra-pure water for several times. The catalyst ink suspension was prepared using the OER catalyst powder samples, a solvent, and a Nafion[®] ionomer solution (5 wt.% ionomer in mixture of lower aliphatic alcohols and water, Sigma Aldrich). The ink composition was adjusted to achieve a desired ionomer content of 1-2 wt.% in the dried coating that consisted of

catalyst and ionomer. The suspension was sonicated for 30 min in a sonication bath (Elmasonic S 30 H, Elma Schmidbauer GmbH) in order to achieve a homogenous ink. The temperature of the bath was maintained below 35 °C in order to prevent solvent evaporation. Finally, 20 μL of the prepared ink was drop-casted onto the polished and cleaned Au working electrode and then dried in air under an infrared (IR) lamp, resulting in a noble metal (Ir or Ru) loading of 0.1-0.4 $\text{mg cm}^{-2}_{\text{disk}}$.

It was noticed that the electrode coating quality of the OER catalysts was highly dependent on the type of solvent used for ink preparation. Therefore, the ink preparation methodology was first optimized using the IrO₂-750-MH catalyst, evaluating several solvent compositions and Nafion[®] ionomer contents (the optimum for the latter was 2 wt.% in the final dried coating). First, ultra-pure H₂O and a H₂O:2-propanol mixture with 4:1 volume ratio were used as the solvents for ink preparation. It can be seen in fig. 2.4a and b that the deposition of the catalyst is inhomogeneous in both cases, resulting in an apparently strong variation of the catalyst loading across the electrode surface. As the quality of the coating has a severe impact on the reproducibility of the RDE measurement results, further efforts were made to improve the coating quality, following the recommendations in the PhD thesis of S. Geiger, where it was shown that a significant improvement of the coating quality of SnO₂ particles can be achieved upon the addition of a small amount of acid or base to the solvent.¹⁴⁶ Therefore, a pH = 3 solution of the high purity H₂SO₄ in ultra-pure water and a pH = 11 solution of NaOH in ultra-pure water were examined as solvents for ink preparation. It can be seen in fig. 2.4b-d that the best coating quality, with a homogeneous deposition of the catalyst material on the disk electrode substrate, is achieved for the pH = 3 solution of H₂O + H₂SO₄ as the ink solvent. The improved coating quality for an optimized solvent pH is attributed to a change in the zeta-potential of the catalyst particles and their associated hindered agglomeration due to achieving a suitable surface charge of the catalyst particles.¹⁴⁶ Therefore, all RDE inks of the as-synthesized OER catalysts were

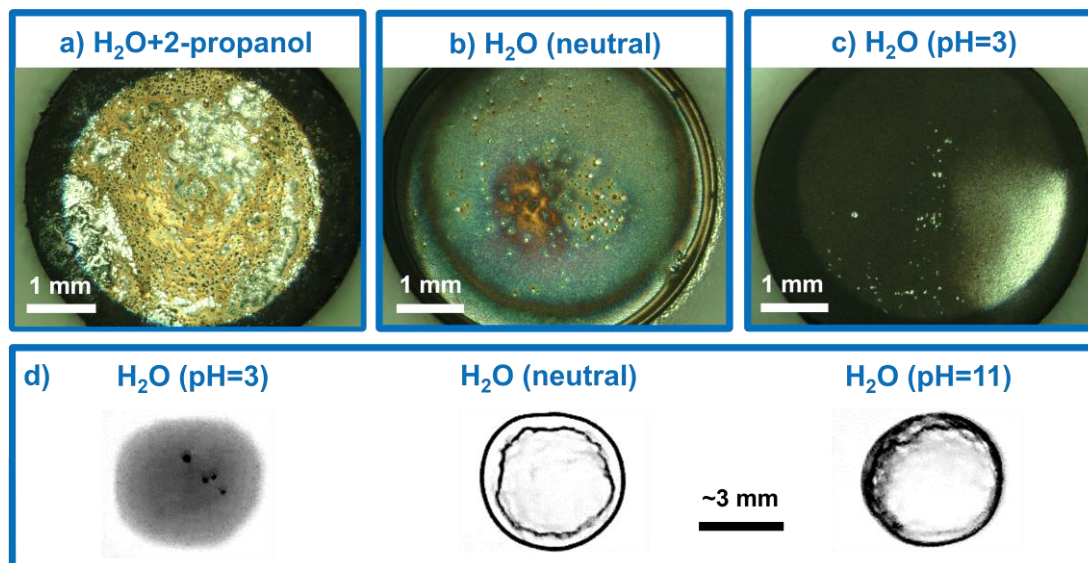


Figure 2.4. Effect of ink solvent composition on the quality of IrO₂-750-MH catalyst coatings, as observed by optical microscopy for: a) a mixture of H₂O + 2-propanol (4:1 volume ratio), b) pure H₂O, and c) a pH = 3 solution of H₂O + H₂SO₄. d) comparison of the results with H₂O-based solvents at varying pH, namely pH = 3 (H₂O + H₂SO₄), neutral pH (only H₂O), and pH = 11 (NaOH + H₂O). A Nafion[®] ionomer solution was added to the inks to achieve an ionomer content of 2 wt.% in the dried coating consisting of catalyst and ionomer. The coatings were achieved by drop-casting 20 μ L of the prepared ink either on a 5 mm diameter glassy carbon RDE electrode (a-c, targeting a loading of 0.4 mg_{Ir} cm⁻²_{disk}) or on a glass microscope slide (d). A portion of the disk electrode is illuminated by an external light source in panels a-c.

prepared using a pH = 3 solution of H₂O + H₂SO₄ as the ink solvent, unless stated otherwise.

All the RDE measurements (using the RRDE assembly) were performed using an Autolab potentiostat (PGSTAT302N, Metrohm AG) and a rotator (Pine Research Instrumentation). During the electrochemical measurements, the electrode rotation rate was fixed at 2500 RPM and the electrolyte temperature was maintained either at 40 °C (using the water jacket) or at room temperature. Freshly coated working electrodes were dipped in Ar-saturated electrolyte and the uncompensated solution resistance between the reference and the working electrodes was determined by electrochemical impedance spectroscopy (EIS) (from 100 kHz to 100 Hz) at open circuit voltage (OCV). Then, cyclic voltammetry (CV) was performed between a lower vertex potential of 0.05 V_{RHE} and an upper

vertex potential of 1.25 or 1.35 V_{RHE} at either 20 or 100 mV s⁻¹. This was performed for 10 cycles in order to record the characteristic voltammetric behavior of the catalysts in this potential range as well as to ascertain the physical stability of the coatings on Au working electrode disk during the experiments. After that, the OER polarization curves were recorded by collecting a CV between 1.3-1.6 V_{RHE} at either 10 or 20 mV s⁻¹, whereby only the very first positive-going scan was used for evaluation of the catalyst materials. The electrolyte was fully saturated with O₂ before recording some of the OER polarization curves, while the rest of OER polarization curves were recorded in Ar-saturated electrolyte. These conditions are specified in detail for each individual work in the results chapter.

The catalyst OER stability tests using the RDE technique were performed using constant current (chronopotentiometry), constant potential (chronoamperometry), and potential cycling experiments in Ar-saturated electrolyte at 40 °C. Due to the decay of the OER currents during the constant potential stability measurements, an online iR compensation was utilized in order to apply a constant iR-free potential to the electrode according to eq. (2.3):

$$E_{iR\text{-free}} = E_{\text{measured}} - |i_{\text{OER}}| \times R \quad (2.3)$$

where R is the uncompensated solution resistance determined by EIS prior to each measurement.

2.5 Catalyst Integration into an MEA

5 cm² MEAs for PEMFC and PEMWE measurements were prepared by the decal transfer method. The MEAs were composed of an IrO₂ or RuO₂-based catalyst at the anode electrode and a platinum supported on Vulcan carbon (50 wt.% Pt/C) at a loading of ~0.3 mg_{Pt} cm⁻²_{MEA} at the cathode electrode. The cathode catalyst layers were provided by Greenerity GmbH and were prepared by using a high-equivalent weight ionomer to achieve an I/C mass ratio of 0.65:1. The inks for the preparation of the anode catalyst layers were prepared by mixing

the IrO₂ or RuO₂-based catalyst powder, a solvent (2-propanol, purity ≥ 99.9% from Sigma Aldrich, Germany), DI water (18 MΩcm), and Nafion ionomer solution (1100 EW, 20 wt.% ionomer; D2021 from IonPower, USA) for 24 h using a roller mill (rotating at 180 rpm). To achieve a homogenous suspension, ~6 g ZrO₂ grinding beads (5 mm diameter) were added to the 2 ml ink dispersion contained in a 8 ml high density polyethylene (HDPE) bottle. The resulting catalyst ink was then coated onto a virgin PTFE decal using a Mayer-rod coating machine. Depending on the catalyst, the ionomer content of the anode electrode was adjusted to ~12-14 wt.% and the anode catalyst loadings referenced to Ir or Ru were in the range of 1.3-2.5 mg_{Ir/Ru} cm⁻²_{MEA}. The MEAs were fabricated by hotpressing the decals either onto 15 μm thick membranes (chemically mitigated, W. L. Gore & Associates GmbH, Germany) for PEMFC measurements or onto 50 μm thick membranes (Nafion[®] 212, from Quintech, Germany) for PEMWE measurements. The hotpressing was performed at 155 °C for 3 min with an applied pressure of 0.11 kNcm⁻².

The gas diffusion layers (GDL) used for the PEMFC measurements were H14C7 (Freudenberg & Co. KG, Germany), and the cell was sealed with PTFE coated fiberglass (Fiberflon, Fiberflon GmbH & Co. KG, Germany) to achieve 15% GDL compression. For PEMWE measurements, sintered titanium porous transport layers (PTLs; from Mott Corporation, USA) with a porosity of ~50 % as well as a carbon fiber paper-based gas diffusion layers (GDLs; TGP-H-120T without MPL, 20 wt% PTFE; from Toray, Japan) were used at the anode and at the cathode, respectively. The cell was sealed with virgin PTFE gaskets with a thickness chosen to achieve ~25% compression of the carbon GDL (assuming the titanium PTL to be incompressible; for further details see Ref.147).

2.6 Investigating the Reduction of Metal Oxides in an MEA

Besides using TGA analysis for a quick benchmarking of the reduction resistance of the various metal oxide catalysts in a H₂-containing atmosphere, the reduction resistance of selected OER catalysts was also investigated in an MEA under the

OCV conditions of a PEMFC anode; for this, 2000 nccm flow of fully humidified H₂ (anode) and 5000 nccm flow of fully humidified air (cathode) at 80 °C and 170 kPa_{abs} cell pressure (inlet controlled) were used (note that nccm refers to a volumetric flow rate in units of cm³min⁻¹, referenced to a pressure of 101.3 kPa and a temperature of 0 °C). The cell was kept under these conditions at OCV for an overall duration of 12 h. At different OCV holding time intervals, CVs of the anode (serving as working electrode) were recorded at ambient pressure and 40 °C, using a Gamry potentiostat (Reference3000, Gamry Instruments, USA) and applying a scan rate of 300 mV s⁻¹ in the potential range of 0.07-1.00 V_{RHE}. For this, fully humidified N₂ (5 nccm) was fed to the anode (serving as working electrode) and fully humidified 5 vol.% H₂/Ar (500 nccm) to the cathode electrode (serving as the counter and reference electrode); an extended N₂ purge of the anode humidifier was conducted before recording the CVs in order to remove any traces of gaseous hydrogen. The reduction resistance of the metal oxide catalysts was judged based on the changes observed in the voltammetric features after different hold times under H₂ at OCV. This is explained in great detail in sections 3.3 and 3.4.

2.7 X-ray Photoelectron Spectroscopy (XPS) Measurements

X-ray photoelectron spectroscopy (XPS) was performed on catalyst powders and on MEAs in order to analyze the surface chemistry of the samples. XPS was measured on a Kratos Axis Supra spectrometer using monochromatic Al K_α radiation at an energy of 1486.6 eV. The spectra were recorded at a total X-ray source power of 225 W (15 kV and 15 mA current). For XPS measurements of the catalyst powders, the samples were drop-casted onto a copper tape placed on a stainless steel sample holder. For XPS measurement of MEAs, the MEA samples were cut into small pieces (~5 × 5 mm) and attached to a self-adhesive copper tape (the electrode to be analyzed facing up), which in turn was attached to a stainless steel sample holder. High-resolution spectra were collected between 58-81 eV in order to detect the Ir 4f (~ 60-68 eV) and the Pt 4f

(~ 70-79 eV) signals, and the shown spectra represent the average of 10 individual spectra. All binding energy values are corrected using the adventitious carbon signal (C 1s = 284.8 eV).

2.8 X-ray Powder Diffraction (XPD) Measurements

X-ray powder diffraction (XPD) was performed using a Stadi P instrument (Stoe & Cie GmbH, Germany) with Cu-K α_1 radiation ($\lambda = 1.54059 \text{ \AA}$, 50 kV, 30 mA, Ge (111) monochromatized) and a Mythen 1 K position-sensitive detector (Dectris Ltd., Switzerland) in transmission mode. About 5 mg of a given catalyst powder sample was smoothly spread onto a scotch tape and placed in the center of the sample holder hole. The XPD patterns were acquired in the 2θ range of 20-90°, recording one data point every 0.015°/2 θ , amounting to a total measurement time of 2 h for each diffractogram.

2.9 N₂-physisorption Measurements

The specific surface area of the samples was measured by N₂ physisorption at 77 K using an Autosorb iQ gas sorption analyzer (Quantachrome Instruments, USA). All samples were evacuated at 120 °C for 12 h prior to the experiments. The sample mass was chosen to achieve a minimum absolute surface area of ~ 2.5 m² inside the sample vial. Adsorption isotherms were measured with 11 data points in the relative pressure range of $0.05 \leq p/p_0 \leq 0.30$, where p represents the gas pressure and p_0 the saturation pressure of N₂. The specific surface area was calculated according to the Brunauer-Emmet-Teller (BET) theory, whereby the ideal linear range was selected by the Micropore BET Assistant of the ASiQwin software (typically 7 out of the 11 points).

2.10 Transmission Electron Microscopy (TEM) Measurements

Transmission electron microscopy (TEM) was used for particle size analysis. A very small amount of sample was dispersed in DI water by ultrasonication and

then deposited onto a carbon-coated copper grid (Cu, 400 mesh, Formvar carbon film, Science Services). The obtained samples were then analyzed using a Philips CM100 electron microscope with an acceleration voltage of 100 kV.

3 Results

In this chapter, the journal articles comprising this PhD thesis are presented. In order to accelerate OER catalyst development, screening tools such as the RDE are necessary to assess the activity and durability of newly developed catalysts. In section 3.1, it will be shown that the shielding of catalyst active sites by oxygen bubbles is one of the major reasons for the rapid performance decay when measuring the activity and durability of OER catalysts using the RDE technique.¹³⁶ Subsequently in section 3.2, the OER catalyst stability data obtained from RDE measurements will be compared to stability data obtained with the same catalysts, when incorporated in an MEA and tested in a single-cell PEMWE.¹³⁵ This reveals that the OER performance of a catalyst decreases rapidly in RDE tests due to the accumulation of oxygen bubbles on/in the catalyst layer while its OER performance remains stable when tested in an MEA.

Section 3.3 investigates the stability challenges of anode OER co-catalysts in a PEMFC.⁵⁶ It is shown that the near-surface layer(s) of a conventional IrO₂ PEMFC anode co-catalyst can be completely reduced to metallic Ir upon exposure to H₂, e.g., under the operating conditions of a PEMFC anode. The formation of metallic Ir on the catalyst surface and its dissolution during the anode potential transients associated with SUSI events lead to an additional MEA performance decay due to iridium cross-over to cathode and a concomitant loss in the ORR activity of the cathode catalyst.⁵⁶ Since the origin of this degradation mechanism is the chemical reduction of the typically employed IrO₂ anode co-catalysts in the PEMFC anode, it is concluded that a reduction resistant OER catalyst would be required. Section 3.4 introduces an unprecedented approach to prepare reduction resistant IrO₂ catalysts by heat treatment,¹²⁰ and

section 3.5 introduces a novel approach to make reduction resistant IrO₂ and RuO₂-based catalysts by forming solid-solution phases of these PGM-oxides with other transition metal oxides.¹²¹

3.1 The Artefact in RDE-based OER Catalyst Durability Tests

This section presents the article “OER Catalyst Durability Tests Using the Rotating Disk Electrode Technique: The Reason Why This Leads to Erroneous Conclusions”, which was published in October 2020 in *ACS Applied Energy Materials*.¹³⁶ It is reprinted (adapted) with permission from the American Chemical Society. The article can be found under the permanent web-link: <https://doi.org/10.1021/acsaem.0c01944>.

This study identifies the main reason why OER catalyst durability tests using the RDE technique lead to erroneous results. While the lifetime of OER catalysts extends over many tens of thousands of hours when measured in an MEA in a PEMWE, durability tests using the RDE technique predict significantly shorter lifetimes.^{132, 148} Different explanations of this discrepancy exist in the literature: (i) passivation of the disk electrode substrate;¹³² (ii) formation of a less active Ir-species;¹³³ (iii) loss of OER active sites;¹³⁴ and (iv) shielding of the active sites by oxygen bubbles.¹³¹

By subjecting the electrochemical cell or the electrolyte to ultrasonication while conducting a typical RDE-based OER activity/stability measurement of a polycrystalline iridium disk electrode, it is demonstrated that the accumulation of microscopic oxygen bubbles is responsible for the rapid OER performance decay observed during the RDE experiments. It is shown that OER catalyst stability measurements at a typical constant current density of 10 mA cm⁻²_{disk} lead to a significant loss in performance within minutes. However, once an ultrasonication horn is placed in close proximity to the electrode and ultrasonication is applied, the performance remains relatively constant throughout the experiment. As a similar behavior is observed during potential cycling experiments, it is concluded

that the surprisingly high degradation rates observed during OER catalyst durability measurements using the RDE technique are clearly adulterated by shielding of catalyst active sites by microscopic oxygen bubbles. Identifying the source of performance deactivation is crucial to the development of reliable RDE measurement protocols that can be used to screen OER catalysts lifetime.

Author contributions

The hypothesis of using ultrasonication for the removal of oxygen bubbles was formulated during a discussion between H.A.E.-S., A.H.-W., and M.F.T., while all the authors contributed to the experimental design. H.A.E.-S. performed the RDE experiments. Analysis and interpretation of the RDE test results were done by H.A.E.-S., A.H.-W., and M.F.T., while A.H.-W. and M.F.T. wrote the manuscript. All authors discussed the experimental results and revised the manuscript.

OER Catalyst Durability Tests Using the Rotating Disk Electrode Technique: The Reason Why This Leads to Erroneous Conclusions

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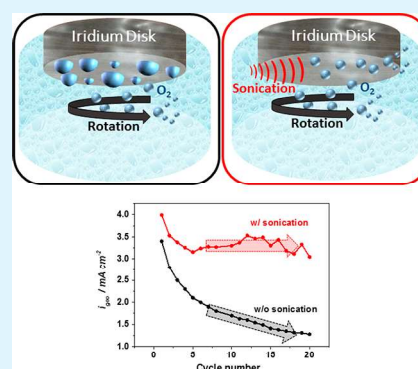


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ABSTRACT: This study reveals the physical origin of the rapid performance decay when measuring the activity and durability of oxygen evolution reaction (OER) catalysts using the rotating disk electrode (RDE) technique or other half-cell test configurations with liquid electrolyte. By subjecting the electrochemical cell or the electrolyte to ultrasonication while conducting a typical RDE-based measurement of the OER performance of a polycrystalline iridium-disk electrode, we demonstrate that it is the accumulation of microscopic oxygen bubbles that is responsible for the rapid OER catalyst performance decay observed during RDE experiments.



KEYWORDS: oxygen evolution reaction, iridium, rotating disk electrode, PEM water electrolysis, accelerated stress tests

Polymer electrolyte membrane water electrolysis (PEM-WE) is considered to be one of the most promising technologies for the production of pure hydrogen.^{1,2} One of its major drawbacks is the sluggish kinetics of the oxygen evolution reaction (OER) of the currently used iridium-based catalysts, and research in this field is thus focused on finding catalysts exhibiting high OER activities as well as long-term stability.^{3–5} It is well-established now that OER activities can be reliably measured in liquid electrolytes using cyclic voltammetry (CV) in stagnant electrolyte, the rotating disk electrode (RDE) technique, and flow-channel approaches,^{5–10} i.e., in half-cell configurations with liquid electrolytes or, alternatively, by testing membrane electrode assemblies (MEAs) in PEM-WEs.^{9,11–13} However, the OER catalyst lifetime determined in half-cell measurements with liquid electrolyte is orders of magnitude less than that measured in a PEM-WE.^{9,10} In order to accelerate catalyst development without the necessity of producing a few grams of newly synthesized catalysts that are needed for PEM-WE measurements, accelerated stress tests (ASTs) using methods that require only several milligrams of catalysts (namely, half-cell tests with liquid electrolyte) are needed. Unfortunately, all OER performance measurements in half-cell configurations with liquid electrolyte exhibit a rapid activity decay that has puzzled researchers for decades;^{14–16} this rapid activity decay also seems to be responsible for the many orders of magnitude shorter catalyst lifetime observed in RDE measurements if compared to measurements with the same catalyst in PEM-WEs.^{9,10} Therefore, identifying the origin of the catalyst

performance decay (with respect to activity and stability) obtained in half-cell experiments with liquid electrolyte is crucial in order to develop meaningful ASTs that can be conducted with small amounts of catalysts and that would thus allow one to accelerate the development of OER catalysts.

Four different hypotheses can be found in the literature explaining the rapid performance decay of OER catalysts measured in half-cells with liquid electrolyte: *Hypothesis I*, formation of an additional contact resistance between the catalyst layer and the electrode substrate due to the passivation of the electrode substrate during the measurement;¹⁷ *Hypothesis II*, the depletion of the OER-active species due to the formation of an anhydrous Ir oxide at the catalyst surface upon continuous polarization of the OER catalyst in the OER potential range;¹⁸ *Hypothesis III*, loss of active sites capable of forming the Ir(V)=O species via progressive cross-linking of iridium atoms¹⁵ (these species, Ir(V)=O, were proposed to be sufficiently electron deficient to undergo nucleophilic attack by substrate water and form the O–O bond); and *Hypothesis IV*, shielding of the catalyst active sites by the trapped oxygen microbubbles at the surface of the electrode and/or within the

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catalyst layer.¹⁰ With the help of ultrasonication, this study provides solid evidence that the microscopic oxygen bubbles shielding the OER-active sites (Hypothesis IV) are the main origin of the rapid OER performance decay in half-cell configurations with liquid electrolyte, as demonstrated by RDE measurements.

A three-electrode cell with a reversible hydrogen electrode (RHE) as a reference electrode and a high surface area Au wire as a counter electrode was used for all electrochemical measurements. As working electrode, a rotating ring-disk electrode (RRDE) consisting of a 5 mm diameter polycrystalline iridium disk (Pine Research Instrumentation, USA) and a platinum ring embedded in a PTFE body (Pine Research) were used. For measurements where the cell or the electrolyte was subjected to ultrasonication, the electrochemical cell was either partially immersed in an ultrasonic bath (S 30 H, Elmasonic, Germany) or the tip of a horn sonicator (Branson 450 Digital Sonifier, Branson Ultrasonics Corp., USA) was directly immersed in the electrolyte in the vicinity of the electrode surface. Prior to each measurement, the reference electrode potential was calibrated in a H₂-saturated electrolyte using the platinum ring of the RRDE assembly, and all potentials are referenced versus RHE. A 0.1 M H₂SO₄ electrolyte was prepared by mixing high purity H₂SO₄ (Ultrapur, 96%, Merck Millipore KGaA, Germany) and ultrapure water (18.2 MΩ cm at 20 °C, Merck Millipore). An Autolab potentiostat (PGSTAT302N, Metrohm AG) and a rotator (Pine Research) with a polyether ketone shaft were used to perform the electrochemical measurements. Electrochemical impedance spectroscopy (EIS) in the frequency range of 100 kHz to 100 Hz at open circuit potential (OCP) was used to determine the noncompensated solution resistance between the reference and working electrodes.

In order to investigate the OER performance decay, the potential of the Ir disk was cycled between 1.2 and 1.65 V_{RHE} at 20 mV s⁻¹. Figure 1A shows the successive anodic sweeps of the iridium disk at a rotation rate of 2500 rpm. A continuous decay in performance of the electrode over the course of potential cycling is observed in the absence of ultrasonication (black curves in Figure 1A). The geometric current densities extracted from the curves in Figure 1A at a potential of 1.55 V_{RHE} are shown in Figure 1B versus the number of potential cycles, illustrating the severe performance loss of the iridium disk, with the current density continuously decreasing from an initial value of ~3.4 to ~1.3 mA cm⁻²_{geo} after 20 cycles (black circles). Since this performance decay of the iridium disk is analogous to the performance decay that is observed with a catalyst layer deposited on a disk electrode substrate (i.e., in a so-called thin-film RDE experiment),^{10,12,19} the formation of an additional contact resistance between the catalyst layer and the disk electrode substrate due to the passivation of the latter (Hypothesis I, proposed by Geiger et al.¹⁷) can be excluded as the main reason for the rapid OER activity performance decay.

Next we will examine Hypothesis IV, namely, whether microscopic oxygen bubbles that form on the surface of the iridium disk are the cause of the observed rapid performance decay. In order to investigate this hypothesis, the RDE cell was placed in an ultrasonic bath in order to facilitate the removal of possibly formed microscopic oxygen bubbles on the surface of the iridium disk. Surprisingly, using an identical potential cycling procedure in the presence of cell ultrasonication, the OER performance remained relatively constant over the course of successive voltage cycles (red curve in Figure 1A). While the

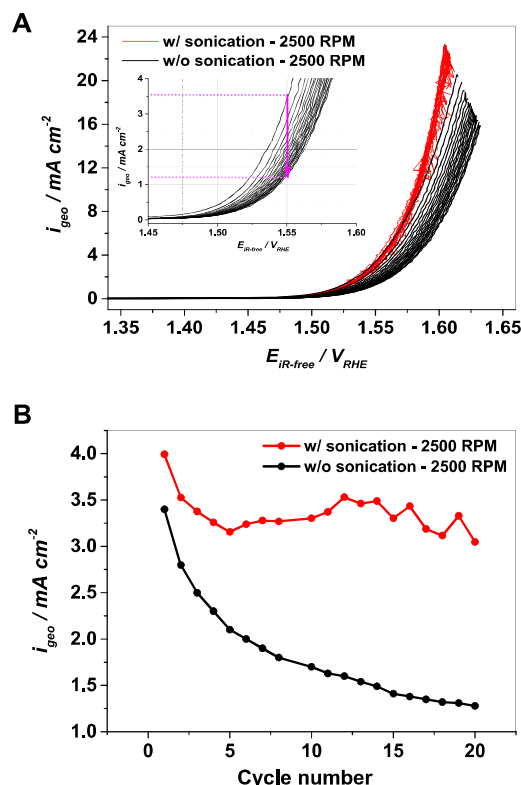


Figure 1. (A) OER cyclic voltammetry (anodic sweeps) of a polycrystalline Ir disk in non-deaerated 0.1 M H₂SO₄ at a scan rate of 20 mV s⁻¹ and a rotation rate of 2500 rpm without ultrasonication (black line) and with ultrasonication (red line) of the cell in an ultrasonic bath. The inset is a close-up of successive anodic sweeps in the absence of ultrasonication. (B) Decay in the OER current density extracted from the OER polarization curves (A) at 1.55 V_{RHE} versus the number of successive sweeps.

application of sonication does not affect the formation of an anhydrous Ir oxide (Hypothesis II) nor the progressive cross-linking of iridium atoms (Hypothesis III), as these are both potential and time dependent processes, ultrasonication is expected to improve the removal of microscopic oxygen bubbles that are forming on the Ir-disk surface or, by extension, on the catalyst layer surface in a thin-film RDE experiment. Hence, the depletion of OER-active sites on the catalyst surface according to Hypotheses II¹⁸ and III¹⁵ does not seem to be responsible for the observed performance decay. At the same time it is noted that the current density measured at 1.55 V_{RHE} decreases within the first 5 cycles from an initial value of ~4.0 to ~3.2 mA cm⁻²_{geo}, even though it remains rather constant (~3.3 mA cm⁻²_{geo}) after 5 cycles (red circles in Figure 1B). This suggests that already within the first cycle, oxygen bubbles are continuously accumulating on the Ir-disk surface, shielding more and more OER-active sites. Therefore, the applied ultrasonication is not strong enough to fully remove the produced microscopic oxygen bubbles, while it is strong enough to demonstrate that the accumulation of microscopic oxygen bubbles is responsible for the observed rapid performance decay.

Applying a constant current (typically 10 mA cm⁻²_{geo}) and monitoring the potential versus time in a half-cell configuration with liquid electrolyte is the prevalent OER catalyst stability test in the literature.^{4,20,21} During this type of experiment, the increase in OER overpotential at constant current is

interpreted as catalyst degradation, ultimately resulting in a rapid jump of the potential to $>2.1 V_{\text{RHE}}$.^{4,10,17} Figure 2A

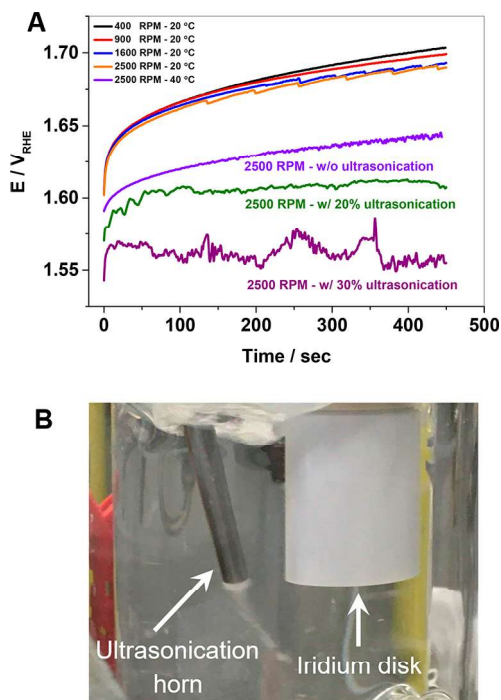


Figure 2. (A) Constant current experiment at $10 \text{ mA cm}^{-2}_{\text{geo}}$ of a polycrystalline Ir disk in non-deaerated $0.1 \text{ M H}_2\text{SO}_4$ without sonication at 400, 900, 1600, and 2500 rpm as well as at 2500 rpm when the electrolyte is subjected to ultrasonication by means of an ultrasonic horn at different ultrasonication power settings of 20% and 30%. (B) Picture of the RDE setup with the ultrasonic horn immersed in the electrolyte and placed in close proximity to the Ir-disk electrode.

shows the initial phase of such a constant current experiment for the iridium disk at $10 \text{ mA cm}^{-2}_{\text{geo}}$, where the first 300 ms after application of the current are not shown due to the strong capacitive contributions to the OER current at $<300 \text{ ms}$. As expected for the case where no ultrasonication is applied and the electrode is only rotated, the voltage rapidly increases within 450 s from $\sim 1.6 V_{\text{RHE}}$ after 300 ms up to $\sim 1.7 V_{\text{RHE}}$ at the lowest rotation rate of 400 rpm (black curve). The effect of the rotation rate is rather weak, showing an only $\sim 10 \text{ mV}$ lower potential after 450 s at the highest rotation rate of 2500 rpm (orange curve).

Next we will examine the effect of ultrasonication on this rapid potential increase within the initial 450 s. However, as ultrasonication of the cell using the ultrasonic bath was shown to be unable to completely suppress the performance decay over the course of the initial sweeps (see red symbols in Figure 1B), it is unlikely that a constant current experiment with this type of ultrasonication would result in a stable OER performance over time. Therefore, a modular cup horn ultrasonicator with adjustable power was placed directly into the electrolyte, in close proximity to the iridium electrode (Figure 2B). Conducting the constant current experiment at the same current density of $10 \text{ mA cm}^{-2}_{\text{geo}}$ at 2500 rpm and at an ultrasonicator power setting of 20% (green curve in Figure 2A), the voltage after the initial 300 ms is now $\sim 30 \text{ mV}$ lower than without ultrasonication ($\sim 1.57 V_{\text{RHE}}$) and the loss of OER performance after 450 s is 80 mV lower (orange curve).

The lower starting potential again implies that the accumulation of oxygen bubbles occurs immediately upon applying a constant current and that strong ultrasonication in conjunction with the rotation of the electrode seems to facilitate the removal of microscopic bubbles that are formed on the Ir-disk surface. However, even in this case, the potential increases within the first 100 s of the experiment before reaching a constant value, which suggests that the applied sonication is still not sufficient to completely prevent the accumulation of oxygen bubbles. Therefore, the sonication power was further increased to 30% (purple curve in Figure 2A), and as a result, the initial potential ($\sim 1.55 V_{\text{RHE}}$) is lower by another $\sim 20 \text{ mV}$. Interestingly, unlike the other potential versus time transients, after $\sim 5 \text{ s}$ the potential now remains constant at a very low value of $\sim 1.56 V_{\text{RHE}}$ until the end of the experiment at 450 s, which implies that the rate of formation and removal of oxygen bubbles on the Ir-disk surface reaches a steady state without any further accumulation of oxygen bubbles. The observed behavior cannot be attributed to thermal effects during ultrasonication as the temperature never exceeded 40°C by the end of the experiment and that performing the constant current experiment without ultrasonication at 40°C (violet curve in Figure 2A) resulted in a continuously increasing potential and a plateau was never observed. This experiment thus firmly proves that the accumulation of microscopic oxygen bubbles is responsible for the performance decay (both with respect to activity and stability) observed in half-cell measurements with liquid electrolyte and that this must be the main origin of the large discrepancy (by many orders of magnitude) in OER catalyst stability when measured in half-cells with liquid electrolyte (e.g., by in RDE measurements) compared to measurements of the same catalyst in an MEA tested in a PEM-WE.⁹

It has to be noted that all experiments in this study were performed using an Ir-disk electrode, where ultrasonication does not affect the physical stability of the catalyst. However, catalysts for application in actual PEM-WEs are generally in particulate form, with primary catalyst particle agglomerate dimensions on the order of several hundred nanometers,²² so that for the evaluation of their OER activity and stability in half-cells with liquid electrolyte the catalysts are drop-cast on an electrochemically inert electrode substrate (e.g., a glassy carbon or gold disk electrode substrate for RDE measurement). In this case, subjecting the cell or the electrolyte to ultrasonication would lead to a physical detachment of the catalyst particles from the electrode substrate, so that ultrasonication is not feasible. Nevertheless, the aim of this study was to prove that the accumulation of microscopic oxygen bubbles forming on the catalyst surface is the main origin of the observed rapid performance decay of OER catalysts in RDE experiments, independent of whether solid disk electrodes (such as the Ir disk in this study) or thin-film catalyst layers deposited on a disk electrode substrate are used.

Assuming that this hypothesis is true, one would perhaps expect that the performance decay should be fully reversible after removal of the oxygen bubbles by, e.g., equilibrating the electrode after the stability test in inter gas purged electrolyte for a long time. This is indeed true in cases where the electrode potential has not increased beyond $\sim 1.65 V_{\text{RHE}}$ over the course of the experiment, but once the OER potential has significantly exceeded this value, a loss of catalyst surface and catalyst dissolution are observed.^{6,10} If iridium or iridium oxide indeed undergo dissolution beyond $\sim 1.65 V_{\text{RHE}}$, it raises the question

as to why this phenomenon would not occur equally in the OER catalyst layer in the MEAs used in PEM-WEs. The answer is surprisingly straightforward: the OER catalyst layer potential (iR -corrected) in PEM-WEs never exceeds $1.6 V_{\text{RHE}}$, even at current densities as high as $3\text{--}4 \text{ A cm}^{-2}_{\text{geol}}$ ^{9,22,23} which thus explains the 4–5 orders of magnitude longer OER catalyst lifetimes observed in PEM-WEs compared to stability tests in half-cell configuration with liquid electrolyte, where the OER catalyst potential rapidly increases beyond $1.65 V_{\text{RHE}}$. The large difference in OER overpotential between these two measurement setups is, we believe, due to a different extent of shielding of the active catalyst by microscopic oxygen bubbles.

In summary, by comparing the OER performance decay of an Ir-disk electrode in an RDE configuration, either in the absence or in the presence of ultrasonication of the cell/electrolyte, we have shown not only that ultrasonication decreases the initial OER overpotential in constant current experiments but that it also can lead to a stable and $\sim 150 \text{ mV}$ lower OER overpotential after 450 s of constant current polarization. Our analysis provides clear evidence that it is the shielding of the OER catalyst by microscopic oxygen bubbles (increasing over time) that is responsible for the observed OER performance decay in half-cell experiments with liquid electrolyte. The accompanied lowering of the OER catalyst utilization at a fixed constant current then increases the OER overpotentials to values high enough to induce iridium dissolution. The fact that the OER overpotentials for the same catalyst and for the same mass specific current density (in $\text{A g}_{\text{Ir}}^{-1}$) are much lower in PEM-WEs suggests a different extent of OER catalyst shielding by microscopic oxygen bubble⁹ and is a straightforward explanation for the 4–5 orders of magnitude higher catalyst lifetime in PEM-WEs compared to that determined in half-cells with liquid electrolyte.

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Notes

The authors declare no competing financial interest.

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3.2 OER Catalyst Activity and Durability Tests: RDE vs MEA

This section presents the article “The Discrepancy in Oxygen Evolution Reaction Catalyst Lifetime Explained: RDE vs MEA - Dynamicity within the Catalyst Layer Matters”, which was published in January 2021 in the *Journal of The Electrochemical Society*.¹³⁵ It is an open access article distributed under the terms of the Creative Commons Attribution 4.0 License (CC BY). The article can be found under the permanent web-link: <https://doi.org/10.1149/1945-7111/abdcc9>. Additionally, the study was presented by Hany A. El-Sayed at the 236th Meeting of the Electrochemical Society (October 13-17, 2019, Atlanta, Georgia, abstract number: I01F-1749).

The development of OER catalysts for PEMWEs requires the use of reliable methods for both activity and stability testing. As long-term stability testing under realistic conditions is not feasible due to the very low degradation rates in PEMWEs, which would require 1000's of hours testing to obtain significant degradation, accelerated degradation tests are typically performed using the RDE method or testing an MEA in PEMWE setup.^{65, 97, 148-151} Unfortunately, the catalyst lifetime estimated on the basis of RDE measurements is orders of magnitude lower than that obtained from MEA-based tests, which results in underestimating the lifetime of many OER catalysts.^{13, 131}

This study reveals the source of discrepancy between the lifetime of OER catalysts determined by RDE measurements and that obtained in an MEA in a PEMWE. A comprehensive comparison of all of the most commonly used accelerated degradation test modes (constant current, constant potential, and potential cycling) for RDE- or MEA-based tests is provided. All the accelerated degradation tests show that the accumulation of microscopic oxygen bubbles in the catalyst layer during OER takes place in both test environments. However, this accumulation was found to be much more significant in RDE measurements, where the shielding of almost all of the catalyst active sites by gas bubbles leads to a rapid catalyst performance deterioration and misleading experimental

artefacts. Therefore, electrochemical cells with liquid electrolytes, such as RDE and flow-channel techniques, are not reliable for OER catalyst lifetime determination. In the end, an explanation is provided as to why the accumulation of microscopic oxygen bubbles in the catalyst layer is much more significant in RDE testing.

Author contributions

M.F.T. fabricated catalyst inks and performed the RDE experiments. A.H.-W. fabricated membrane electrode assemblies and performed electrochemical testing in a PEMWE. M.F.T and A.H.-W. analyzed the experimental test results. A.H.-W. and M.F.T. wrote the manuscript and H.A.G. and H.A.E.-S. edited it. All authors discussed the experimental results and revised the manuscript.



The Discrepancy in Oxygen Evolution Reaction Catalyst Lifetime Explained: RDE vs MEA - Dynamicity within the Catalyst Layer Matters

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This study reveals the source of discrepancy between the lifetime of oxygen evolution reaction (OER) catalysts determined by rotating disk electrode (RDE) measurements vs that obtained in a membrane electrode assembly (MEA) in an electrolyzer. We show that the accumulation of microscopic oxygen bubbles in the pores of the electro-catalyst layer during the OER takes place in both RDE and MEA measurements. However, this accumulation was found to be much more significant in RDE measurements, where the shielding of almost all of the catalyst active sites by gas bubbles leads to rapid performance deterioration. This decrease in performance, albeit largely reversible, was found to also induce irreversible catalyst degradation, which could be avoided if the accumulation of microscopic bubbles is prevented. This type of artefact results in vastly under-estimated catalyst lifetimes obtained by RDE experiments, resulting in values that are orders of magnitude shorter than those obtained using MEA measurements, and a hypothesis for this discrepancy will be proposed. Therefore, electrochemical cells with liquid electrolytes are not reliable for OER catalyst lifetime determination.

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The slow kinetics of the oxygen evolution reaction (OER) is a major challenge in the electrochemical production of hydrogen from water by proton exchange membrane water electrolysis (PEM-WE). To date, IrO₂ and RuO₂ are the most investigated catalysts in the literature for OER catalysis.^{1–3} In order to identify a suitable OER catalyst, its activity and long-term stability are of an equally critical importance. Reliable methods for screening the activity have been established using rotating disk electrode (RDE) and flow-channel techniques or testing membrane electrode assemblies (MEAs) in PEM-WEs.^{4–10} However, the evaluation of the long-term stability of OER catalysts under realistic conditions is not feasible due to the rather low degradation rate in PEM-WEs, which would require 1000's of hours of testing to obtain significant degradation.^{11,12} Therefore, accelerated degradation tests are required, which are typically performed in cells with liquid electrolyte or in PEM-WEs.^{12–17} Generally, accelerated degradation tests are performed using one or more of three different methods: i) constant current holds (chronopotentiometry), ii) constant potential holds (chronoamperometry), and iii) potential cycling.¹⁸

Applying a constant current is the prevalent testing method in the literature.¹⁹ In this method, which is carried out in an RDE setup, the increase in OER overpotential at constant current operation is taken as a measure for catalyst stability, where a drastic potential jump is interpreted as the end of life (EOL) of the catalyst.^{15,20–22} Alternatively, constant potential and potential cycling methods are also utilized to perform accelerated degradation tests in which the deterioration of current as a function of time or cycle number is taken as representative of catalyst stability.^{8,23–29}

It is well established now that there is a discrepancy between a catalyst lifetime obtained from RDE and PEM-WE under similar operating conditions.^{14,30,31} The extremely short lifetime of a

catalyst obtained from RDE testing using the constant current method and indicated by the sudden potential jump was attributed to the disk electrode substrate passivation, making the catalyst no longer electrochemically accessible due to the high contact resistance.¹¹ On the other hand, Tan et al. evaluated a variety of Ir-based catalysts and showed that the phase transformation of the active sites from the highly OER-active hydrous Ir oxy-hydroxide to the less OER-active anhydrous-IrO_x exerts a harsher oxidative condition (higher potentials) on the electrode.³²

The OER catalyst performance loss during RDE based stability measurements can, at least in part, be ascribed to the passivation of the RDE disk material, to the dissolution and/ or the physical detachment of the OER catalyst (as evidenced by the quantification of dissolved Ir after RDE tests),³² and to the accumulation of microscopic oxygen bubbles within the catalyst layer. In our recent studies, we discovered the effect of the latter on the stability results obtained from RDE experiments.^{31,33} We have shown that the accumulation of microscopic oxygen bubbles in the pores of a catalyst layer during constant current electrolysis in RDE measurements is causing the apparent catalyst deactivation and failure.³¹ The effect of such microscopic bubbles on the performance loss of a catalyst during a gas-evolving reaction was further proven by subjecting the electrochemical cell or the electrolyte to ultrasonication while conducting a typical RDE-based measurement.^{33,34}

In this study, we demonstrate that the accumulation of microscopic oxygen bubbles in the catalyst layer strongly affects the outcome of RDE based durability tests, independent of whether they are based on constant current, constant potential, or potential cycling methods. In addition, we show that the same phenomenon leads to a decay of OER catalyst activity in PEM water electrolyzer based aging tests, in which case, however, the OER activity loss can be fully recovered, even after 100's of hours. We also provide an explanation as to why the accumulation of microscopic oxygen bubbles in the catalyst layer is detrimental in RDE testing, while in MEA based tests in an electrolyzer it only causes reversible degradation processes that are fully recoverable.

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Experimental

Rotating disk electrode (RDE).—Electrochemical measurements were carried out in a water jacketed three-electrode cell using a reversible hydrogen electrode (RHE) as a reference electrode, a high surface area Au wire as a counter electrode and a rotating ring-disk electrode (RRDE) consisting of a 5 mm diameter polycrystalline Au disk and Pt ring supported by PTFE body (Pine Research Instrumentation, USA) as a working electrode. The reference electrode potential was calibrated in a H₂-saturated electrolyte prior to each experiment using the Pt ring of the RRDE.

A 0.05 M H₂SO₄ aqueous solution was used as electrolyte, which was prepared by mixing high purity H₂SO₄ (Ultrapur, 96%, Merck Millipore KGaA, Germany) and ultra-pure water (18.2 MΩ cm at 20 °C, Merck Millipore KGaA, Germany). High purity Ar and H₂ (6.0-grade, Westfalen AG) were used to purge the electrolyte.

All RDE electrochemical measurements were performed using an Autolab potentiostat (PGSTAT302N, Metrohm AG) and a rotator (Pine Research Instrumentation) with a polyether ketone shaft. The electrode rotation rate was fixed at 2500 RPM and the electrolyte temperature was maintained at 40 °C using the water jacket. Freshly coated electrodes were dipped in Ar-saturated electrolyte and the non-compensated solution resistance between the reference and working electrode was determined by electrochemical impedance spectroscopy (EIS) from 100 kHz to 100 Hz at open circuit potential (OCP). Then, cyclic voltammetry (CV) was performed between 0.05–1.25 V vs RHE with 20 mVs⁻¹ scan rate for 10 cycles. Afterwards, the OER polarization curve was recorded between 1.2–1.55 V vs RHE at 10 mVs⁻¹. The catalyst OER stability tests were performed by the constant current, constant potential and potential cycling methods in Ar-saturated electrolyte. The initial 100 ms of the constant current and constant potential measurements were excluded in the final graphs in order to eliminate the capacitive contributions to the OER current. This time approximately corresponds to five times the time constant (RC) of the RDE configuration, as calculated by EIS results (not shown here). Due to decay of the current during the constant potential stability measurements, an online iR compensation was utilized in order to apply a constant iR-free potential of 1.53 V_{RHE} to the electrode according to the following equation:

$$E_{iR-free} = E_{measured} - i_{OER} \times R$$

where R is the high frequency resistance measured by EIS prior to each measurement.

Before each measurement, the Au working electrode was polished with 0.3 μm alumina polishing suspension (Buhler AG) and sonicated in ultrapure water for several times. The catalyst ink suspension was prepared using 10.46 mg of IrO₂ supported on TiO₂ (IrO₂/TiO₂ with 75 wt.% iridium, Elyst Ir75 0480 from Umicore, Germany), 2 ml ultrapure water, and 2.4 μl Nafion[®] ionomer solution (5 wt.% ionomer, Sigma Aldrich) in order to achieve ≈1 wt.% ionomer content in the final coating. The suspension was sonicated for 30 min in a sonication bath (Elmasonic S 30 H, Elma Schmidbauer GmbH) in order to achieve a homogenous ink. The temperature of the bath was maintained below 35 °C in order to prevent solvent evaporation. Finally, 20 μl of the prepared ink was drop-casted on the cleaned Au working electrode in order to achieve an iridium loading of 0.4 mg_{Ir} cm⁻²_{disk}. Since RDE is known to be a thin-film technique with controlled mass-transport, high loadings and thus, thick catalyst layers, should be avoided.³⁵ Due to the rather high packing density of the IrO₂/TiO₂ catalyst (≈2.3 g_{Ir}cm⁻³),³⁶ a loading of 0.4 mg_{Ir} cm⁻²_{disk} already results in a ≈1.7 μm thick catalyst layer. Since this is already quite thick, a higher loading was not feasible within the RDE setup.

Membrane electrode assembly (MEA) preparation and cell assembly.—Using the decal transfer method, MEAs with an active area of 5 cm² were prepared. Platinum supported on Vulcan XC72

carbon (45.8 wt.% Pt/C, TEC10V50E from Tanaka, Japan) was used as a hydrogen evolution reaction (HER) catalyst on the cathode electrode and IrO₂ supported on TiO₂ (same as above) as an OER catalyst on the anode electrode. The inks were prepared by mixing de-ionized (DI) water (18 MΩ cm), 2-propanol (purity ≥ 99.9% from Sigma Aldrich) and Nafion[®] ionomer solution (20 wt.% ionomer, D2021 from IonPower, USA) together with the respective amount of catalyst. After mixing the suspension for 24 h using a roller mixer, where ZrO₂ grinding balls (5 mm diameter) were added to achieve a homogenous suspension, the ink was coated onto a thin plastic foil (PTFE, 50 μm thick, from Angst + Pfister, Germany) using the Mayer rod technique. After drying, 5 cm² decals were cut from the coating and hot-pressed onto a Nafion[®] 212 membrane (50 μm thick, from Quintech, Germany) at 155 °C for 3 min at a pressure of 2.5 MPa. The actual weight of the decals was determined by weighing the decals before and after the hot-pressing. Throughout the study, the loading was kept constant at 0.3 ± 0.1 mg_{Pt} cm⁻²_{MEA} for the hydrogen cathode and 1.9 ± 0.2 mg_{Ir} cm⁻²_{MEA} for the oxygen anode, respectively. Since low loadings (<0.6 mg_{Ir}cm⁻²_{geo}) lead to additional performance losses due to an inhomogeneous catalyst³⁷ and in order to be more representative of state-of-the-art loadings (≈2.3 g_{Ir}cm⁻³),³⁸ a rather high loading compared to the RDE setup was chosen for the MEA configuration. The ionomer content was ≈11 wt.%. Sintered titanium (from Mott Corporation, USA) with a porosity of ≈50% and a thickness of 280 ± 10 μm was used as a porous transport layer (PTL) on the anode, whereas on the cathode, a carbon fiber paper (TGP-H 120 T from Toray, no MPL, 20 wt.% PTFE) with a thickness of 370 ± 10 μm was used. The MEA and the PTLs were placed between the flow fields of the electrolyzer cell, and additional virgin PTFE sheets were used as gaskets. A compression of 25% for the carbon PTL was achieved by choosing the right thickness of the gaskets. Specific details about the cell hardware are reported elsewhere.³⁹

Electrochemical characterization of MEAs.—An automated test station from Greenlight Innovation was used to perform all the electrochemical measurements of the MEAs. Throughout the whole test, the anode was supplied with 5 ml min⁻¹ deionized (DI) water, which was pre-heated to 80 °C for the MEA conditioning procedure and to 40 °C before the stability measurements. During the stability measurements, the cell temperature was kept constant at 40 °C and the produced gas on the anode side was diluted with nitrogen (100 nccm) to avoid the formation of an explosive gas mixture due to hydrogen permeation through the membrane into the anode compartment. Initially, the cell was conditioned at 1 A cm⁻² for 30 min at 80 °C under nitrogen atmosphere. Subsequently, three consecutive polarization curves were taken at ambient pressure (1 bar_a) and 80 °C, by increasing the current density from 0.01 to 4 A cm⁻² stepwise and holding at each current for 5 min to ensure a stable cell voltage. The last 10 s of the cell voltage at each current density were averaged. Considering these polarization curves as part of the conditioning, they were not included in the analysis. Subsequently, another polarization curve was recorded at 40 °C, which was used as a reference (beginning of test, BOT). Additionally, AC impedance measurements were performed at each current density in a range from 100 kHz to 1 Hz. The amplitude of the current perturbation was adjusted for each step individually in order to fulfill the criteria of linearity, while still maintaining a sufficient signal to noise ratio. The high-frequency intercept with the real axis in a Nyquist plot was used to determine the high frequency resistance (HFR). At the beginning of test (BoT) as well as at the end of test (EoT), cyclic voltammograms (CVs) of the anode electrode were recorded by flushing the cathode counter electrode with dry H₂ (50 ml min⁻¹) to ensure a stable reference potential and supplying the anode electrode with DI water (5 ml min⁻¹). The CVs were recorded in a potential range of 0.05 V–1.25 V at 20 mV s⁻¹ and 40 °C. Moreover, a linear sweep voltammogram (LSV) was recorded at BoT in a potential range of 1.25–1.65 V at 10 mV s⁻¹ and 40 °C to determine the OER activity under CV conditions. During the chronoamperometric aging

test, the measured decay in current was found to lead to a small difference in Ohmic overpotential (BoT ($61 \text{ A/g}_{\text{Ir}}$) $\approx 10 \text{ mV}$; EoT ($33 \text{ A/g}_{\text{Ir}}$) $\approx 5 \text{ mV}$), therefore, no iR-compensation was required in this test.

Results and Discussion

Activity comparison of RDE and MEA measurements.—To identify the main reason for the remarkably different catalyst lifetimes estimated using MEA and RDE, we have employed a variety of OER catalyst durability testing procedures using a commercially available OER catalyst ($\text{IrO}_2/\text{TiO}_2$). As stability measurements require comparing applied potentials with corresponding currents or vice versa, it is important to confirm that both RDE and MEA measurements result in comparable OER activities. Therefore, the activities recorded from the two techniques were assessed.

Figure 1a shows the iridium mass-specific LSVs of the $\text{IrO}_2/\text{TiO}_2$ catalyst in the OER potential region for three RDE measurements (green lines) and two MEA measurements (blue circles and squares); Fig. 1b shows the corresponding Tafel plots. The results clearly indicate that within each technique, the measurements are quite reproducible. However, comparing the two techniques, the mass-specific OER activities obtained in RDE measurements are higher than those obtained in MEAs. This difference in activity may be explained either by the poor utilization of the catalyst in the MEAs, by the different loadings used in the two techniques, or by the effect of the ionomer content (Further details can be found in supplementary note A-1 available online at stacks.iop.org/JES/168/014512/mmedia). A poor utilization of the catalyst in the MEAs is excluded as the mass-specific capacitive currents of the MEAs (blue lines in Fig. 1c) are almost twice as large as the ones recorded in RDE experiments (green lines in Fig. 1c). A closer look shows that the polarization curve measured in MEA seems to be off by a constant value of $\approx 20 \text{ mV}$ over a wide range of current density. Bernt et al.⁴⁰ showed that a local increase in partial pressure of oxygen at the electrode can lead to an additional loss in performance. The same holds true for an increase in partial pressure of hydrogen. By using a similar approach as Bernt et al., the 20 mV higher potential measured in MEA would equate to a difference in oxygen partial pressure of $\approx 10 \text{ bar}$ or in hydrogen partial pressure of $\approx 2 \text{ bar}$ ($\Delta p = p_{\text{gas,cat}} - p_{\text{gas,channel}}$). Although the values seem to be reasonable, Bernt et al. also showed a dependency on current density, which cannot be observed in this case. Hence, it is rather unlikely that an increase in partial pressure of oxygen and/or hydrogen within the catalyst layer is responsible for this discrepancy in activity.

It is, however, well known for platinum that high ionomer loadings can negatively impact the ORR activity³⁵ and thus the higher ionomer content used within the MEA configuration might explain the lower activity measured. As can be seen in figure A-1 within the supporting information the application of a higher ionomer content (20 wt.%) within the RDE configuration results in a significantly lower activity (≈ 3.5 -times at $1.5 \text{ V}_{\text{RHE}}$ (HFR-corrected)). Additionally, Bernt et al. showed that with increasing ionomer content, the activity is slightly decreasing.³⁹ Although no further studies were carried out to measure the change in activity as a function of ionomer content within the RDE configuration, we believe that the different ionomer contents used (1 wt.% ionomer in RDE measurements vs 11 wt.% in MEA measurements) are the origin of the discrepancy in OER activity measured by RDE and MEA. Nevertheless, the results obtained by both techniques are in reasonably good agreement; and therefore stability measurements were successfully assessed as shown in the next sections.

Chronopotentiometric (CP) aging test.—CP is the most frequently used method in the literature to estimate the stability of an OER catalyst by RDE measurements, where the observed increase in potential while applying a constant current is attributed to catalyst degradation, and ultimately to a complete loss of active

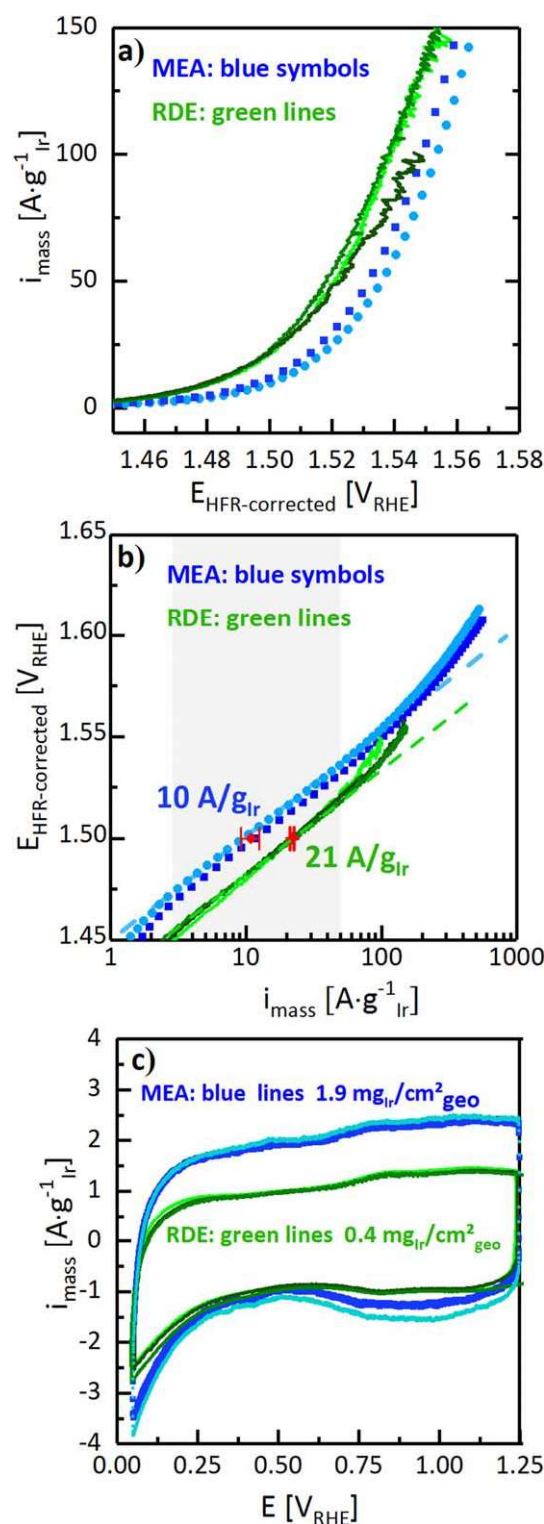


Figure 1. (a) Iridium mass-specific linear sweep voltammograms of the $\text{IrO}_2/\text{TiO}_2$ catalyst at 40°C and 10 mV s^{-1} in MEAs (blue circles and squares) and in RDE experiments (green lines, $0.05 \text{ M H}_2\text{SO}_4$, Ar-saturated); (b) Tafel-plots (constructed from a) for three RDE measurements (green lines) and two MEA measurements (blue circles and squares), including the averaged activity determined at $1.50 \text{ V}_{\text{RHE}}$ (HFR-corrected) indicated by the red symbols; (c) Cyclic voltammograms in the purely capacitive voltage region at 20 mV s^{-1} for three RDE measurements in Ar-saturated electrolyte (green lines) and for two MEA measurements with 50 ncm H_2 at the cathode side (blue lines).

material.^{41–44} Figure 2a shows the potential transient recorded in

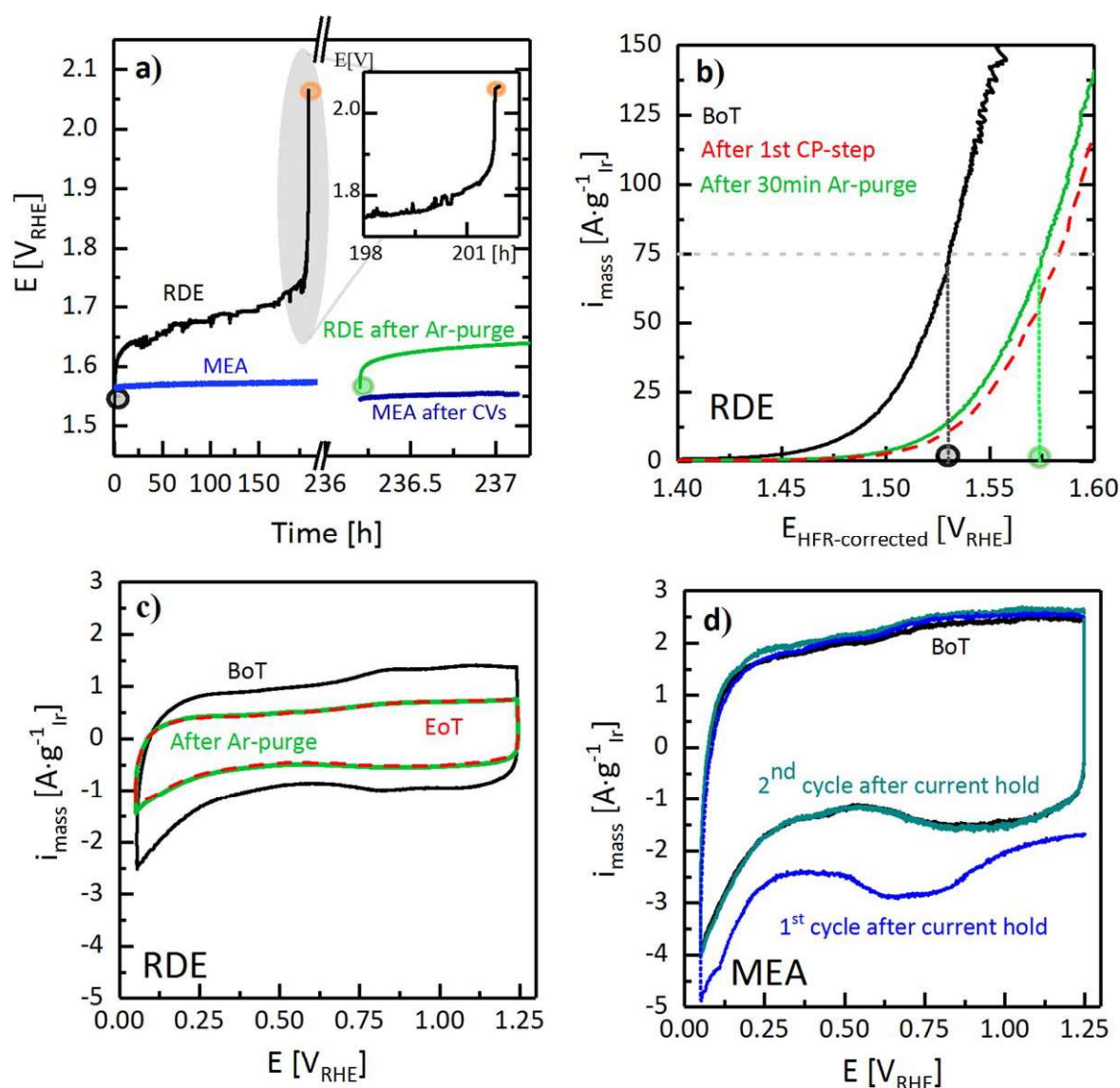


Figure 2. (a) Chronopotentiometry at $70 \text{ A g}^{-1}_{\text{Ir}}$ of RDE measurements at BoT (black) and after purging with Ar for 30 min. (Ar-CV; 20 mVs^{-1}) (green curve) and MEA measurements at BoT (light blue) and after CV (50 ncm H_2 at the cathode) (dark blue). Inset shows the last hours of the first CP-step of the RDE measurements. (b) Mass-specific polarization curves for RDE measurements at BoT (black), after first CP-step and Ar-CV (green) and after second CP-step (EoT) and Ar-CV (red) recorded at 10 mV s^{-1} . (c) Cyclic voltammograms for RDE measurements recorded at BoT (black), after first CP-step (green) and after second CP-step (dotted red) at 20 mV s^{-1} in an Ar-purged electrolyte. (d) Cyclic voltammograms recorded for MEA measurements at BoT (black) and after first CP-step at 20 mV s^{-1} , where the first (blue) and the second (cyan) cycles after first CP-step are shown.

MEA and RDE measurements at a current density of $70 \text{ A g}^{-1}_{\text{Ir}}$. In the RDE experiment, the potential increases continuously (black line in Fig. 2a) reaching $\approx 1.75 \text{ V}$, at which a sudden potential jump occurs. Subsequently, the potential levels out at $\approx 2.1 \text{ V}$ (orange circle, Fig. 2a inset), a potential one would measure when the same geometric current is applied to a bare Au-disk.³¹ This behavior is typically interpreted in the literature by the degradation of the catalyst.^{32,44} According to Eq. 1, an increase in OER overpotential (η) by one Tafel slope (TS; ca. 50 mV in this case) at a constant current (i), should correspond to a 90% loss of electrochemically active surface area or electrode roughness factor Ref. 31. Therefore, and according to this degradation hypothesis, no catalyst should remain after a total potential increase of $>400 \text{ mV}$ (black line in Fig. 2a).

$$\eta = TS \cdot \left[\lg \left(\frac{i}{i_0} \cdot \frac{1}{rf} \right) \right] \quad [1]$$

However, after the applied current was stopped and the electrolyte was purged with Ar for 30 min at 2500 rpm, followed by applying the same current ($70 \text{ A g}^{-1}_{\text{Ir}}$), the starting potential of this second CP-step was almost the same as that of the first CP-step, showing the same gradual increase of potential (green line in Fig. 2a). This result indicates that the catalyst did not collapse as suggested by the potential jump and that a correlation between this increase in potential and catalyst degradation seems highly unlikely. This increase in potential is related to an accumulation of microscopic oxygen bubbles and the concomitant shielding of active sites within the catalyst layer.³¹ The formation and stability of such microscopic gas bubbles on the surface of gas evolving catalysts has been also shown by different imaging techniques such as total-internal reflection fluorescence (TIRF) microscopy, atomic force

microscopy (AFM) and X-ray radiography.^{45–47} However, after the first CP-step was completed, the accumulated microscopic oxygen bubbles were removed by diffusion during the 30 min rotation in Ar-saturated electrolyte, which led to the re-exposure of active sites and performance recovery.

The potential increase was not detected in an MEA measurement in a PEM-WE, in fact, the performance was stable throughout the whole measurement period (~ 9 d) (light blue line in Fig. 2a). This drastic difference in the potential transient obtained in MEA vs RDE demonstrates that the RDE-based CP test cannot be reliably used to test the stability of OER catalysts.

After the initial CP-step with the MEA in the PEM-WE, OER polarization curves along with CVs are recorded and the same current is applied again (second CP-step, dark blue line Fig. 2a). Surprisingly, the initial potential of the second CP-step within the MEA configuration is even 10 mV smaller than that of the first CP-step and again showed a stable performance, a phenomenon observed elsewhere in literature, but never explained.⁴⁸ During operation, an increase in local partial pressure within the catalyst layer as well as the accumulation of oxygen bubbles is possible, however, distinguishing between the two is not trivial. The enhanced cell performance observed for the second CP-step within the MEA configuration might be related to either the microscopic oxygen bubbles formed and/or accumulated in the catalyst layer during the first CP-step or a developing local increase in oxygen and/or hydrogen partial pressure. Assuming that the increase in potential is only related to either an increase in partial pressure of oxygen or hydrogen, this would result in a pressure difference ($\Delta p = p_{\text{gas, catalyst}} - p_{\text{gas, channel}}$) of ≈ 2 bar and ≈ 0.5 bar respectively, both of the values being reasonable. While an increase in oxygen or hydrogen partial pressure can subside during OCV or zero current, the trapped oxygen bubbles can either be physically detached/diffuse away during the recorded CV under the water flow, or reduced electrochemically by scanning to low cathodic potentials (< 1.0 V) within the MEA configuration. The latter is indicated by the additional cathodic current observed in the first CV (blue line in Fig. 2d) obtained after the first CP-step that is not observed in the second subsequent CV (cyan line in Fig. 2d).

To prove that the active sites are indeed shielded by microscopic oxygen bubbles, CVs and polarization curves were recorded for the RDE measurements subsequent to each CP-step and a 30 min. Ar purge. Figure 2b shows the mass-specific polarization curves recorded at the BoT (black line), after the first CP-step, a 30 min. Ar purge, and a subsequent CV (green line), and after the second CP-step, a 30 min Ar purge, and a subsequent CV (red dotted line). Quite nicely, the potentials corresponding to the $70 \text{ A g}^{-1}_{\text{Ir}}$ in the polarization curves are in good agreement with the initial values of both CP-steps (black and green circles in Figs. 2a and 2b), proving that the polarization curves and the initial potentials of the CP measurements can indeed be correlated. According to Eq. 1, no catalyst should remain after the potential jump. However, the polarization curves reveal that there is still a sufficiently high OER activity compared to a bare Au-disk,³¹ although significantly smaller compared to the initial activity. Accordingly, comparing the OER activities at $1.5 \text{ V}_{\text{RHE}}$ suggests that only $\approx 20\%$ of the initial catalyst layer seems to remain, whereas $\approx 80\%$ is lost due to “microscopic bubbles-induced degradation.” The accumulation of oxygen in the catalyst layer and partial shielding of the active sites result in an increasing potential at the remaining active sites to provide the same applied current. Consequently, the increased potential on the remaining active sites inevitably enhances iridium dissolution.^{49–52} In fact, if the accumulation of microscopic bubbles could be avoided, no significant dissolution is expected to occur, since shielding a fraction of the catalyst layer is the main cause for the increasing potential and the accompanied iridium dissolution happening at the still accessible sites.

Figure 2c shows CVs measured at the BoT (black line), after the first CP-step (green line) and at EoT (red dotted line), each recorded after purging with Ar for 30 min to ensure a catalyst layer free of

microscopic bubbles. The CVs recorded after the both CP-steps show that at least half of the initial catalyst layer is still electrochemically accessible. Conclusively, this comparison demonstrates that using chronopotentiometry for estimating the stability of an OER catalyst in RDE measurements is not reliable, since the observed increase in potential seems to be exclusively caused by the accumulation of microscopic oxygen bubbles and the by subsequent shielding of active sites within the catalyst layer.

Chronoamperometric (CA) aging test.—The observed decrease in current during a constant potential measurement is attributed to catalyst degradation and is commonly correlated to the lifetime of an OER catalyst.^{14,29} In this study, a constant potential of $1.53 \text{ V}_{\text{RHE}}$ (iR-corrected) is applied and the corresponding current is recorded during the RDE and MEA measurements. Within the first few minutes of a CA measurement in an RDE, a rapid decrease in the mass-normalized current of almost 75% can be observed (Fig. 3a, black curve), followed by a more gradual decrease in current over the subsequent 6 h. The initial OER activity of $56 \text{ A g}^{-1}_{\text{Ir}}$ is taken after 100 ms, so that capacitive contributions are negligible (see experimental section). If this drop in current over the first hour were related to catalyst degradation, then almost 85% of the catalyst would have to be lost, even though this catalyst was proven to be stable in a PEM-WE over hundreds of hours.¹⁷ Therefore, this rapid drop in current must be related to the fast filling of the catalyst layer with microscopic oxygen bubbles, shielding a significant fraction of the active sites, so that the current decreases.³¹ Applying the same potential after purging for 30 min with Ar resulted in an initial current that is only 60% ($34 \text{ A g}^{-1}_{\text{Ir}}$, green circle in Fig. 3a) of the initial current recorded for the first CA-step (gray circle in Fig. 3a), which again rapidly decays within the first hour of the second CA-step before it levels out ($\sim 5 \text{ A g}^{-1}_{\text{Ir}}$). While the rapid decay in current during the CA-step can undoubtedly be related to the partial shielding of active sites by microscopic oxygen bubbles, the 40% lower initial current in the subsequent second CA-step suggests that the catalyst also partially degraded during first CA-step. Polarization curves recorded at BoT, after the first CA-step, and at EoT, are provided at the supplementary note A-2.

Figure 3c shows that the CVs recorded after the first and second CA-steps (each preceded by a 30 min Ar purge) are $\sim 30\%$ smaller compared to the one measured at BoT (black curve in Fig. 3c), suggesting that roughly one third of the catalyst is degraded by the end of the experiment and that the decrease in current during a CA-step does not correlate to catalyst degradation. In summary, these results confirm that the stability of an OER catalyst cannot be examined by applying a constant potential in RDE measurements, since the current decrease is largely due to the shielding of active sites by microscopic oxygen bubbles, which are trapped in the catalyst layer.

Using the same catalyst in an MEA and testing it in a PEM-WE, it was found that the current decreased by $\sim 50\%$ after ~ 24 h (black curve in Fig. 3b), suggesting that half of the catalyst is either shielded or has degraded. The current at $1.53 \text{ V}_{\text{RHE}}$ derived from a subsequently measured polarization curve after the first CA-step ($33 \text{ A g}^{-1}_{\text{Ir}}$, purple star in Fig. 3b) closely matches the steady-state current ($32 \text{ A g}^{-1}_{\text{Ir}}$) at $1.53 \text{ V}_{\text{RHE}}$ after the 24 h CA-step. The current at $1.53 \text{ V}_{\text{RHE}}$ also remains essentially constant ($30 \text{ A g}^{-1}_{\text{Ir}}$) over a subsequent potential hold (dark blue curve in Fig. 3b), which either means that the catalyst has indeed degraded or that the O_2 bubbles are remaining in the catalyst layer.

Scanning the potential to below 1 V_{RHE} to remove the oxygen bubbles or to subside a local increase in oxygen and/or partial pressure in the catalyst layer, followed by a CA-step (turquoise curve in Fig. 3b), the same initial current at $1.53 \text{ V}_{\text{RHE, HFR-corrected}}$ ($63 \text{ A g}^{-1}_{\text{Ir}}$) as that obtained for the first CA-step ($61 \text{ A g}^{-1}_{\text{Ir}}$) was obtained. This firmly proves that the performance decay during a CA step was solely due to shielding the active sites by oxygen bubbles or the increase in local partial pressure of oxygen and/or hydrogen. An increase in partial pressure, however, would occur instantly and not

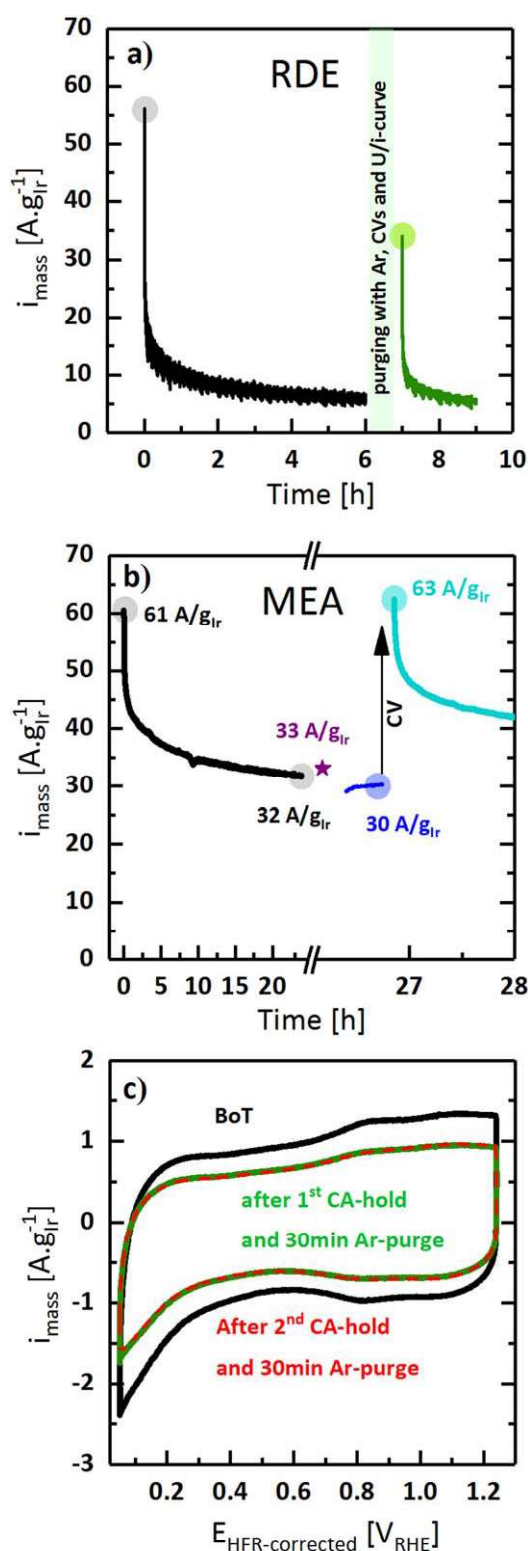


Figure 3. (a) Chronoamperometry at $1.53 \text{ V}_{\text{RHE}}$ (internal iR -correction was applied) measured by RDE at BoT (black) and after first CA-hold (green). After each CA-hold, the electrolyte was purged with Ar for 30 min and a CV (see Fig. 3c) was recorded. (b) Chronoamperometry at $1.53 \text{ V}_{\text{RHE}}$ (HFR-corrected) measured in an MEA at BoT (black), the purple star represents the activity measured at $1.53 \text{ V}_{\text{RHE}}$ during a subsequent polarization curve, directly after the polarization curve (blue) and after a subsequent CV (turquoise). (c) Cyclic voltammograms recorded at BoT (black), after a 30 min. Ar-purge after the first CA-hold (green) and after a 30 min. Ar-purge after the second CA-hold at EoT (red dotted) at 20 mV s^{-1} .

over hours (see gradual decay in current over hours in Fig. 3b), wherefore an increase in partial pressure seems rather unlikely. So far, it is not trivial to give a solid explanation for whether this reversible degradation in an MEA is due to the electrochemical reduction of O_2 , due to the removal of O_2 by diffusion, or an even more complex phenomenon.

Although the testing time in the MEA was much longer than that in the RDE configuration, no catalyst degradation was observed in the MEA, while for the RDE test, about 40% of the current could not be recovered. This confirms that using RDE measurements to predict the lifetime of a catalyst by applying a constant potential is not a valid approach, since the recorded drop in current is mostly due to the shielding of active sites by trapped microscopic oxygen bubbles and since the observed loss in OER activity is most likely a consequence of it. On the other hand, in MEA measurements, the current loss is reversible and it can be avoided by a proper design of the stability test.

Potential cycling aging test.—Undeniably, the OER catalyst stability during transient operation is of vital interest, since it will be an important consideration when coupling a PEM water electrolyzer with renewable energies that are inherently intermittent in power output.^{53–56} By cycling the potential between idle periods (OCV) and times of operation ($>1.4 \text{ V}_{\text{RHE}}$), the fluctuating power supply is commonly mimicked in RDE durability tests, and the observed decrease in OER activity is attributed to catalyst degradation.^{5,7,14} In this study, the potential was cycled between $1.3 \text{ V}_{\text{RHE}}$ and $1.6 \text{ V}_{\text{RHE}}$, avoiding reducing conditions, which can affect the performance of a PEM water electrolyzer.¹⁷ Figure 4a depicts the mass-normalized current [$\text{A g}^{-1}_{\text{Ir}}$] extracted at $1.5 \text{ V}_{\text{RHE}}$ from the anodic scan of the respective cycle during RDE measurements as a function of cycle number. Evidently, the current significantly drops within the first two cycles by $\sim 40\%$ (cycles 1 and 2 in Fig. 4a), whereas the decrease slows down afterwards. After 20 cycles, only 40% of the initial activity is remaining ($10 \text{ A g}^{-1}_{\text{Ir}}$, Fig. 4a), which means that 20 cycles would be enough to degrade more than half of the catalyst, assuming that this deactivation is owing only to catalyst degradation. However, after purging with Ar for 30 min and recording a CV, showing that roughly 70% of the initial activity can be recovered ($\sim 15 \text{ A g}^{-1}_{\text{Ir}}$, red dotted circle). While a significant fraction of the catalyst degradation can be recovered, some irreversible catalyst degradation must have occurred, although this irreversible degradation is not expected in the here used potential range.^{17,57} Again, the microscopic oxygen bubbles must be directly responsible for the reversible degradation, and indirectly responsible for the irreversible degradation.

The anodic scans of the individual cycles in the above RDE experiment are shown in Fig. 4c, where it becomes quite clear that the second cycle (dark green curve) during the first cycling test and the first one (red dotted line) recorded after a 30 min. Ar purge and a CV are perfectly identical, clearly demonstrating the partial recovery of activity. It can therefore be concluded that part of the catalyst layer degraded during the cycling test since only 70% of the current can be recovered by Ar purge. The CVs recorded for the potential cycling stability test at the BoT and at EoT are shown in Fig. A3.

The same stability protocol was executed in an MEA and the results are shown in Fig. 4b. Obviously, the current ($\sim 12 \text{ A g}^{-1}_{\text{Ir}}$) recorded at $1.50 \text{ V}_{\text{RHE}}$ during a polarization curve (purple diamond, measured galvanostatically beforehand) is similar to the current ($\sim 12.5 \text{ A g}^{-1}_{\text{Ir}}$) obtained during the first anodic cycle at the same potential, whereas during the subsequent 200 cycles (light blue squares) the activity slightly decreases by $\sim 10\%$. This decrease is often interpreted in the literature as degradation of the catalyst,⁵ however, after recording a polarization curve and a subsequent CV between 0.05 – $1.25 \text{ V}_{\text{RHE}}$, the activity increases to $16 \text{ A g}^{-1}_{\text{Ir}}$ at $1.50 \text{ V}_{\text{RHE}}$ (blue circles in Fig. 4b), i.e., to a value even higher than the one recorded during the very first cycle.

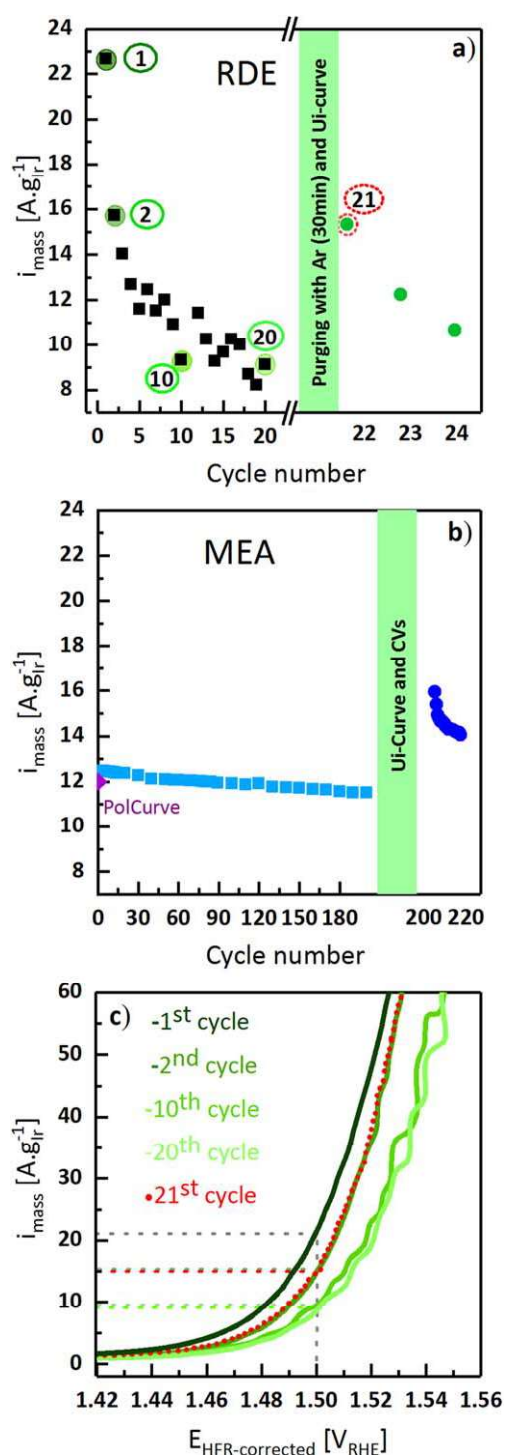


Figure 4. (a) Mass-specific currents, extracted at $1.50 \text{ V}_{\text{RHE}}$ of the anodic scan during cycling between $1.3\text{--}1.60 \text{ V}_{\text{RHE}}$ ($i_{\text{R}}\text{-corrected}$) at 10 mV s^{-1} in RDE configuration, recorded for the initial 20 cycles (black squares) and for 3 cycles after a 30 min. Ar-purge, a CV and a polarization curve (green circles). (b) Mass-specific currents, extracted at $1.50 \text{ V}_{\text{RHE}}$ during cycling between $1.3 \text{ V}_{\text{RHE}}\text{--}1.60 \text{ V}_{\text{RHE}}$ (HFR-corrected) with 10 mV s^{-1} in an MEA, for the initial 200 cycles (light blue squares) and for 20 cycles (dark blue circles) recorded after obtaining a polarization curve and a CV. The purple diamond represents the extracted current at $1.50 \text{ V}_{\text{RHE}}$ from the polarization curve recorded directly before the 200 cycles, and (c) Mass-specific anodic cycles (from RDE) recorded at 10 mV s^{-1} during cycling depicted for the first (dark green line), 2nd (green line), 10th (light green line), 20th (bright green line) and for the 22nd (red dotted line).

In contrast to the activity decrease over the course of the first 200 cycles, the decrease observed during the subsequent cycles is much more severe ($\sim 13\%$ within 20 cycles). Both, the higher activity measured along with the observed fast decrease is related to the CV recorded directly before the second cycling, whereas the first cycling was recorded directly after measuring a polarization curve, during which large OER currents were drawn. By cycling the cell to lower cathodic potentials ($<1.0 \text{ V}_{\text{RHE}}$), as it was already shown in the previous section (Fig. 2d), the microscopic oxygen bubbles trapped within the catalyst layer can be removed and/or an increase in oxygen and/or hydrogen partial pressure can decay. Since the cell was polarized at high potentials prior to the first cycling, a certain fraction of the catalyst layer must have already been shielded or a partial pressure difference was already developed and hence, did already affect the performance. This would explain the apparently lower activity along with the smaller decrease in activity during the first 200 cycles (light blue squares). On the other hand, once the catalyst layer is free of any microscopic oxygen bubbles after a CV into the potential range where O_2 can be reduced and any partial pressure buildup did subside, the catalyst can be fully utilized, which results in a high initial activity that, however, decays more rapidly due to the fast filling by microscopic oxygen bubbles and/or the increase in local partial pressure. In summary, this comparison shows that potential cycling cannot be used in RDE measurements to predict the lifetime of an OER catalyst, since the claimed degradation is caused by a shielding of active sites via trapped microscopic oxygen bubbles within the catalyst layer.

MEA aging for the three different aging protocols.—Each of the three investigated aging protocols showed that during MEA measurements in a PEM-WE, a fraction of the catalyst layer is shielded by microscopic oxygen bubbles and that by recording a CV to low potentials, the activity can be fully recovered. This suggests that there are no irreversible changes to the catalyst and the catalyst layer of the MEA during the test. Hence, the polarization curves recorded at BoT and at EoT should be identical, independent of which aging protocol is applied. The polarization curve representing the initial activity at BoT (black squares) and those recorded at the EoT for each aging protocol are depicted in Fig. 5a. In fact, the polarization curves at the end of the different stability tests match quite well with BoT performance, especially when the HFR-corrected curves are considered, thereby confirming that none of these aging tests caused any degradation of the catalyst and the catalyst layer. The corresponding HFRs as well as Tafel plots at BoT and at EoT are depicted in Fig. 5b. Further details regarding this figure can be found in supplementary note A-4.

We provide here a possible hypothesis (Fig. 6) as to why the effect of trapped oxygen bubbles is more pronounced in case of the RDE compared to MEA measurements. For this, we first focus on the processes occurring during MEA measurements in a PEM-WE. Since the through-plane electrical resistance within the catalyst layer is quite small ($\approx 0.04 \text{ m}\Omega \text{ cm}^2_{\text{geo}}$)¹⁷ compared to the proton sheet resistance ($14\text{--}30 \text{ m}\Omega \text{ cm}^2_{\text{geo}}$),³⁷ the OER reaction should mainly occur at the membrane/electrode interface (Fig. 6a).³⁹ Thus, although the reaction is occurring throughout the whole catalyst layer, the utilization of the catalyst layer should be highest at the membrane/electrode interface. The catalyst layer thickness at a loading of $2 \text{ mg}_{\text{Ir}} \text{ cm}^{-2}_{\text{geo}}$ is $\approx 8\text{--}10 \mu\text{m}$,³⁷ through which the produced oxygen has to escape. Within the OER catalyst layer, the local partial pressure of oxygen must thus increase, resulting in a pressure gradient from the membrane | electrode ($\text{P}_{\text{O}_2, \text{ME}}$) to the electrode | PTL interface ($\text{P}_{\text{O}_2, \text{E|PTL}}$), illustrated by the blue curved line in Fig. 6a (marked as ①). This pressure difference might enhance the removal of oxygen within the catalyst layer towards the PTL, thereby minimizing the accumulation of oxygen within the catalyst layer.

The above consideration is only true, however, if a sufficiently large flux of water can be sustained from the electrode | PTL to the membrane | electrode interface. This, we believe, is provided by the

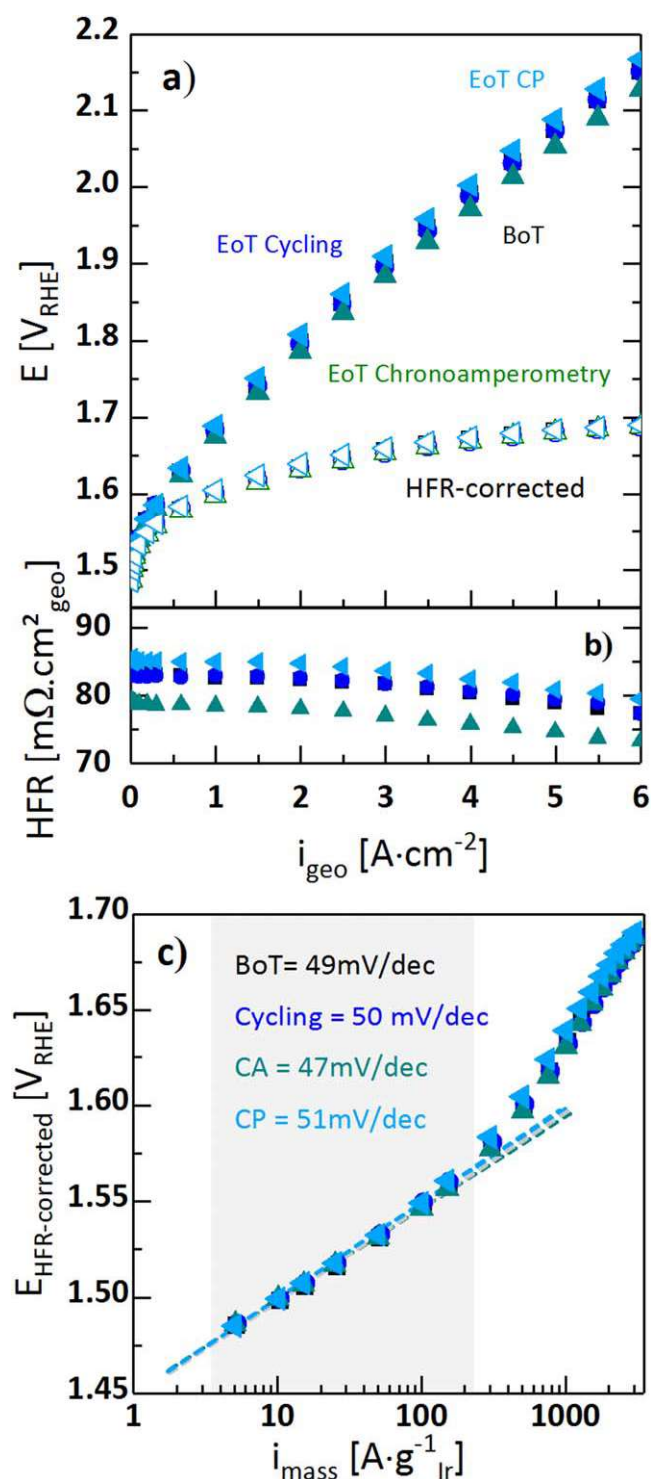


Figure 5. (a) Galvanostatically measured polarization curves at 40 °C recorded at BoT (black squares) and at EoT after 223 potential cycles between 1.3–1.60 V_{RHE} (blue circles), after ~26 h of CA at 1.53 V_{RHE} (green triangles), and after ~10 d of CP-hold at 70 A g⁻¹_{Ir} (light blue triangles); The open symbols represent the HFR-corrected polarization curves. (b) The corresponding HFRs as a function of current density. (c) Mass-specific Tafel-plots (data replotted from (a) at BoT (red line) and at EoT after 223 cycles (blue circles), after ~26 h at 1.53 V_{RHE} (green triangles) and after ~10 d at 70 A g⁻¹_{Ir} (light blue triangles). Please note that in many instances the data points overlap so closely that not all of the four different symbols can be discerned in each instance.

electro-osmotic water drag from anode to cathode through the membrane (Fig. 6a, ②). The drag coefficient under electrolyzer

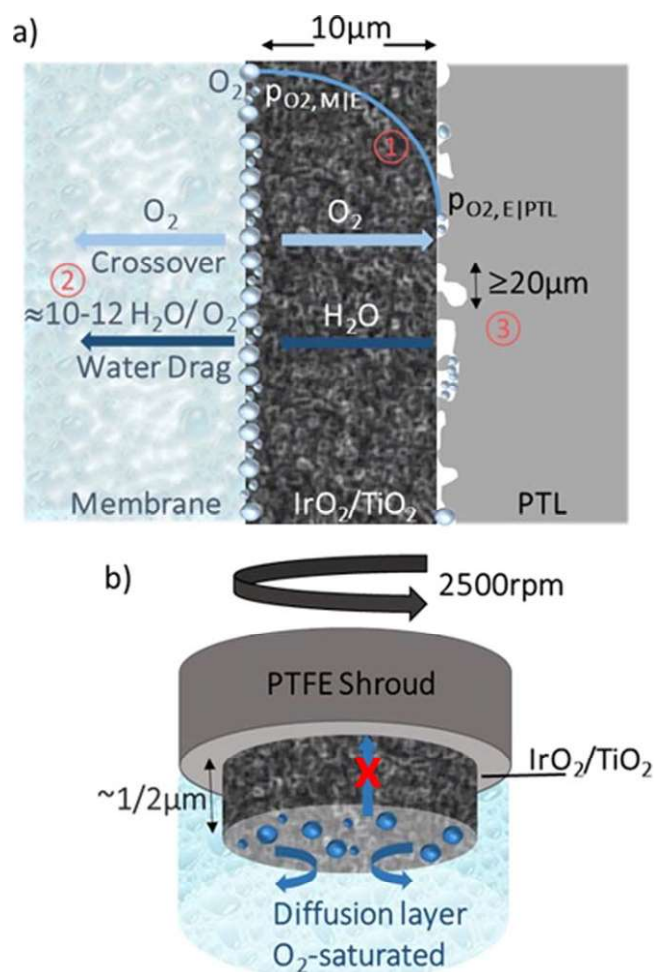


Figure 6. (a) Scheme of a single cell (MEA), illustrating possible reasons for a different degradation rate in MEA compared to an RDE: 1) pressure build-up within the catalyst layer; 2) electro-osmotic water drag and oxygen permeation; 3) restricting the size of a micro-bubble formed in an MEA | PTL interface to the pore diameter of the PTL. (b) Scheme of an RDE tip during OER operation.

operating conditions ranges between 2.5–3.2 H₂O/H⁺, so that roughly 10–12 water molecules per produced oxygen molecule (4 H⁺ per generated O₂) are dragged through the membrane and, consequently, through the anode catalyst layer, i.e., ~5–6 times the amount required to produce one O₂ molecules.⁵⁸ This electro-osmotic water drag will thus sustain a sufficiently large flux of water to the membrane | electrode interface, so that the current density distribution across the anode catalyst layer will be governed by the proton conduction resistance. In this case, oxygen will be produced at a higher rate near the membrane | electrode interface (see above), producing the p_{O_2} gradient sketched by ① in Fig. 6a, which in turn allows for an efficient removal of O₂ gas bubbles from the anode catalyst layer. Additionally, the pore size of the PTL ($\geq 20 \mu\text{m}$) may prevent the formation of macroscopic oxygen bubbles (0.1 – 1 mm) and thus the blockage of larger sections of the anode catalyst layer (Fig. 6, ③). Commonly, however, a pressurized operation is desirable, while the whole study was conducted at ambient pressure. Bernt et al. showed that an increase in pressure leads to a higher hydrogen crossover.⁵⁹ Assuming the same holds true for oxygen crossover, an even more efficient removal of oxygen bubbles is expected for operations at higher pressure. Since there was already no degradation observed in the case of ambient pressure operation, none is expected in the case of pressurized operation.

On the other hand, in the RDE configuration, the oxygen can only be removed by diffusion within the catalyst layer or by convection in the radial direction at the outer surface of the catalyst layer (blue arrows, Fig. 6b) into an O₂-saturated electrolyte. Even in the absence of water transport resistances into the catalyst layer, the primary (i.e., conductivity-controlled) current distribution in this case favors the highest current density at the catalyst | electrolyte rather than at the disk | electrolyte interface, so no positive p_{O_2} gradient would be established from the disk | electrolyte to the catalyst | electrolyte interface to drive O₂ removal. In conclusion, the electro-osmotic drag of water across the catalyst layer of an MEA and the skewing of the OER current density distribution towards the membrane | electrode interface due a minimized proton conduction resistance are the most likely reason for the apparently more effective O₂ bubble removal in an MEA configuration. If one would be able to design a measurement setup, where one can stimulate dynamics within the catalyst layer during the measurement in liquid electrolyte, one might be able to predict the lifetime of a catalyst without the need of an MEA setup. One possibility to prevent the accumulation of bubbles would be the application of sonication during operation,³³ which, however, is not feasible with catalyst in nano-particulate form. To the best of our knowledge, up to now there is no other technique other than assessing the long-term stability within in an MEA configuration, which can be used to reliably predict the lifetime of OER catalysts.

Conclusions

In this study, the most commonly used methods to predict the lifetime of OER catalysts, namely chronoamperometry, chronopotentiometry and potential cycling, were conducted in both RDE and MEA cells and directly compared with each other. It was demonstrated that none of the three investigated aging tests in an RDE configuration provides a measure of OER catalyst degradation/dissolution. This is mainly attributed to the accumulation of oxygen bubbles within the catalyst layer, shielding most of the active sites in case of an RDE test, resulting in a rapid increase in potential, for a CP test, or a rapid decrease in current, for a CA or potential cycling test, which is commonly interpreted as degradation of the catalyst. The accumulation of bubbles was found to induce irreversible degradation of the catalyst, a phenomenon that we did not observe in an MEA test. In fact, we demonstrated that while a local increase in partial pressure of oxygen and/or hydrogen seems rather unlikely, the accumulation of microscopic oxygen bubbles takes place also in an MEA, but to a much less extent compared to RDE. Therefore, the degradations observed in MEA for all the methods were fully reversible and almost no irreversible catalyst degradation was observed.

In summary, none of the most commonly used methods in RDE measurements is applicable to predict the lifetime of OER catalysts, since the observed decrease in performance is solely caused by the shielding of active sites via trapped microscopic oxygen bubbles. If it would be possible to prevent the accumulation of the microscopic oxygen bubbles within the catalyst layer during the measurement, it might be possible to design a proper stability protocol for testing OER catalysts using RDE measurements.

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Appendix

Supplementary information is available.

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3.3 Degradation of Anode OER Co-catalysts in a PEMFC

This section presents the article “Degradation Mechanism of an IrO₂ Anode Co-Catalyst for Cell Voltage Reversal Mitigation under Transient Operation Conditions of a PEM Fuel Cell”, which was published in June 2021 in the *Journal of The Electrochemical Society*.⁵⁶ It is an open access article distributed under the terms of the Creative Commons Attribution 4.0 License (CC BY). The article can be found under the permanent web-link: <https://doi.org/10.1149/1945-7111/ac0d39>. Additionally, the study was accepted for an oral presentation by Mohammad Fathi Tovini at the 237th Meeting of the Electrochemical Society (May 10-14, 2020, Montreal, Canada, abstract number: I03-1636). However, this meeting was later on cancelled due to the COVID-19 pandemic.

One strategy to mitigate the damages of H₂ starvation in PEMFCs is the addition of a co-catalyst to the anode electrode, which catalyzes the OER, so that the non-damaging OER rather than the damaging COR (carbon oxidation reaction) takes place.³⁷ A commonly used anode co-catalyst to facilitate the OER over the COR during cell reversal events is IrO₂.^{34, 36} Since the OER activity of a co-catalyst directly correlates with the effectiveness of the catalyst for mitigating cell reversal damages in a PEMFC, numerous studies have focused on improving the OER activity of IrO₂ co-catalysts.^{46, 53} However, the stability of the OER co-catalyst under the normal and transient operating conditions of a PEMFC also has to be considered. This study shows that two major degradation phenomena happen in PEMFCs when using IrO₂ as an anode co-catalyst:

- i) The near-surface layer(s) of the IrO₂ catalyst get chemically reduced to metallic Ir by H₂ during the normal operation of the fuel cell, which is in agreement with experiments in a PEMWE configuration that demonstrated that the surface reduction of a typical IrO₂ catalyst occurs upon its exposure to H₂.^{65, 66} Such alteration of the near-surface layers of IrO₂ drastically affects its stability over the course of the anode potential transients that occurs during SUSD events in a

PEMFC. The anode potential cycles surface-reduced IrO_2 materials leads to the dissolution of metallic Ir and cross-over of the dissolved Ir^{n+} species through the membrane to the cathode electrode, where iridium deposits on the Pt/C cathode catalyst and deteriorates its ORR activity.

- ii) SUSD transients in a PEMFC cause an OER activity loss of a typical IrO_2 anode co-catalyst, which is shown to be mainly due to the re-deposition of Pt dissolved from the anode HOR catalyst onto the reduced IrO_2 anode co-catalyst, blocking its OER active sites.

These findings suggest that the stability of IrO_2 -based anode co-catalysts in H_2 -containing atmosphere should be carefully assessed, for which a new methodology is proposed to be used prior to the implementation of these catalysts in a PEMFC anode. It is based on an extended isothermal TGA experiment at the operational temperatures of PEMFCs and under a dilute H_2 atmosphere, from which the reducibility of the IrO_2 catalyst can be reliably and quantitatively examined. After these isothermal TGA experiments, the catalyst material can be investigated by a series of physical/chemical and electrochemical analyses in order to determine the effect of the exposure of the catalyst to a reducing H_2 atmosphere on its physical-chemical and electrochemical properties. It is concluded that future research towards the development of a more stable anode co-catalyst to mitigate cell reversal degradation should focus on materials-based stabilization strategies to prevent the chemical reduction of IrO_2 -based catalysts by H_2 at the operational temperatures of PEMFCs, along with designing high OER active IrO_2 catalysts.

Author contributions

J.S. fabricated the 38 cm^2 MEAs and performed their electrochemical testing in a PEMFC. A.M.D. fabricated the 5 cm^2 MEA and performed its electrochemical testing in a PEMFC. M.F.T., A.M.D., and J.S. analyzed the experimental test results of the MEAs. M.F.T. performed all the other physical-chemical and electrochemical experiments and analyzed these data. M.F.T. wrote the

manuscript and H.A.G., A.M.D., and H.A.E.-S. edited it. All authors discussed the experimental results and revised the manuscript.



Degradation Mechanism of an IrO₂ Anode Co-Catalyst for Cell Voltage Reversal Mitigation under Transient Operation Conditions of a PEM Fuel Cell

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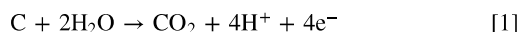
IrO₂ is the most stable oxygen evolution reaction (OER) catalyst in acidic media and it has been widely used as co-catalyst to mitigate cell reversal damages in the anode of PEM fuel cells (PEMFCs). In this study, a mechanistic understanding of the degradation of an IrO₂ anode co-catalyst under transient operation of a PEMFC is provided. Thermogravimetric analysis (TGA) in reductive atmosphere (3.3 vol.% H₂/Ar) shows that IrO₂ is not stable in H₂ containing atmosphere at operational temperatures of PEMFCs. By conducting a series of physical-chemical and electrochemical analyses, it is proven that H₂ under the operating conditions in a PEMFC anode can chemically reduce a few outer monolayers of the surface of IrO₂ nanoparticles to metallic Ir. The metallic Ir formed on the IrO₂ surface can then dissolve during fuel cell start-up/shut-down (SUSD) cycles. At least part of the dissolved Ir species formed in the anode electrode are shown to diffuse through the membrane to the cathode electrode, where they lead to a deterioration of the oxygen reduction reaction (ORR) activity of the Pt cathode catalyst. The consequences of Ir dissolution on the cell reversal tolerance of the anode are also discussed.

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One of the challenges that hinders the widespread commercialization of fuel cell electric vehicles is meeting long-term durability targets.¹ Among several conditions that can cause a substantial degradation of membrane electrode assemblies (MEAs), cell (voltage) reversal has recently received a great attention.^{2–4} Cell reversal can occur during the transient operation of proton exchange membrane fuel cells (PEMFCs) on account of a temporary under-supply of H₂ to one or several cells in a fuel cell stack.^{2–5} During cell reversal events, the anode potential rises to $\gg 1$ V vs the reversible hydrogen electrode (RHE) potential, causing a transient dissolution of platinum and a continuous oxidation of the carbon support:



The carbon oxidation reaction (COR) according to Eq. 1 is thermodynamically favorable at potentials >0.2 V_{RHE}, but due to its slow kinetics, considerable rates are only observed at potentials >0.9 V_{RHE}.^{6–8} Such high anode potentials occur during cell reversal and lead to a collapse of the anode catalyst layer and to cell failure. There are three main strategies to mitigate the damages caused by cell reversal: i) replacing the carbon support by corrosion resistant support materials such as metal oxides;^{9,10} ii) application of system-mitigation strategies;^{11,12} and, iii) addition of a co-catalyst to the anode electrode which catalyzes the oxygen evolution reaction (OER), so that the non-destructive OER, rather than the destructive COR, will take place.^{2,4,5,13,14} The application of corrosion resistant non-carbon support materials has been limited due to their generally lower electrical conductivity, their often insufficient stability particularly at transient fuel cell operating conditions, the risk of cationic contamination and/or degradation of the ionomer in membrane and electrodes, and cost considerations^{15–17}; therefore, graphitized carbons are the currently used support materials for Pt-based anode catalysts for the hydrogen oxidation reaction (HOR) in PEMFC stacks.⁵ On the other hand, the implementation of system-mitigation strategies adds complexity and cost to the PEMFC system: as cell

reversal damages can be substantial even if the cell reversal only occurs over time scales of tens of milliseconds, the control system has to be able to detect cell reversals on a millisecond time scale and to respond very quickly to prevent MEA damage. Therefore, addition of an OER co-catalyst to the anode electrode would seem to be the most simple strategy to mitigate cell reversal damages, and a commonly used anode co-catalyst to facilitate the OER over the COR during cell reversal events is iridium oxide (IrO₂).^{2,4,14,18–20}

Numerous studies have investigated the effect of IrO₂ co-catalysts on mitigating cell reversal degradation in PEMFC anodes. It is well known that the OER activity of an IrO₂ catalyst reliably correlates with the effectiveness of the catalyst for mitigating cell reversal degradation in a PEMFC.²⁰ The low onset potential of the OER on IrO₂ prevents the anode potential from reaching high values during cell reversal, and thus significantly reduces the extent of the COR at the anode side. Therefore, the focus of the research in this field is to attain highly OER-active IrO₂ catalysts by different synthesis approaches and to modify the anode catalyst layer design such as to achieve a uniform dispersion of IrO₂ in the anode catalyst layer.^{18–21} Typically, the mitigation performance of an anode OER co-catalyst is evaluated by simulated cell reversal tests (CRTs) in single-cell PEMFCs, in which a constant current (typically 0.2 Acm⁻²) is applied with air flowing through the cathode compartment and N₂ (rather than H₂) flowing through the anode compartment.^{5,22,23} Due to the lack of H₂ on the anode electrode during the CRT, the cell potential vs time rapidly drops to large negative values in the beginning of the CRT and then reaches a nearly constant potential plateau whose value gradually decreases over time, until it results in a drastic potential drop that is considered to mark the complete degradation of the anode catalyst layer. The time spent until this final potential drop is usually taken as a figure-of-merit to compare the performance of different anode co-catalysts during cell reversal. The negative cell potential during the CRT corresponds to the difference between the positive cathode potential that is established at the cell current by the ORR on the cathode catalyst and the more positive anode potential at which the cell current can be supplied by the OER and the COR reaction at the anode. Thus, the higher the OER activity of the anode co-catalyst, the less positive will be the anode potential during the CRT,

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resulting in a lower rate of the COR at the anode and, consequently, in a higher cell reversal tolerance.

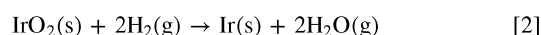
In addition to the high OER activity of the anode co-catalyst, another requirement a co-catalyst needs to fulfil is that it should be stable under the normal operating conditions of a PEMFC anode. While we are not aware of any comprehensive study on the stability of IrO₂ in the H₂ atmosphere in a PEMFC anode, experiments in a PEM water electrolyzer configuration show that it will undergo surface reduction under these conditions.²⁴ This could ultimately affect the stability of an IrO₂ anode co-catalyst, particularly during the repetitive transitions between normal operating conditions, where the anode potential is at ~ 0 V_{RHE}, and the high anode potentials (≥ 1 V_{RHE}) that occur during cell reversal and system start-up/shut-down (SUSD) transients. An SUSD transient takes place when a H₂/air_{anode}-front passes through the anode flow field due to the replacement of the H₂ gas by air during shut-down and vice versa during start-up.²⁵ The underlying degradation mechanism during SUSD and the effect of various conditions were subject to many studies. It has been shown that SUSD does not only invoke oxidative currents in the cathode electrode, which leads to carbon corrosion and loss of Pt electrochemical surface area (ECSA) at the cathode,^{26,27} but that it also leads to a significant Pt ECSA loss at the anode induced by the anode potential cycling between ~ 0 and ~ 1 V_{RHE} upon the passage of H₂/air_{anode} front.²⁸ These anode voltage cycles enhance the dissolution of an IrO₂ catalyst that has been exposed to H₂ at elevated temperatures (80 °C), as indicated in a recent publication from our group. There, we have shown that H₂ permeating through the membrane from the hydrogen cathode to the oxygen anode of a PEM water electrolyzer (PEMWE) during open circuit voltage (OCV) conditions leads to a surface reduction of an IrO₂ OER catalyst to metallic Ir, which in turn gets oxidized to an amorphous IrO_x during the subsequent normal operation period of the PEMWE at the high OER potentials.²⁹ The repetitive cycling between the reducing conditions during OCV periods, where the surface of the IrO₂ catalyst is reduced to metallic Ir, and oxidizing conditions during operation, where the IrO₂ surface is re-oxidized to an amorphous IrO_x, were shown to cause an enhanced dissolution of iridium, concomitant with iridium redeposition in the membrane.

In this study, we examine the cell reversal tolerance in the presence of an IrO₂ anode co-catalyst as well as its degradation and concomitant poisoning of the cathode catalyst activity upon SUSD cycles. Thermogravimetric analysis (TGA) in reductive atmosphere (3.3 vol.% H₂/Ar) is used to simulate the reductive environment of PEMFC anode during normal operation, and shows that the near-surface region of IrO₂ can be completely reduced to metallic Ir under the operating conditions of a PEMFC anode. The formation of metallic iridium surfaces after TGA experiments to different temperature is proven by X-ray photoelectron spectroscopy (XPS), and we show that the same surface reduction occurs in an MEA upon extended exposure of IrO₂ to H₂ in a PEMFC anode. Finally, it is shown that anode potential transients, such as those caused by SUSD events, lead to the dissolution of iridium from the IrO₂ based anode co-catalyst. Subsequently, the dissolved iridium is shown to diffuse through the membrane and to poison the oxygen reduction reaction

(ORR) activity of the cathode catalyst, which deteriorates the cell performance. In summary, we will investigate the fundamental aspects of the stability of IrO₂ in the presence of H₂ using different physical-chemical and electrochemical diagnostics (see left panel of Fig. 1). Following this, the effect of partial reduction of IrO₂ in a PEMFC anode condition when used as an anode co-catalyst is investigated on the durability of PEMFCs upon intermittent operation, namely cell reversal and SUSD (see right panel of Fig. 1).

Experimental

IrO₂/TiO₂ catalyst specification.—A commercial benchmark IrO₂ supported on TiO₂ OER catalyst (IrO₂/TiO₂ with 75 wt.% iridium, Elyst Ir75 0480 from Umicore, Germany) is used throughout this study. According to the patent, the IrO₂ deposited onto the high surface area TiO₂ is heat-treated ($T_{\text{heat-treatment}} \approx 400$ °C in air atmosphere),³⁰ and it has previously been shown by our group that it is an active and stable OER catalyst for PEMWE applications.^{31,32} A stoichiometric IrO₂ (iridium(IV) oxide) consists of 85.7 wt.% Ir and 14.3 wt.% O. Considering that the here used IrO₂/TiO₂ catalyst consists of 75 wt.% Ir, its nominal composition can be calculated as: 87.5 wt.% IrO₂ (75 wt.% Ir, 12.5 wt.% O_{IrO2}) and 12.5 wt.% TiO₂ (7.5 wt.% Ti, 5 wt.% O_{TiO2}). During TGA experiments under H₂, the IrO₂ phase of this catalyst can be reduced according to the following reaction:



Considering that TiO₂ cannot be reduced at temperatures where IrO₂ will be fully reduced (i.e., at 350 °C, as will be shown later), the total mass loss of the IrO₂/TiO₂ catalyst upon the complete reduction of IrO₂ to Ir would be accompanied by the total loss of O_{IrO2}, which would amount to a mass loss of the IrO₂/TiO₂ catalyst of 12.5 wt.%.

Next we will estimate the mass loss upon the reduction of a monolayer of IrO₂, assuming a core-shell morphology, with the surface of the TiO₂ support covered completely by IrO₂ particles. This assumption should be quite reasonable in view of the fact that the IrO₂ that is deposited on the TiO₂ support has a volume fraction of $\sim 72\%$ in the final IrO₂/TiO₂ catalyst (based on $\rho_{\text{IrO}_2} = 11.7 \text{ g cm}^{-3}$ and $\rho_{\text{TiO}_2} = 4.23 \text{ g cm}^{-3}$). Furthermore, since no Ti signal is detected in the XPS Ti2p spectrum of as-received IrO₂/TiO₂ catalyst (see Fig. A-1), it can be deduced that the TiO₂ support particles are completely covered by the IrO₂ particles. Based on the patent,³⁰ the pristine TiO₂ particles for the preparation of this IrO₂/TiO₂ catalyst have a specific surface area of $50 \text{ m}^2 \text{ g}^{-1} \text{ TiO}_2$. This corresponds to an average calculated TiO₂ particle size of $d \approx 28 \text{ nm}$. Considering that the final IrO₂/TiO₂ catalyst contains 87.5 wt.% IrO₂ along with the assumption that TiO₂ particles are covered by a uniform and compact film of crystalline IrO₂, an equivalent IrO₂ film thickness of $\sim 7.5 \text{ nm}$ covering TiO₂ support particles can be calculated for the IrO₂/TiO₂ catalyst. The specific surface area of this catalyst determined by the Brunauer–Emmett–Teller (BET) method is $27.2 \text{ m}^2 \text{ g}^{-1} \text{ IrO}_2/\text{TiO}_2$. By assuming a complete coverage of the TiO₂ support by IrO₂ particles (the schematic in Fig. A-1, inset, shows such a structural assumption), all of the physisorbed N₂ determined by the BET measurement would be adsorbed on the outermost IrO₂ surface, so that the BET surface area of $27.2 \text{ m}^2 \text{ g}^{-1} \text{ IrO}_2/\text{TiO}_2$ would represent the area of exposed IrO₂ in 1 g of catalyst ($S_{\text{BET}(\text{IrO}_2)}$). For a zero order estimate of the molar amount of IrO₂ in the outermost monolayer of the IrO₂ phase, we consider the hypothetical case that all of the IrO₂ in the IrO₂/TiO₂ catalyst would be in the rutile phase, so that the IrO₂ surface area can be calculated from the theoretical ionic radii of O²⁻ and Ir⁴⁺ in a rutile structure. While a significant fraction of the IrO₂ phase is actually amorphous, it still has an oxidation state of +4 (see discussion of Fig. 2a), so that the thus estimated surface area should still be reasonable. With this approximation and the above determined BET surface area, one can then estimate the molar amount of IrO₂ in the outermost monolayer of the IrO₂ phase in 1 g of the

Fundamental aspects	Implications for use in PEMFCs
IrO ₂ stability in H ₂	IrO ₂ -based anode co-catalyst in PEMFC
- TGA analysis in H₂ - XPS - Cyclic voltammetry and OER activity	- Cell reversal tolerance - Catalyst/MEA degradation during SUSD

Figure 1. A schematic overview of the two main experimentally designed sections in this work and the experiments which are performed in each section.

IrO₂/TiO₂ catalyst ($n_{\text{IrO}_2(\text{ML})}$):

$$\begin{aligned} n_{\text{IrO}_2(\text{ML})} &= \frac{S_{\text{BET}(\text{IrO}_2)}}{S_{\text{IrO}_2} \cdot N_A} = \frac{27.2 \text{ m}^2_{\text{IrO}_2}}{(1.18 \cdot 10^{-19} \text{ m}^2_{\text{IrO}_2}) \cdot (6.022 \cdot 10^{23})} \\ &= 3.83 \cdot 10^{-4} \text{ mol}_{\text{IrO}_2} \text{ g}_{\text{IrO}_2/\text{TiO}_2}^{-1} \end{aligned} \quad [3]$$

where S_{IrO_2} is the cross-sectional area of an IrO₂ unit, estimated from the area of two O²⁻ ions and one Ir⁴⁺ ion based on their ionic radii (O²⁻ = 126 pm, Ir⁴⁺ = 76.5 pm),³³ yielding $S_{\text{IrO}_2} = 1.18 \cdot 10^{-19} \text{ m}^2_{\text{IrO}_2}$, and where N_A is Avogadro's number ($6.022 \cdot 10^{23}$). Considering that the catalyst contains 87.5 wt.% IrO₂ with a molecular mass of 224 g mol^{-1} , the total moles of IrO₂ in the IrO₂/TiO₂ catalyst is $n_{\text{IrO}_2(\text{total})} = 3.90 \cdot 10^{-3} \text{ mol}_{\text{IrO}_2} \text{ g}_{\text{IrO}_2/\text{TiO}_2}^{-1}$. Therefore, the molar fraction of IrO₂ that is on the outermost surface of the assumed iridium shell amounts to:

$$x_{\text{IrO}_2(\text{ML})} = \frac{n_{\text{IrO}_2(\text{ML})}}{n_{\text{IrO}_2(\text{total})}} = \frac{3.83 \cdot 10^{-4} \text{ mol}}{3.90 \cdot 10^{-3} \text{ mol}} = 0.098 \quad [4]$$

According to this estimate, one monolayer of IrO₂ (ML_{IrO₂}) on the IrO₂/TiO₂ catalyst corresponds to ~10% of the total moles of IrO₂ in the catalyst. Therefore, the reduction of 1 ML_{IrO₂} and, consequently, the formation of 1 monolayer metallic Ir (ML_{Ir}) on the surface of the IrO₂/TiO₂ catalyst via reaction [2], corresponds to the reduction of ~10% of the total moles of IrO₂ in the IrO₂/TiO₂ catalyst. Referred to the overall IrO₂/TiO₂ mass, the reduction of 1 ML_{IrO₂} thus corresponds to an overall mass loss of $\sim 0.1 \cdot 12.5 \text{ wt.}\% \approx 1.25 \text{ wt.}\%$, a value which can be used to judge the extent of IrO₂ reduction during the later shown TGA experiments with the IrO₂/TiO₂ catalyst.

Rotating disk electrode (RDE) measurements.—Electrochemical measurements were carried out in a three-electrode cell using a static H₂ reference electrode (RE) consisted of a Pt wire sealed into one end of a glass tube which was drawn to a capillary and filled with electrolyte and a bubble of evolved H₂ (all voltages of RDE experiments throughout this work are quoted vs the potential of this reversible hydrogen electrode (V_{RHE})).³⁴ a high surface area Au wire as a counter electrode (CE), and a 5 mm diameter polycrystalline Au disk working electrode (WE) assembled in an interchangeable rotating ring-disk electrode (RRDE) shaft made of polyether ketone (Pine Research Instrumentation, USA). The reference electrode potential was calibrated in a H₂ saturated electrolyte prior to each experiment using the Pt ring of the RRDE. A 0.05 M H₂SO₄ aqueous solution was used as electrolyte, which was prepared by mixing high purity H₂SO₄ (Ultrapur, 96%, Merck Millipore KGaA, Germany) and ultrapure water (18.2 MΩ cm at 20 °C, Merck Millipore KGaA, Germany). High purity Ar and H₂ (6.0-grade, Westfalen AG) were used to purge the electrolyte.

Before each measurement, the Au working electrode disk was removed from the RRDE shaft and was polished with 0.3 μm alumina polishing suspension (Buhler AG) and then sonicated in ultrapure water for several times. The catalyst ink suspension was prepared using the as-received or the partially reduced IrO₂/TiO₂ catalyst powders after the TGA experiments, ultrapure water, and Nafion® ionomer solution (5 wt.% ionomer in mixture of lower aliphatic alcohols and water, Sigma Aldrich). The ink composition was adjusted to achieve 0.98 mg_{Ir}·ml⁻¹_{ink} and 2 wt.% ionomer content in the final dried coating consisting of catalyst and ionomer (note: the Ir content of the partially reduced IrO₂/TiO₂ powders after the TGA experiments was re-calculated based on their mass loss during the TGA experiments). The suspension was sonicated for 30 min in a sonication bath (Elmasonic S 30 H, Elma Schmidbauer GmbH) in order to achieve a homogenous ink. The temperature of the bath was maintained below 35 °C in order to prevent solvent evaporation. Finally, 20 μl of the prepared ink was drop-casted on

the polished and cleaned Au working electrode, resulting in a catalyst loading of 0.1 mg_{Ir}·cm⁻²_{disk}.

All the RDE measurements (using the RRDE assembly) were performed using an Autolab potentiostat (PGSTAT302N, Metrohm AG) and a rotator (Pine Research Instrumentation). The electrode rotation rate was fixed at 2500 rounds per minute (RPM) and the electrolyte temperature was maintained at room temperature during the electrochemical measurements. Freshly coated working electrodes were dipped in Ar-saturated electrolyte and the uncompensated solution resistance between the reference and working electrode was determined by electrochemical impedance spectroscopy (EIS) from 100 kHz to 100 Hz at open circuit voltage (OCV). Then, cyclic voltammetry (CV) was performed between 0.05–1.35 V_{RHE} with 20 mVs⁻¹ scan rate for 10 cycles (the CVs were started with a positive going scan from OCP to 1.35 V_{RHE} followed by 10 cycles in 0.05–1.35 V_{RHE}, see Fig. A-2), in order to record the characteristic voltammetry behavior of the as-received or the partially reduced IrO₂/TiO₂ catalyst powders in this potential range as well as to make sure of the physical stability of the coatings on Au working electrode disk during the experiments. After that, an OER polarization curve was recorded by collecting a CV between 1.2–1.57 V_{RHE} with 20 mVs⁻¹ scan rate where only the very first positive-going scan is used for evaluations; during both types of measurements, the electrolyte was purged by bubbling argon in the electrolyte.

Membrane electrode assembly (MEA) preparation and cell assembly.—The stability of IrO₂ under the OCV condition of a PEMFC anode was investigated using a 5 cm² single-cell in a self-designed flow field hardware³⁵ and a G60 fuel cell test station (Greenlight Innovation Corp., Canada). These MEAs had an IrO₂/TiO₂ loading of 2.0 mg_{Ir}·cm⁻²_{MEA} at the anode (no platinum was used at the anode) and platinum supported on Vulcan XC72 carbon (45.8 wt.% Pt/C, TEC10V50E, Tanaka, Japan) with 0.4 mg_{Pt}·cm⁻²_{MEA} loading at the cathode, hot-pressed onto a Nafion® 212 membrane (50 μm thick, from Quintech, Germany). The ionomer content of the electrodes was 12 wt.% on the anode and corresponded to an ionomer/carbon mass ratio of 0.65/1 on the cathode, using a Nafion ionomer solution (20 wt.% ionomer, D2021 from IonPower, USA). More details on the ink composition and the decal transfer to produce the catalyst coated membranes can be found in our previous study.³¹ The gas diffusion layer (GDL) used for this experiment was H14C7 (Freudenberg & Co. KG, Germany), and the cell was sealed with PTFE coated fiberglass (Fiberflon, Fiberflon GmbH & Co. KG, Germany) to achieve 20% GDL compression.

The SUS cycling and the CRT measurements were conducted using a 38 cm² single cell. The MEAs for these experiments were prepared using platinum supported on Vulcan carbon (50 wt.% Pt/C) with 0.3 mg_{Pt}·cm⁻²_{MEA} loading at the cathode and platinum supported on graphitized Vulcan carbon (20 wt.% Pt/C) with 0.05 mg_{Pt}·cm⁻²_{MEA} loading at the anode. Mitigated anode electrodes were prepared by mixing the as-received IrO₂/TiO₂ catalyst with the aforementioned Pt/C anode catalyst to achieve a loading of 0.05 mg_{Pt}·cm⁻²_{MEA} + 0.05 mg_{Ir}·cm⁻²_{MEA} (Pt:Ir ratio of 1:1). For simplicity, the MEAs containing the non-mitigated anode (i.e., Pt/C only) and the mitigated anode (Pt/C + IrO₂/TiO₂) will further on be referred to as “non-mitigated MEA” and “mitigated MEA,” respectively. Catalyst layers were prepared with a high equivalent weight ionomer and an ionomer:carbon ratio of 0.65:1. The MEAs were prepared by decal transfer method on 18 μm thick membranes. In this case, the Freudenberg gas diffusion layer H14C10 was used, and the cell was sealed with PTFE-coated fiberglass to achieve 10% GDL compression.

Electrochemical measurements of the MEAs.—The stability of crystalline IrO₂ under the OCV condition of a PEMFC anode was

investigated in a 5 cm² single-cell using 2000 nccm flow of fully humidified H₂ (anode) and 5000 nccm flow of fully humidified air (cathode) at 80 °C and 170 kPa_{abs} cell pressure; nccm refers to a volumetric flow rate in units of cm³min⁻¹, referenced to a pressure of 101.3 kPa and a temperature of 0 °C. The cell was kept under these conditions at the OCV for an overall duration of 3 h (pre-conditioning of the MEA was not done prior to this experiment). As soon as H₂ is introduced into the anode at 80 °C, metallic Ir sites begin to form on the surface of the catalyst due to the reduction of IrO₂ by H₂ through Eq. 2. Since the hydrogen oxidation reaction and hydrogen evolution reaction (HOR/HER) activities on iridium are very high,³⁶ the metallic Ir sites on the catalyst surface initiate an open circuit potential of the anode electrode of ~0 V vs RHE and an open circuit potential of the cathode electrode of ~0.90–0.95 V vs RHE (corresponding to the OCV of a H₂/air cell) throughout the entire 3 h of this OCV experiment. Every half an hour, cyclic voltammograms (CVs) of the anode (serving as working electrode) at ambient pressure and 40 °C were recorded using a Gamry potentiostat (Reference3000, Gamry Instruments, USA), applying a scan rate of 150 mVs⁻¹ in the potential range of 0.07–1.00 V. For this, fully humidified N₂ was fed to the anode (5 nccm) and fully humidified 5 vol.% H₂/Ar to the cathode electrode (500 nccm; serving as the counter and reference electrode); an extended N₂ purge of the anode humidifier was conducted before recording the CVs.

Prior to the SUSD cycling and CRT experiments using the 38 cm² single-cells, the cells were conditioned under H₂/air for 8 h at 1 Acm⁻²_{MEA} at 80 °C, an outlet pressure of 150 kPa_{abs}, and 100% relative humidity (RH). After conditioning, an H₂/air polarization curve was recorded at 80 °C and 100% RH with an outlet pressure of 150 kPa_{abs} and controlled H₂/air stoichiometries of 1.5/2. Polarization curves were recorded in galvanostatic mode, with 5 min hold at each current.

SUSD cycling was performed according to the US DRIVE Fuel Cell Technical Team Roadmap protocol at 35 °C, ambient cell pressure, and a constant cathode air flow rate corresponding to a stoichiometry of 2 at 1.0 Acm⁻²_{MEA}.¹ A single SUSD cycle consists of five steps: i) operating the cell in fuel cell mode at 0.4 Acm⁻²_{MEA} and 100% RH for 60 s, with an anode H₂ flow corresponding to a stoichiometry of 1.2; ii) setting the anode gas flow and the current to 0, and holding the resulting OCV for 10 s (pre-shutdown step); iii) introducing dry air to the anode compartment at a flow rate that corresponds to a residence time of 0.3 s (shutdown step); iv) setting the air flow rate in the anode to a flow corresponding to a stoichiometry of 1 at 0.1 Acm⁻²_{MEA} for 55 s (idle step); and, finally, v) introducing fully humidified H₂ to the anode compartment at a flow rate corresponding to a stoichiometry of 1.2 at 1.0 Acm⁻²_{MEA} (corresponding to a residence time of 0.3 s) and keeping the cell at OCV for 10 s (start-up step). H₂/air polarization curves at 80 °C (100% RH, 150 kPa_{abs}, H₂/air stoichiometries of 1.5/2.) were recorded after different SUSD cycling intervals, and the potential that corresponds to 1.2 Acm⁻²_{MEA} was taken to compare the performance loss of MEAs upon SUSD cycling as shown in Fig. 6a.

CRTs were carried out at 80 °C and 100% RH with a gas outlet pressure of 150 kPa_{abs}. The CRT was initiated by switching the anode gas feed from H₂ to N₂ (both at 166 nccm) while flowing air in the cathode (333 nccm) and then drawing a constant current of 0.2 Acm⁻²_{MEA}. As a result of fuel starvation in the anode, the cell potential rapidly drops to negative values in the beginning of the CRT; the end-of-life (EOL) criterion was defined as the time once the potential reached -1.5 V.

Thermogravimetric analysis (TGA).—Thermogravimetric analysis (TGA) of the as-received IrO₂/TiO₂ catalyst powder was performed by a Mettler Toledo TGA/DSC 1 instrument. ~10 mg IrO₂/TiO₂ raw powder was weighed into a sapphire crucible (volume 70 μl) closed with a perforated sapphire lid and directly inserted into

the TGA furnace. All the gases used in TGA experiments were 5.0-grade and supplied by Westfalen AG. Ar (20 mlmin⁻¹) was used as the cell carrier gas in addition to the reactive gases during all TGA experiment steps. Each TGA experiment was composed of two main steps: i) an initial in situ drying/cleaning step in oxidative atmosphere (mass profiles of this step are not shown in the figures) and ii) a subsequent metal oxide reduction step in reductive atmosphere.

The in situ drying/cleaning step was used in order to desorb all the adsorbed water and to oxidatively remove organic molecules from the surface of the as-received catalyst powder, so that the mass losses during the subsequent reduction step are only due to the reduction of IrO₂. The procedure of the in situ drying/cleaning step was as follows: flushing the TGA furnace with Ar (100 mlmin⁻¹) for 5 min at 25 °C, ramping the temperature from 25 to 200 °C (10 Kmin⁻¹) in O₂ (100 mlmin⁻¹), holding the temperature at 200 °C for 10 min in O₂ (100 mlmin⁻¹), cooling down the furnace from 200 to 25 °C (-10 Kmin⁻¹) in O₂ (100 mlmin⁻¹), and finally purging the TGA furnace with Ar (100 mlmin⁻¹) for 5 min at 25 °C. Since the as-received IrO₂/TiO₂ catalyst is already heat-treated in air atmosphere at a temperature of ~400 °C (as stated in the patent),³⁰ the drying/cleaning step at 200 °C in O₂ at the beginning of each TGA experiment is not expected to have a significant influence on the as-received catalyst's physical/chemical properties (surface area, particle size, oxidation state, etc.).

After the initial drying/cleaning step, the metal oxide reduction step was carried out in two different modes: i) a temperature ramp mode and ii) an isothermal mode. During the temperature ramp experiment, the temperature was ramped from 25 to 500 °C with different heating rates (1, 2.5, 5, and 10 Kmin⁻¹) while supplying 5 vol.% H₂/Ar (40 mlmin⁻¹), which was followed by cooling the furnace from 500 to 25 °C (-20 Kmin⁻¹) in Ar (100 mlmin⁻¹). Since IrO₂ was fully reduced at T = 350 °C during the heating step under reductive atmosphere, only the mass profiles up to 350 °C are shown in the graphs. The isothermal reduction experiments were carried out by heating the TGA furnace from 25 °C to a given target temperature (80, 100, 120, 160, or 240 °C) with a heating rate of 5 Kmin⁻¹ in Ar (100 mlmin⁻¹), followed by switching the gas supply from Ar to 5 vol.% H₂/Ar (40 mlmin⁻¹) and keeping the furnace at the chosen target temperature for 60 min. After this, the furnace was cooled down to 25 °C (-20 Kmin⁻¹) in Ar (100 mlmin⁻¹). Since IrO₂ reduction by H₂ occurs only during the 60 min holding temperature period, only the mass profile of this period of the entire experiment is shown in the graphs. For the extended isothermal reduction experiment in Fig. 5a, the experimental procedure was identical, except that different longer holding times under reductive conditions at the target temperature of 80 °C were applied. It should be noted that during all the IrO₂ reduction steps in TGA experiments, the effective H₂ concentration was 3.3 vol.% H₂/Ar, since in addition to the 40 mlmin⁻¹ 5 vol.% H₂/Ar an extra 20 mlmin⁻¹ flow of Ar as cell carrier gas was supplied.

IrO₂ reduction kinetics analysis.—The kinetic analysis of the TGA data was performed based on an isoconversional method to determine the Arrhenius activation energy of the IrO₂ reduction step. In this study, we used the Flynn-Wall-Ozawa (FWO) integral method, based on the procedure described in ASTM E1641–16.^{37,38} This test method is based on the general rate equation derived from Arrhenius equation:

$$\frac{d\alpha}{dt} = A \cdot f_{(\alpha)} \cdot \exp\left(\frac{-E_a}{RT}\right) \quad [5]$$

where α is the reaction extent (fraction of IrO₂ reduced to Ir), t is time (min), A is pre-exponential factor, $f_{(\alpha)}$ is the reaction kinetic model, E_a is the activation energy (Jmol⁻¹), R is the gas constant (8.314 Jmol⁻¹K⁻¹), and T is the absolute temperature (in K). By applying a constant heating rate β (in Kmin⁻¹), Eq. 5 can be

rewritten as:

$$\frac{d\alpha}{dT} = \frac{A}{\beta} \cdot f_{(\alpha)} \cdot \exp\left(\frac{-E_a}{RT}\right) \quad [6]$$

Equation 6 can then be solved based on the FWO method for a given constant α to determine the activation energy:

$$\ln(\beta) = \ln\left(\frac{A \cdot E_a}{R \cdot g_{(\alpha)}}\right) - 5.523 - 1.053 \cdot \frac{E_a}{RT} \quad [7]$$

where $g_{(\alpha)}$ is the integral form of the kinetic model ($f_{(\alpha)}$). According to Eq. 7, the activation energy at $\alpha = \text{constant}$ can thus be calculated by a linear regression of $\ln(\beta)$ vs $1/T$, where T are the temperatures at which the chosen constant α is reached at different heating rates β (in this study, heating rates of 1, 2.5, 5, and 10 Kmin⁻¹ were used). This analysis can be performed for different constant α values, yielding the corresponding activation energies E_a vs α . It has to be noted that Eq. 7 is valid for $20 < \frac{E_a}{R \cdot T_c} < 60$ values, where T_c is the temperature corresponding to the chosen $\alpha = \text{constant}$ value obtained for the TGA curve with a heating rate that is closest to the midpoint of the experimental heating rates (i.e., $\beta = 5$ Kmin⁻¹ in this study). For $\frac{E_a}{R \cdot T_c}$ values outside this range, Flynn and Wall suggested corrections to determine accurate E_a values.³⁷ However, all the E_a values in this study fall within the $20 < \frac{E_a}{R \cdot T_c} < 60$ range, so that Eq. 7 is valid for calculating the E_a values.

Other analytical methods.—X-ray photoelectron spectroscopy (XPS) was performed on a Kratos Axis Supra spectrometer using monochromatic Al K α radiation at an energy of 1486.6 eV. The spectra were recorded at a total X-ray source power of 225 W (15 kV and 15 mA current). For XPS measurements, as-received IrO₂/TiO₂ catalyst powder and catalyst powders after partial reduction in TGA experiments were drop-casted on a copper tape placed on a stainless steel sample holder (in floating mode, where the sample holder was electrically insulated from the copper tape), and then outgassed overnight in the ultrahigh vacuum (UHV) sample-introduction chamber to remove moisture and contaminants, so that the pressure in the analysis chamber during the XPS data acquisition remained below $1.0 \cdot 10^{-8}$ Torr. For XPS measurements on SUSD-cycled and as-prepared MEAs, the MEA samples were cut into small pieces ($\sim 5 \times 5$ mm) and attached to a self-adhesive copper tape (the electrode to be analyzed facing up) that in turn was attached to a stainless steel sample holder (in floating mode). Prior to inserting the MEA samples into the UHV sample introduction chamber, they were outgassed for 24 h in a vacuum oven at 80 °C.

High-resolution Ir 4f and Pt 4f spectra were collected using a step size of 0.05 eV, 0.6 s/step, and a pass energy of 20 eV; the shown spectra represent the average of 10 individual spectra. All binding energy values are corrected using the adventitious carbon signal (C 1s = 284.8 eV). The XPS data analysis was performed using the Casa XPS software. A Shirley function was used as background. As it is reported that Ir 4f spectra exhibit a distinct asymmetric line shape,^{39,40} a Functional Lorentzian line shape was used for metallic iridium and for iridium oxides, with the parameters set to LF (0.6, 1, 150, 300) and LF (0.3, 1.5, 25, 150), respectively. The fits of the doublets of Ir 4f7/2 and Ir 4f5/2 were fixed to have the same FWHM (full width at half maximum) and to have a (4f7/2)/(4f5/2) peak area ratio of 4:3.

X-ray diffraction was performed using a Stadi P instrument (Stoe & Cie GmbH, Germany) with Cu K α 1 radiation ($\lambda = 1.54059$ Å, 50 kV, 30 mA, Ge(111) monochromatized) and a Mythen 1 K areal detector (Dectris Ltd., Switzerland) in transmission mode. About 5 mg of each powder sample was smoothly spread onto a scotch tape and placed in the center of the sample holder hole. The XRD patterns

were recorded in the 2θ range of 20°–90° with a step size of 0.015° and a hold time of 0.8 s per step.

Results and Discussion

To our knowledge, the reduction of IrO₂ in a H₂-containing atmosphere has not been considered when using this material as an anode co-catalyst for mitigating cell reversal damages in PEMFCs; recent data, however, showed that IrO₂ can be partially reduced to metallic Ir when subjecting an IrO₂/TiO₂ anode catalyst in a PEM water electrolyzer to cross-over hydrogen at OCV and 80 °C.^{24,29} In the following, a mechanistic understanding of IrO₂ reduction in H₂-containing atmospheres is provided. Following this, the long-term stability of IrO₂ is evaluated in an isothermal condition at a temperature of 80 °C in a H₂-containing atmosphere (simulated PEMFC anode reductive environment). Lastly, the effect of partial reduction of IrO₂ in a PEMFC anode condition when used as an anode co-catalyst is investigated on the long-term durability of PEMFCs.

Fundamental aspects of IrO₂ reduction in H₂-containing atmospheres.—TGA is a well-established technique that can be used to unveil the underlying mechanism of metal oxide reduction even for complex multi-step reactions.^{41–43} Figure 2a shows the TGA temperature ramp curves of the as-received IrO₂/TiO₂ catalyst in 3.3 vol.% H₂/Ar carried out at four different heating rates ($\beta = 1, 2.5, 5,$ and 10 Kmin⁻¹). The TGA curves show the onset of a mass loss at temperatures of ~ 85 °C– 110 °C, depending on the heating rate. The mass loss vs temperature curves are approaching the theoretical mass loss that would be expected for the full reduction of IrO₂ in the IrO₂/TiO₂ catalyst to metallic Ir (i.e., a loss of 12.5 wt.%, see experimental section) at ~ 350 °C. Since TiO₂ is completely inert to reduction by H₂ at this temperature range,^{44–46} the TGA curves imply that the entire mass loss between 80 °C–350 °C corresponds to the reduction of IrO₂ in the IrO₂/TiO₂ catalyst through Eq. 2. The agreement between the experimental mass loss and that predicted by Eq. 2 indicates that iridium in the here used IrO₂/TiO₂ catalyst is, at least predominantly, in the form of iridium (IV) oxide. It should be noted that desorption of adsorbed water or any other organic residues on the surface of the catalyst does not contribute to the observed mass loss in the initial stage due to the in situ drying/cleaning step prior to the TGA measurement under reducing conditions (see experimental section).

As only IrO₂ can be reduced under these conditions and as the weight loss up to 500 °C (data only shown up to 350 °C in Fig. 2a) corresponds to the complete reduction of IrO₂ to Ir, the mass loss plotted on the left y-axis in Fig. 2a can be converted to the fraction of IrO₂ reduced to metallic Ir (α), marked by the right y-axis. From this it can be seen that the TGA curves are composed of an initially fast mass loss with increasing temperature for $\alpha < 60\%$, followed by a much more gradual mass loss with temperature for α ranging between 60%–100%. This might suggest that the kinetics of the IrO₂ reduction in the IrO₂/TiO₂ catalyst follows multi-step reaction kinetics, characterized by an initially high rate that gradually slows down as the reduction reaction extent proceeds to $\alpha > 60\%$. In order to get better insights into the IrO₂ reduction kinetics for the IrO₂/TiO₂ catalyst, the Flynn-Wall-Ozawa (FWO) method described in the experimental section is used to perform a kinetic analysis and to calculate the activation energy for the reduction of the IrO₂ phase of the IrO₂/TiO₂ catalyst. The FWO method is a kinetic model-independent analysis method, which can provide the activation energy at each reaction extent α , which is also suitable when several reaction steps are occurring simultaneously and when the activation energy varies with the reaction extent α .^{47,48} Figure 2b shows the linear regressions of the $\ln(\beta)$ vs $1/T$ points which are collected from the TGA curves in Fig. 2a at constant reaction extents α , selected between $\alpha = 5\%$ – 90% . The horizontal and vertical black

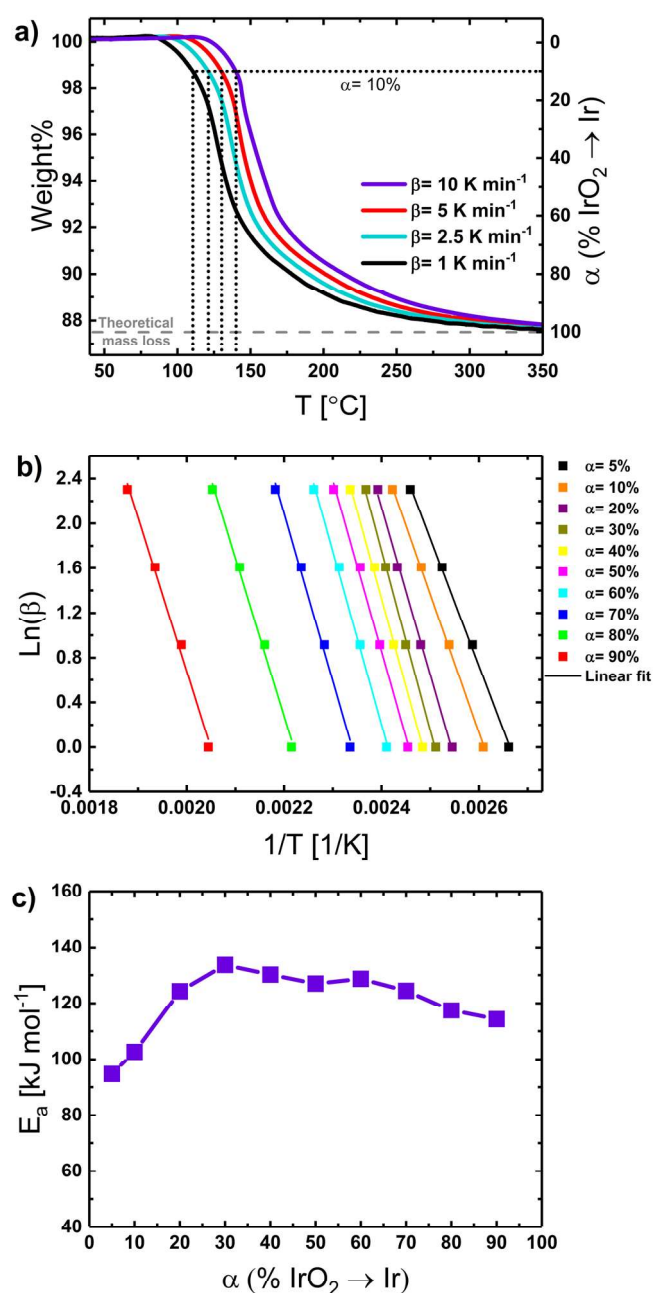


Figure 2. (a) TGA temperature ramp experiments with the as-received $\text{IrO}_2/\text{TiO}_2$ catalyst powder under 3.3 vol.% H_2/Ar at heating rates of 1, 2.5, 5, and 10 K min^{-1} (following the drying/cleaning step; see experimental section). The left y-axis represents the weight% mass loss of the $\text{IrO}_2/\text{TiO}_2$ catalyst versus temperature, while the fraction of the IrO_2 phase that is reduced to metallic Ir (α) is given on the right y-axis. The gray horizontal dashed line marks the theoretical mass loss (12.5 wt.%) of the $\text{IrO}_2/\text{TiO}_2$ catalyst upon the complete reduction of the IrO_2 phase by H_2 to metallic Ir (see Eq. 2). The black horizontal and vertical dotted lines illustrate the data that are used for the analysis in b) for a reaction extent of $\alpha = 10\%$. (b) Linear regression of $\text{Ln}(\beta)$ vs $1/T$ points collected from a) at constant α values selected between 5%–90%. The squares represent the data points at different constant α values, and the solid lines are the linear regression fits of the data points at each set of α values. (c) Plot of activation energy vs α for the reduction of the IrO_2 phase of the $\text{IrO}_2/\text{TiO}_2$ catalyst, calculated based on FWO method (Eq. 7), using the regression line slopes in b).

dotted lines in Fig. 2a exemplarily illustrate the data collection at $\alpha = 10\%$. All of the regression lines in Fig. 2b fit to the data points with $R^2 > 0.99$. The activation energy at each α value is calculated from Eq. 7, using the slopes of the fitted lines in Fig. 2b, and the thus

determined activation energies E_a vs α are plotted in Fig. 2c. It can be seen in Fig. 2c that the activation energy of $\text{IrO}_2/\text{TiO}_2$ reduction is ~ 95 and $\sim 105 \text{ kJ mol}^{-1}$ for low reaction extents α of 5% and 10%, respectively; at α ranging between 20%–70% the activation energy is $\sim 130 \pm 5 \text{ kJ mol}^{-1}$, then decreasing to $\sim 115 \text{ kJ mol}^{-1}$ as α reaches 90%. Interestingly, the clearly lower activation energies up to $\alpha = 10\%$ corresponds to the reduction of approximately one monolayer of the IrO_2 phase (see above estimates), suggesting that the outermost monolayer can be reduced more easily than the bulk of the IrO_2 phase. This has also already been suggested for the same catalyst based on differential scanning calorimetry data.²⁴ One possible explanation for the apparently more facile reduction of the outermost surface layer(s) of the iridium oxide phase would be that this near-surface region is amorphous, as amorphous iridium oxide was shown to be more readily reducible by H_2 (at temperatures of $\sim 80^\circ\text{C}$) compared to crystalline rutile type IrO_2 .^{40,49}

In summary, the above data suggest that the one or two outermost monolayers of the IrO_2 phase of the catalyst consist of an iridium oxide phase that on account of OH surface terminations and/or surface imperfections is amorphous (furtheron referred to A- IrO_x), and that has a lower activation energy for reduction to metallic Ir by H_2 . As the reduction reaction proceeds further into the sub-surface layers of the IrO_2 phase, the reduction of more stable crystalline iridium oxide (C- IrO_2) in the bulk of the catalyst starts to take place, indicated by a higher apparent activation energy for mixtures of A- IrO_x and C- IrO_2 . The initially fast mass loss with increasing temperature for $\alpha < 60\%$ (see Fig. 2a) suggests that the A- IrO_x species are mainly reduced at $\alpha < 60\%$; on the other hand, the more gradual mass loss for α ranging between 60%–100% suggests that the innermost IrO_2 phase becomes more and more crystalline, i.e., less reducible.

Although TGA temperature ramp experiments are a useful method to compare the temperature range for the reduction of different IrO_2 catalysts in an H_2 -containing atmosphere, they do not provide sufficient information to project the long-term stability of the iridium oxide phase under the isothermal working condition of a fuel cell anode. Therefore, TGA isothermal experiments were designed to study the reduction behavior of the IrO_2 phase of the $\text{IrO}_2/\text{TiO}_2$ catalyst at different temperatures of 80°C – 240°C over a period of 1 h. The mass losses over the course of this isothermal reduction step in 3.3 vol.% H_2/Ar (marked here as time = 0) at a given target temperature are plotted in Fig. 3a, whereby the mass profiles for the initial temperature ramp from 25°C to the target temperature that is performed in Ar atmosphere are not shown in Fig. 3a. Looking at the entire 1 h time span of the isotherms, it becomes clear that the reduction of the IrO_2 phase occurs at temperatures as low as 80°C , although the reaction is much faster at higher temperatures such as 160°C or 240°C , where respectively $\sim 65\%$ or $\sim 85\%$ of the iridium oxide phase are reduced within only ~ 11 min. An interesting feature is the initial mass gain of ~ 0.1 – 0.2 wt.% when the gas is switched from Ar to 3.3 vol.% H_2/Ar at the targeted temperature, as shown in the magnified isotherms in Fig. 3b. This mass gain is likely due to the adsorption of hydrogen on the iridium oxide surface of the $\text{IrO}_2/\text{TiO}_2$ catalyst, as this is reported to be one of the initial steps during the reduction of a metal oxide by H_2 gas.^{40,49,50} Assuming that each of the surface oxygens in the outermost monolayer of the iridium oxide phase were to bond to one H-atom, the molar H-uptake would be two times the moles of IrO_2 in the outermost surface layer ($n_{\text{IrO}_2(\text{ML})} = 3.83 \cdot 10^{-4} \text{ mol IrO}_2 \text{ g}^{-1}_{\text{IrO}_2/\text{TiO}_2}$, see Eq. 3), corresponding to $7.66 \cdot 10^{-4} \text{ mol H g}^{-1}_{\text{IrO}_2/\text{TiO}_2}$ or ~ 0.08 wt.%, which, within the error of measurement, is in the same range as the mass gain observed in Fig. 3b.

Next we will examine the surface chemistry and the structure of the $\text{IrO}_2/\text{TiO}_2$ catalyst samples after the TGA experiments under 3.3 vol.% H_2/Ar in order to identify the nature of reduction products. Figure 4a and b show the XPS $\text{Ir}4f$ spectra and XRD patterns, respectively, of the as-received $\text{IrO}_2/\text{TiO}_2$ catalyst and of several (partially) reduced $\text{IrO}_2/\text{TiO}_2$ powders after the TGA experiments.

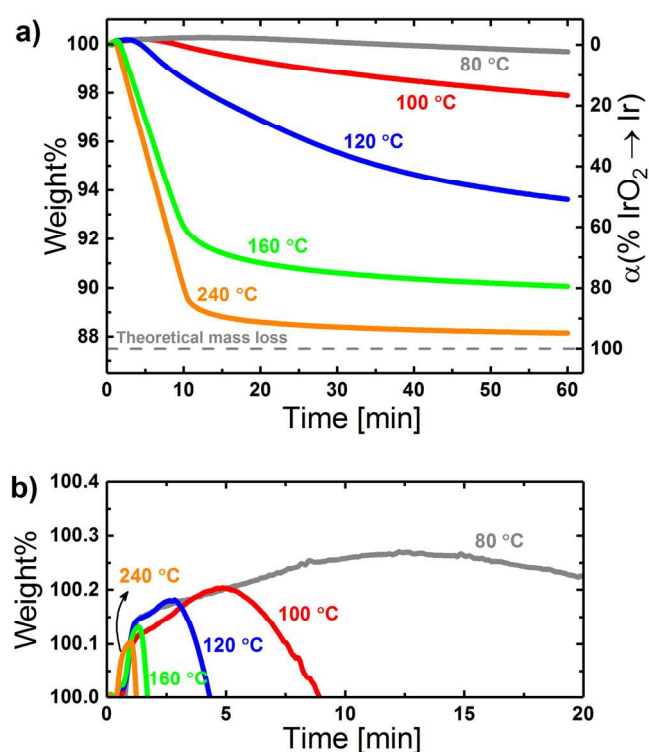


Figure 3. (a) Isothermal TGA experiments on the reduction of the iridium oxide phase of the $\text{IrO}_2/\text{TiO}_2$ catalyst in 3.3 vol.% H_2/Ar at 80, 100, 120, 160, and 240 °C (following the drying/cleaning step; see experimental section). The left y-axis represents the mass loss in wt.% of the $\text{IrO}_2/\text{TiO}_2$ catalyst vs temperature, while the fraction of the IrO_2 phase that is reduced to metallic Ir (α) is given on the right y-axis. The gray horizontal dashed line marks the theoretical mass loss (12.5 wt.%) of the $\text{IrO}_2/\text{TiO}_2$ catalyst upon the complete reduction of the IrO_2 phase by H_2 to metallic Ir (see Eq. 2). (b) Magnification of the initial 20 min of (a).

Table I summarizes the XPS Ir4f peak deconvolution parameters and the calculated composition of each sample based on the fitted spectra. The Ir4f XPS spectrum of the as-received $\text{IrO}_2/\text{TiO}_2$ catalyst (see Fig. 4a) can be fitted to C- IrO_2 and A- IrO_x components, yielding a composition ratio of A- IrO_x :C- IrO_2 = 41:59 (for the fitting procedure, see experimental section), with no contributions from metallic iridium being detected. The XRD pattern of the as-received $\text{IrO}_2/\text{TiO}_2$ catalyst (see Fig. 4b) is composed of broad crystallite reflections of rutile C- IrO_2 from the crystalline portion of the iridium oxide phase (main reflections marked by the red dotted lines) and the anatase TiO_2 (main reflections marked by the green dotted lines) from the TiO_2 support of the catalyst. Next, we will examine the XPS and XRD data for the $\text{IrO}_2/\text{TiO}_2$ catalyst after the 1 h isothermal TGA experiment at 120 °C (see blue line in Fig. 3a). The clear detection of metallic Ir in the XPS spectrum of the thus treated $\text{IrO}_2/\text{TiO}_2$ catalyst confirms that the observed mass loss in Fig. 3a corresponds to the partial reduction of IrO_2 by H_2 through Eq. 2, with metallic Ir being the product of this reaction. The XRD pattern of this sample shows that the metallic Ir forms crystalline domains, indicated by the unique reflection at $2\theta \approx 89^\circ$ (see right-most gray dotted line in Fig. 4b). In addition, strong diffractions for C- IrO_2 and anatase TiO_2 are still observed, so that the sample is composed of all three crystalline phases. Based on the XPS analysis (Table I), the surface composition of the sample with respect to metallic iridium and the crystalline and amorphous iridium oxide phases corresponds to Ir:C- IrO_2 :A- $\text{IrO}_x \approx 42:47:11$, indicating that the overall fraction of amorphous iridium oxide ($\sim 11\%$) in the near-surface region has greatly decreased compared to the as-received $\text{IrO}_2/\text{TiO}_2$ sample ($\sim 41\%$), which is also reflected by the much lower A- IrO_x :C- IrO_2 ratio in the reduced sample ($11/47 = 0.23/1$) compared

to the as-received sample ($41/59 = 0.69/1$). This observation is in line with the reaction mechanism proposed in the context of the discussion of Fig. 2, namely that A- IrO_x is being reduced predominantly in the beginning of the reduction reaction. Increasing the isothermal reaction temperature to 240 °C or ramping the temperature from 25 to 500 °C leads to the full reduction of iridium oxide to metallic Ir, which can be seen clearly by an inspection of the XPS data (Fig. 4a) and the XPS peak fitting results (Table I) as well as by the XRD data (Fig. 4b), where all of the features unique to C- IrO_2 have disappeared. The sharper diffraction lines for the sample ramped to 500 °C is indicative of more pronounced growth of the metallic Ir domains at this higher final reduction temperature.

Overall, both TGA temperature ramp and isothermal experiments can in principle be used to study the reduction of IrO_2 in H_2 -containing atmospheres, but the choice of the method depends on the question to be answered. The temperature ramp is a quick experiment for comparing the temperature stability window of different catalysts, while the time consuming isothermal experiment might be more useful when trying to get information at conditions that more closely reflect those in real applications. The latter point will be demonstrated in the next section, showing that isothermal TGA experiments can be used to project the behavior of an $\text{IrO}_2/\text{TiO}_2$ catalyst under the conditions of a PEMFC anode.

IrO_2 reduction in a simulated PEMFC anode reductive environment.—When using IrO_2 as an anode co-catalyst in PEMFCs, it is crucial to know the effect of the strongly reducing conditions in the hydrogen anode (~ 1 bar H_2 , 80 °C, and ~ 0 V vs RHE) on the chemical stability of IrO_2 . While probing the stability of IrO_2 directly in the anode of a PEMFC is possible, this approach has several disadvantages: i) it requires the time-consuming preparation/optimization of electrodes and their integration in membrane electrode assemblies (MEAs); ii) MEA preparation requires a considerable amount of catalyst (at least a few hundred milligrams), which often is a significant hurdle when exploring new catalysts synthesized by different methods; iii) the electrochemical characterization methods performed in a fuel cell are mainly sensitive to the chemical changes in the near-surface regions of a catalyst, and the analysis of bulk phases (e.g., via XRD) requires cumbersome post-mortem analysis; and, iv) MEA characterization in a fuel cell introduces additional complexity due to multiple reactions occurring in parallel. On the other hand, isothermal TGA experiments can be designed to simulate the reductive environment of PEMFC anodes, whereby no sample preparation is required, only a few milligrams of a sample are needed, and the observed sample mass loss can be directly and quantitatively correlated to the amount of reduced IrO_2 (surface and bulk). Therefore, long-term (up to 24 h) isothermal TGA experiments have been performed at 80 °C to investigate the stability of the iridium oxide phase of the $\text{IrO}_2/\text{TiO}_2$ catalyst in the presence of hydrogen, and the results are shown in Fig. 5a. To aid the interpretation of the data, the $\text{IrO}_2/\text{TiO}_2$ catalyst is assumed to have a core-shell morphology, with the surface of the TiO_2 support covered completely by IrO_2 particles or by an IrO_2 film (the latter is sketched in Fig. 5c). Nevertheless, Fig. 5c is a simplified sketch of the $\text{IrO}_2/\text{TiO}_2$ catalyst that is used here. All the assumptions regarding the calculation of the monolayer of IrO_2 (ML_{IrO_2}) on the $\text{IrO}_2/\text{TiO}_2$ catalyst surface in the experimental section are made while being based on a morphology that TiO_2 support is completely covered by IrO_2 particles; that is similar to Fig. A-1, inset.

The $\text{IrO}_2/\text{TiO}_2$ catalyst mass loss vs time for the long-term isothermal TGA experiment (Fig. 5a) reveals that a continuous IrO_2 reduction occurs over the entire course of the experiment, not showing any plateau in the mass loss even after 24 h. Based on our estimate (see experimental section) for the mass loss or the reaction extent α which correspond to the reduction of a monolayer of the iridium oxide phase (1 ML_{IrO_2} amounts to ~ 1.25 wt.% mass loss or to $\alpha \approx 10\%$), the estimated numbers of IrO_2 monolayers that are

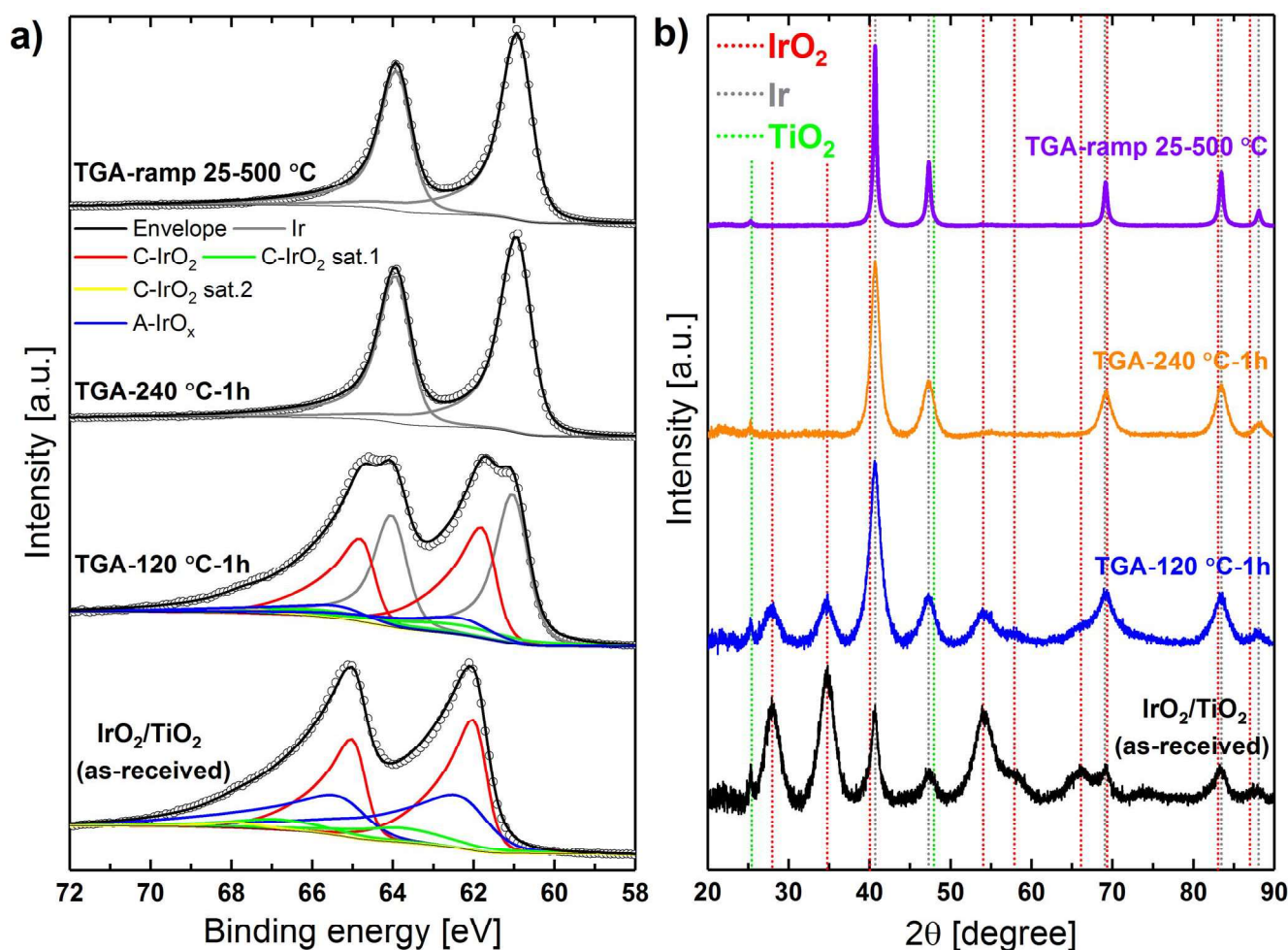


Figure 4. Post characterization of the as-received $\text{IrO}_2/\text{TiO}_2$ catalyst and of (partially) reduced $\text{IrO}_2/\text{TiO}_2$ catalyst powders after the TGA experiments in Fig. 3 by: (a) XPS $\text{Ir}4f$ spectra and (b) XRD. Sample notations: TGA-120 °C-1h and TGA-240 °C-1h refer to the materials obtained after the 1 h isothermal TGA experiments (see Fig. 3a) and TGA-ramp 25 °C–500 °C refers to the material obtained after the TGA temperature ramp experiment at a heating rate of $\beta = 5 \text{ Kmin}^{-1}$ (see Fig. 2a). Detailed peak deconvolution parameters and the ratios between different Ir species in (a) can be found in Table I. The vertical dotted lines in (b) are the main reference crystalline peak positions for metallic Ir (gray), rutile C-IrO_2 (red), and anatase TiO_2 (green).

reduced to metallic iridium are marked by the orange dotted lines in Fig. 5a. This analysis implies that the reduction of the iridium oxide phase of the $\text{IrO}_2/\text{TiO}_2$ catalyst at 80 °C is not limited to the outermost monolayer(s) of the iridium oxide phase, but that it rather proceeds further towards its bulk; after 24 h in 3.3 vol.% H_2/Ar at 80 °C, the data suggest that more than four ML_{IrO_2} equivalents of the IrO_2 phase have been reduced, corresponding to $\alpha > 40\%$.

Next, we will show that the above described surface and sub-surface reduction of the IrO_2 phase of the $\text{IrO}_2/\text{TiO}_2$ catalyst has a strong impact on its electrochemical behavior. For this, $\text{IrO}_2/\text{TiO}_2$ powder samples were subjected to different isothermal TGA intervals of 0.5, 3, 12, and 24 h (marked by the asterisks in Fig. 5a), and their electrochemical behavior was then characterized by RDE measurements and compared with that of the as-received $\text{IrO}_2/\text{TiO}_2$ catalyst. Figure 5b shows the CVs (first scans out of the 10 measured scans for each sample are shown, the starting positive sweeps from OCP to 1.35 V_{RHE} are removed, see Fig. A-2) of these samples in an Ar saturated 0.05 M H_2SO_4 electrolyte at a scan rate of 20 mVs^{-1} . Although the surface composition of the as-received $\text{IrO}_2/\text{TiO}_2$ is composed of two different IrO_2 species, namely A- IrO_x and C- IrO_2 (see Table I), the voltammetric features of this sample are resembling those of a highly crystalline and heat-treated IrO_2 ; this is indicative of an electrochemically stable IrO_2 phase in the as-received $\text{IrO}_2/\text{TiO}_2$ catalyst.⁵¹ It can be seen that after only 0.5 h of the isothermal TGA experiment (green asterisk in Fig. 5a), the

capacitive currents are increased by ~ 3 -fold (green line) compared to those of the as-received $\text{IrO}_2/\text{TiO}_2$ (black line), due to the formation of sub-monolayer amounts of metallic Ir on the catalyst surface. Nevertheless, the CV features still closely resemble that of the as-received catalyst.

Further reduction of the iridium oxide phase of the $\text{IrO}_2/\text{TiO}_2$ catalyst, equating to the reduction of roughly 1 ML_{IrO_2} (i.e., after 3 h, blue asterisk in Fig. 5a), leads to the appearance of voltammetric features for the hydrogen under-potential deposition (H_{upd}) between 0.05–0.40 V_{RHE} , characteristic of metallic polycrystalline iridium or carbon-supported iridium nanoparticles.^{52,53} This suggests that the reduction of $\sim 1 \text{ ML}_{\text{IrO}_2}$ and thus the formation of $\sim 1 \text{ ML}_{\text{Ir}}$ on the surface of the $\text{IrO}_2/\text{TiO}_2$ catalyst is sufficient to completely change its voltammetry from that corresponding to heat-treated IrO_2 to that corresponding to metallic Ir. After reducing the $\text{IrO}_2/\text{TiO}_2$ catalyst for longer times of 12 or 24 h, where ~ 3 or $>4 \text{ ML}_{\text{IrO}_2}$ equivalents are reduced, the CVs reach a steady-state, indicating that the reduction of sub-surface layers of the iridium oxide phase does not further increase the H_{upd} region. This is due to the fact that H adsorption/desorption occurs only on the outermost surface of the apparently compact and dense metallic Ir phase that is formed during reduction at 80 °C. The reduction of the iridium oxide phase of the $\text{IrO}_2/\text{TiO}_2$ catalyst during the extended isothermal TGA experiment is schematically shown in Fig. 5c.

In order to validate that the results obtained in the isothermal TGA experiment are representative of what happens to the

Table I. XPS Ir4f peak deconvolution parameters and the calculated composition of as-received and (partially) reduced IrO₂/TiO₂ samples based on the fitted XPS Ir4f spectra in Fig. 4a. C-IrO₂ refers to crystalline IrO₂, A-IrO_x refers to amorphous iridium oxide. Details of the fitting procedure are described in the experimental section.

Sample	Peak	B.E. [eV]	FWHM [eV]	Area [%]	Composition
IrO ₂ /TiO ₂ (as-received)	C-IrO ₂ 4f7/2	61.92	0.81	26.24	C-IrO ₂ : 59% A-IrO _x : 41%
	C-IrO ₂ 4f5/2	64.92	0.81	19.72	
	C-IrO ₂ 4f7/2 (sat.1)	63.80	2.91	6.83	
	C-IrO ₂ 4f5/2 (sat.1)	66.80	2.91	4.94	
	C-IrO ₂ 4f5/2 (sat.2)	67.90	1.53	1.32	
	A-IrO _x 4f7/2	62.20	1.79	23.38	
	A-IrO _x 4f5/2	65.20	1.79	17.57	
TGA-120 °C-1h	Ir 4f7/2	60.99	0.90	23.84	metallic Ir: 42% C-IrO ₂ : 47% A-IrO _x : 11%
	Ir 4f5/2	63.99	0.90	17.92	
	C-IrO ₂ 4f7/2	61.71	0.85	20.56	
	C-IrO ₂ 4f5/2	64.71	0.85	15.45	
	C-IrO ₂ 4f7/2 (sat.1)	63.5	3.6	5.61	
	C-IrO ₂ 4f5/2 (sat.1)	66.5	3.6	4.06	
	C-IrO ₂ 4f5/2 (sat.2)	67.71	1.57	1.04	
	A-IrO _x 4f7/2	62.21	1.8	6.63	
TGA-240 °C-1h	Ir 4f7/2	60.90	0.87	57.09	metallic Ir: 100%
	Ir 4f5/2	63.90	0.87	42.91	
TGA-ramp 25 °C-500 °C	Ir 4f7/2	60.88	0.86	57.09	metallic Ir: 100%
	Ir 4f5/2	63.88	0.86	42.91	

IrO₂/TiO₂ catalyst in a PEMFC anode, its stability was tested in an MEA. An MEA with an active area of 5 cm² was prepared, where IrO₂/TiO₂ was used in the anode electrode and a Pt/C catalyst was used in the cathode electrode. The MEA was held at OCV ($E_{\text{anode}} \approx 0$ V vs RHE and $E_{\text{cathode}} \approx 0.9$ – 0.95 V vs RHE, see experimental section) at 80 °C, with a constant flow of fully-humidified H₂ (2000 nccm) through the anode compartment pressurized at 170 kPa_{abs} (corresponding to a H₂ partial pressure of 123 kPa). Every 30 min, anode CVs were recorded at 40 °C, and were compared to the CV of the as-received IrO₂/TiO₂ catalyst (before ever flowing H₂ through the anode), as shown in Fig. 5d. The observed gradual formation of H_{upd} features of metallic Ir in Fig. 5d suggests that, similar to the TGA experiment, IrO₂ reduction upon exposure to H₂ also occurs in an MEA in a PEMFC (analogous to what was shown previously for a PEM water electrolyzer configuration^{24,29}). However, the reduction kinetics of the IrO₂ phase seems to be faster in the MEA, where it takes ~2 h for the surface of the IrO₂ phase to completely convert to metallic Ir and for the CVs to reach a steady-state. This is most likely due to the higher H₂ partial pressure in the MEA experiment ($P_{\text{H}_2} = 123$ kPa) compared to that in the TGA experiment ($P_{\text{H}_2} = 3.3$ kPa). It has to be noted that although the CVs recorded in the MEA reach a steady state after ~2 h of OCV (see Fig. 5d), it is speculated based on the TGA results (and based on the analogy of the TGA and MEA experiments) that the reduction of the IrO₂ phase of the IrO₂/TiO₂ catalyst also proceeds to subsurface layers of IrO₂, even though the formation of bulk metallic Ir is not further traceable by measuring CVs in the MEA. It is also worth mentioning that the high iridium loading of 2.0 mg_{Ir}cm⁻²_{MEA} used in this section is not relevant for the application of IrO₂ as an anode co-catalyst in a PEMFC, and it is only used to show the instability of IrO₂ in the reductive atmosphere of a PEMFC anode. The following sections of the paper will show that a more relevant loading of 0.05 mg_{Ir}cm⁻²_{MEA} will be used in the CRT and SUSD experiments.

A more active OER catalyst facilitates the OER over the COR during cell reversal in a PEMFC, resulting in longer cell reversal tolerance times.^{19,20} Measuring the OER activity of a catalyst using the RDE technique is a quick and reasonably reliable approach to predict its OER activity in an MEA.^{54,55} Therefore, Fig. 5e shows the RDE-based OER polarization curves of the as-received

IrO₂/TiO₂ catalyst (black line) and the catalyst after the respective isothermal TGA hold times shown in Fig. 5a. The polarization curves were recorded after 10 CVs in the potential window of 0.05–1.35 V_{RHE} in the Ar-saturated electrolyte (shown in Fig. A-2), whereby the potential that corresponds to the electrode current of 10 mAcm⁻²_{disk} is frequently taken as a measure of the OER activity.⁵⁶ It can be seen in Fig. 5e that the OER activity of the electrodes is increasing with increasing isothermal hold times at 80 °C, whereby the OER activity is improved by 38 mV after a 24 h hold time compared to the as-received IrO₂/TiO₂ catalyst. Analogous improvements of the OER activity (between 20–40 mV) were also observed when subjecting the same IrO₂/TiO₂ catalyst in the anode catalyst layer of a PEM water electrolyzer to cross-over hydrogen at OCV and 80 °C.^{24,29} Based on the analysis of Figs. 5a and 5e, such OER activity improvement is directly correlated to the reduction of IrO₂ and the formation of metallic Ir in the near-surface layer of the IrO₂ phase. It is well known that the product of electrochemical oxidation of metallic Ir (furtheron referred to as E-IrO_x, denoting a highly porous, hydrated iridium oxy-hydroxide) has a substantially higher OER activity than heat-treated IrO₂,^{57–59} which explains why the OER activity of the IrO₂/TiO₂ catalyst increases with increasing reduction time in Fig. 5a. The transformation of metallic Ir to E-IrO_x over the course of 10 CVs in the potential window of 0.05–1.35 V_{RHE} prior to the measurement of the OER polarization curves can be seen in Fig. A-2, where the appearance of voltammetric features in the potential range of ~0.7–1.2 V_{RHE} upon cycling is indicative of the transformation of the near-surface region metallic Ir to E-IrO_x. In fact, this feature is more prominent for the samples reduced for 12 and 24 h (Figs. A-2c and A-2d), which showed a nominal reduction of ~3 and ~4.5 ML_{IrO₂}, respectively. This is due to the fact that upon cycling the electrodes between 0.05–1.35 V_{RHE}, further oxidation of sub-surface metallic Ir leads to the formation of a thicker porous E-IrO_x layer on the catalyst surface and to an incorporation of the near-surface active sites to the electrochemical processes.^{60,61} This phenomenon, so called three-dimensional electrocatalysis,⁵⁹ explains the higher OER activity of the samples reduced for 12 and 24 h (reduction of ~3 and ~4.5 ML_{IrO₂} on IrO₂ surface) compared to the sample reduced for 3 h (reduction of ~1 ML_{IrO₂} on IrO₂ surface).

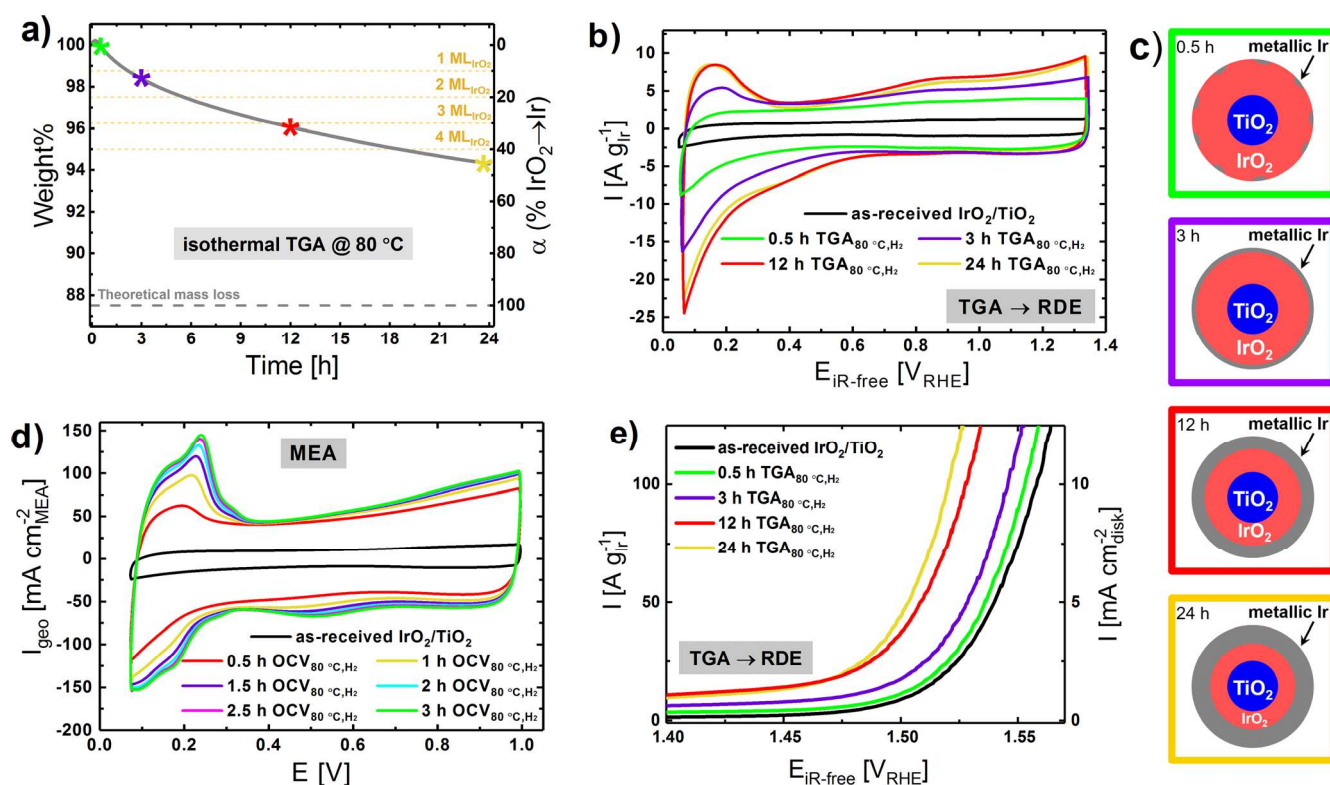


Figure 5. (a) Extended-time isothermal TGA experiments on the reduction of the iridium oxide phase of the $\text{IrO}_2/\text{TiO}_2$ catalyst in 3.3 vol.% H_2/Ar at 80 °C, aiming to simulate the PEMFC hydrogen anode reductive environment. The left y-axis represents the mass loss in wt.% of the $\text{IrO}_2/\text{TiO}_2$ catalyst vs time, while the fraction of the IrO_2 phase that is reduced to metallic Ir (α) is given on the right y-axis. The orange dotted lines represent the reduction of 1–4 monolayers of IrO_2 (ML_{IrO_2}), whereby the reduction of 1 ML_{IrO_2} corresponds to an estimated mass loss of ~ 1.25 wt.% or to a reaction extent of $\alpha \approx 10\%$; the gray dashed line marks the theoretical mass loss (12.5 wt.%) of the $\text{IrO}_2/\text{TiO}_2$ catalyst upon the full reduction of the IrO_2 phase to Ir (see experimental section). The asterisks mark the reduction times for the independently prepared samples for the electrochemical measurements in (b) and (e). (b) Cyclic voltammograms (CVs) of the as-received $\text{IrO}_2/\text{TiO}_2$ catalyst and of the partially reduced $\text{IrO}_2/\text{TiO}_2$ samples marked in a); they were recorded in an RDE configuration at room temperature between 0.05–1.35 V_{RHE} at a scan rate of 20 mVs^{-1} in Ar saturated 0.05 M H_2SO_4 (loading of $0.1 \text{ mgIr cm}^{-2}_{\text{disk}}$) at a rotation rate of 2500 RPM (1st cycle; all 10 cycles are shown in figure A.2). (c) Schematic representation of the reduction of the $\text{IrO}_2/\text{TiO}_2$ surface to metallic Ir during the extended-time isothermal TGA experiment in a), assuming a core/shell morphology. (d) CVs at 150 mVs^{-1} of the as-received $\text{IrO}_2/\text{TiO}_2$ catalyst incorporated as anode in a 5 cm^2 MEA ($2.0 \text{ mgIr cm}^{-2}_{\text{MEA}}$) with a Pt/C cathode ($0.4 \text{ mgPt cm}^{-2}_{\text{MEA}}$). The CVs, taken after a series of 30 min holds at OCV (80 °C, 170 $\text{kPa}_{\text{abs.}}$, 2000 nccm H_2 (anode)/5000 nccm air (cathode)), were acquired between 0.07–1.00 V at 40 °C and ambient pressure with fully-humidified N_2 (anode) and 5 vol.% H_2/Ar (cathode). (e) OER polarization curves of the as-received $\text{IrO}_2/\text{TiO}_2$ catalyst and of the partially reduced $\text{IrO}_2/\text{TiO}_2$ samples taken at 20 mVs^{-1} and 2500 RPM in Ar-saturated 0.05 M H_2SO_4 at room temperature ($0.1 \text{ mgIr cm}^{-2}_{\text{disk}}$).

Based on the conclusions drawn from the TGA and RDE experiments, and their confirmation by the MEA experiments in a PEMFC, it is clear that at least the near-surface layers of the IrO_2 phase of the $\text{IrO}_2/\text{TiO}_2$ catalyst can be reduced to metallic Ir by H_2 under the conditions of a PEMFC anode. This formation of metallic Ir at/near the catalyst surface also alters the electrochemical properties of the catalyst, leading to a drastic increase in its OER activity. A consequence of this phenomenon is that OER catalyst testing in an RDE, where the potential is usually kept above 1 V vs RHE, can yield a vastly different OER activity from that of the same catalyst, when it is used as an anode co-catalyst in a PEMFC. For example, the OER activity of the here used $\text{IrO}_2/\text{TiO}_2$ catalyst (corresponding to the black line in Fig. 5e) will be much lower than its activity as a cell reversal mitigation catalyst in a PEMFC anode (more closely corresponding to the yellow line in Fig. 5e). By the same token, IrO_2 based catalysts that are made by different synthesis routes could, e.g., be predominantly amorphous (or consisting of hydrous iridium oxide) or highly crystalline, which in turn would lead to a different degree of reducibility under H_2 (the higher degree of reducibility of amorphous iridium oxide is suggested by Figs. 2 and 3). As a more easily reducible IrO_2 catalyst would be expected to have a higher OER activity, it would also be expected to show a better cell reversal mitigation performance when used as an anode co-catalyst in a PEMFC. This phenomenon might explain the occasional discrepancy observed between the OER activity of a series of catalysts

measured by the RDE technique, and their performance as anode co-catalysts in cell reversal tests (CRTs) in a PEMFC (for example, compare Figs. 3a and 5a in Roh et al.,¹⁹ and Figs. 4a and 5a in Moore et al.²⁰). Therefore, the possibly different surface state of an IrO_2 based catalyst in conventional RDE based OER activity measurements vs that when used as anode co-catalyst in a PEMFC must be considered. In the next section, further consequences of the near-surface reduction of the IrO_2 phase of the $\text{IrO}_2/\text{TiO}_2$ catalyst when used as anode co-catalyst on PEMFC durability will be discussed.

Degradation of an $\text{IrO}_2/\text{TiO}_2$ anode co-catalyst by SUSD cycling.—Based on the results of the previous section it is now clear that during the normal operating conditions of a PEMFC, the IrO_2 phase of the $\text{IrO}_2/\text{TiO}_2$ catalyst when used as anode co-catalyst will get (partially) reduced to metallic Ir and, accordingly, its electrochemical behavior will change substantially. This phenomenon could eventually affect the stability of such an anode co-catalyst during the transient operation of a PEMFC, e.g., during SUSD and cell reversal events. In this regard, an accelerated SUSD test was performed with 38 cm^2 active area MEAs with a Pt/C catalyst in the cathode electrode and two different types of anode electrodes, namely either only with Pt/C (furtheron referred to as *non-mitigated MEA*) or with a mixture of Pt/C and the $\text{IrO}_2/\text{TiO}_2$ as anode co-catalyst (furtheron referred to as *mitigated MEA*). The

accelerated SUSD experiments are performed at a temperature of 35 °C, according to the US DRIVE Fuel Cell Technical Team Roadmap protocol (see experimental section), so that the strongly temperature-dependent Pt/C catalyst degradation during SUSD events is minimized²⁶ and any degradation that may be caused by the IrO₂/TiO₂ anode co-catalyst can be more easily determined. Figure 6a shows the cell potential profiles at a current density of 1.2 A cm⁻²_{MEA} as a function of performed SUSD cycles, determined from H₂/air (*s* = 1.5/2) performance curves at 80 °C, 100% RH, and 150 kPa_{abs,outlet} pressure. For the non-mitigated MEA (turquoise line/symbols in Fig. 6a), the H₂/air performance at 1.2 A cm⁻²_{MEA} drops by ~15 mV over the first 10 cycles and then remains roughly constant up to 100 cycles, after which it continuously decreases. The nearly constant performance over the first 100 cycles is likely due to a compensation of the SUSD losses by an activation of the Pt/C cathode catalyst caused by the positive potential excursion during the initial SUSD cycles.⁶² The overall SUSD induced performance loss with an unmitigated MEA is predominantly due to carbon support corrosion at the cathode, leading to a collapse of the cathode electrode (the so-called cathode thinning) and concomitant O₂ transport losses, and to a loss of Pt surface area at the cathode.²⁶ It should be noted that for each SUSD cycle, the anode electrode experiences a potential cycling between ~0–1.05 V_{RHE} upon the H₂/air_{anode} gas front passage, which also causes Pt dissolution and loss of electrochemically active surface area (ECSA) at the anode.²⁸ However, at least for a pure Pt/C anode, the contribution of anode ECSA loss to the overall losses caused by SUSD is negligible, due to the fast hydrogen oxidation reaction (HOR) kinetics on Pt, as long as the anode loadings are not ultra-low (i.e., not << 0.05 mg_{Pt} cm⁻²_{MEA}).²⁸

In order to quantify the degradation rate of the non-mitigated MEA upon SUSD cycling, the H₂/air front residence time normalized SUSD degradation rate at 35 °C for the non-mitigated MEA was calculated according to Mittermeier et al.²⁶ Considering a potential loss of ~80 mV over the 500 SUSD cycles (neglecting the initial activation effect of the Pt/C cathode catalyst) and the H₂/air front residence time of ~0.3 s, an average degradation rate of ~0.5 mV cycle⁻¹ s⁻¹ at 1.2 A cm⁻²_{MEA} is obtained. This is in reasonable agreement with the degradation rate of ~0.3 mV cycle⁻¹ s⁻¹ obtained for SUSDs conducted at 40 °C for cathodes with non-graphitized Vulcan carbon support reported by Mittermeier et al.²⁶ The mitigated MEA was also tested by the same SUSD protocol and the potential profile measured at 1.2 A cm⁻²_{MEA} vs SUSD cycling is compared to the non-mitigated MEA in Fig. 6a (dark purple line/symbols). The potential profile of the mitigated MEA at 1.2 A cm⁻² is clearly distinct from that of the non-mitigated MEA, as it shows a much larger potential loss in the initial 100 SUSD cycles. This initially rapid degradation is followed by a more gradual voltage decay, so that between 200 and 500 SUSD cycles the residence time normalized degradation rate for the mitigated and the non-mitigated MEA become essentially identical (~0.4 mV cycle⁻¹ s⁻¹). While both types of MEAs have the same initial performance (i.e., ~0.64 V at 1.2 A cm⁻²), owing to its initially faster SUSD degradation, the mitigated MEA has a ~40 mV lower performance after 500 SUSD cycles compared to the non-mitigated MEA. This overall ~40 mV larger voltage loss of the mitigated MEA is apparently due to its initial rapid performance loss and must thus be related to some additional degradation phenomenon originating from IrO₂/TiO₂ anode co-catalyst in the mitigated MEA.

To further explore this hypothesis, it is instructive to first examine the changes of the anode potential over the course of an SUSD cycle. Under the normal operating conditions of an H₂-fed PEMFC anode, the anode potential (and thus the potential of the IrO₂/TiO₂ anode co-catalyst) is at ~0 V vs RHE. On the other hand, once the H₂ gas in the anode compartment has been replaced by air during an SUSD half-cycle, the anode potential increases to ~1.05 V vs RHE.²⁸ During a subsequent SUSD half-cycle (i.e., when replacing the air in the anode again by H₂), the anode potential will be decreased again to ~0 V vs RHE. Thus, over the course of a complete SUSD cycle, the anode potential is being moved in a

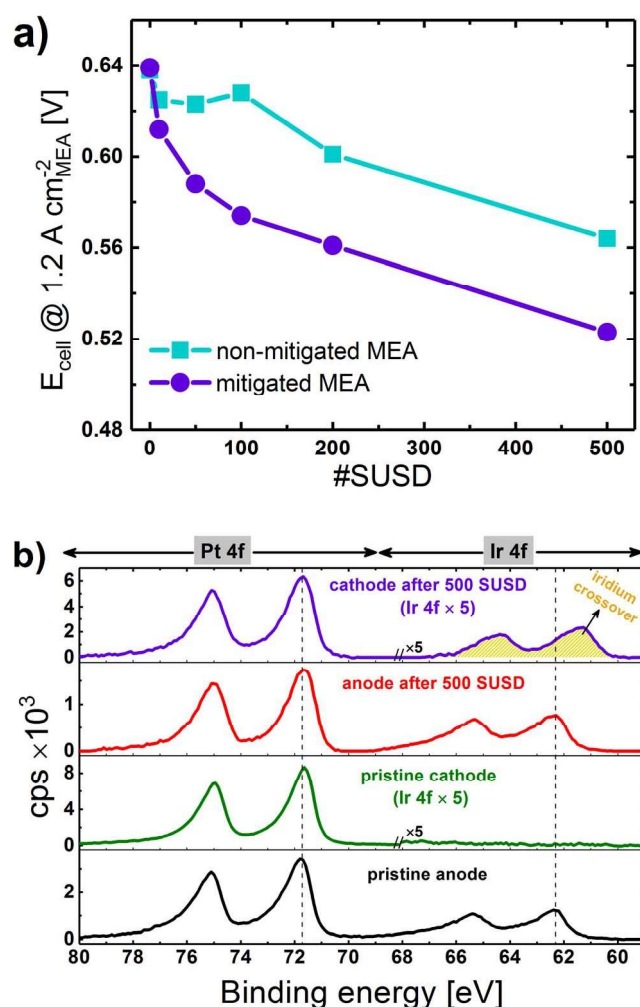


Figure 6. (a) Cell voltages at 1.2 A cm⁻² (taken from H₂/air performance curves, not shown here) as a function of the performed start-up/shut-down (SUSD) cycles (acc. to the US DRIVE Fuel Cell Technical Team Roadmap protocol at 35 °C, see experimental section) for *non-mitigated* and *mitigated* MEAs. H₂/air performance curve condition: T_{cell} = 80 °C, RH = 100%, P_{cell} = 150 kPa_{abs,outlet}, *s* = 1.5H₂/2air. MEA specifications: i) cathode with 0.3 mg_{Pt} cm⁻²_{MEA} loading, ii) anodes with 0.05 mg_{Pt} cm⁻²_{MEA} (*non-mitigated* MEA) or with 0.05 mg_{Pt} cm⁻²_{MEA} + 0.05 mg_{Ir} cm⁻²_{MEA} (Pt/C + IrO₂/TiO₂, *mitigated* MEA) loading. (b) Shirley background-corrected XPS Pt 4f and Ir 4f spectra of the anode and cathode electrodes of the pristine and 500-SUSD cycled mitigated MEAs. The vertical dashed line in the Pt 4f region shows the position of the Pt 4f_{7/2} peaks in the spectra of all electrodes. The vertical dashed line in the Ir 4f region shows the position of the Ir 4f_{7/2} peaks of the spectra of the anode electrodes (corresponding to the binding energy of A-IrO_x, see Table I). For better visualization of iridium crossover into the cathode electrode, the cps values in the Ir 4f regions of the cathode electrodes have been multiplied by 5.

square-wave like fashion from ~0 to ~1.05 and back to ~0 V vs RHE. These potential cycles, repeated for each SUSD cycle, are well known to lead to the dissolution of iridium (via the formation of Irⁿ⁺ ions), a mechanism called transient dissolution^{61,63} (the same process is also responsible for the accelerated dissolution of platinum during the current- or voltage-cycling of fuel cell cathodes).⁶² The stability of iridium against transient dissolution strongly depends on its chemical and morphological nature. It has been previously shown that transient dissolution rates are ~2 orders of magnitude higher for metallic Ir compared to highly crystalline IrO₂ (usually obtained by heat-treatment),⁶⁴ and comparable transient dissolution rates have been observed between metallic Ir surfaces and E-IrO_x (the product of electrochemical oxidation of

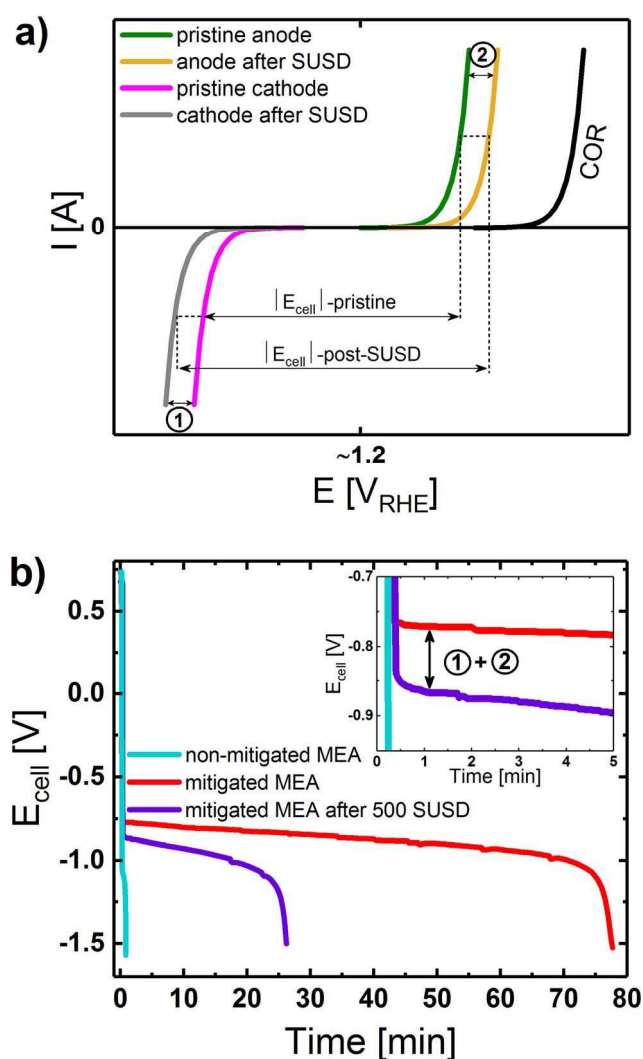


Figure 7. (a) Schematic representation of the current vs potential (referenced vs RHE) relationships of the anode and cathode half-cell reactions during a CRT. For the pristine mitigated MEA with an anode co-catalyst (Pt/C + IrO₂/TiO₂) and a Pt/C cathode these are: i) ORR on the pristine cathode (pink line); ii) OER on the pristine anode (green line); iii) carbon oxidation reaction (COR; black line), whose kinetics are much slower than that of the OER on an iridium based OER catalyst. For the mitigated MEA after SUSD testing, the loss of ORR performance of the cathode electrode (see Fig. 6a) leads to a negative-shift of the ORR (gray line) by a value marked as $\textcircled{1}$, while a decrease of the OER activity of the anode co-catalyst would lead to a positive-shift of the OER (yellow line) by a value marked as $\textcircled{2}$. The negative cell voltage during a CRT for a pristine mitigated MEA is marked by $|E_{cell}|_{\text{pristine}}$ and that of the mitigated MEA after SUSD testing by $|E_{cell}|_{\text{post-SUSD}}$; the difference between these two cell voltages corresponds to the loss of OER and ORR performance caused by SUSD testing, i.e., to $\textcircled{1} + \textcircled{2}$. (b) Cell reversal tests (CRTs) of the pristine non-mitigated MEA (turquoise line) as well as of the mitigated MEAs either in pristine state (red line) or after the 500 SUSD cycles shown in Fig. 6a (dark purple line); the MEA specifications are the same as given in Fig. 6a. CRT condition: $i = 0.2 \text{ A cm}^{-2}_{\text{MEA}}$, $T_{\text{cell}} = 80^\circ\text{C}$, $\text{RH} = 100\%$, $P_{\text{cell}} = 150 \text{ kPa}_{\text{abs, outlet}}$, N_2/air flows (166/333 nccm) in anode/cathode. The inset is a magnified view of the first 5 min of the CRTs, marking the initial cell potential difference between the two mitigated MEAs, corresponding to the sum of the ORR and OER activity losses (denoted as $\textcircled{1} + \textcircled{2}$ in the inset of panel b).

metallic Ir by potential cycling between ~ 0 – 1.05 V vs RHE)^{61,63} rendering metallic Ir and E-IrO_x substantially less stable than heat-treated IrO₂ when subjected to voltage cycles. Considering that the here used IrO₂/TiO₂ catalyst was heat-treated above 300°C

according to the patent⁶⁵ and that its voltammetric features are indicative of highly crystalline IrO₂ (see black line in Fig. 5b), one would expect it to have a high stability against transient dissolution during SUSD cycling. However, according to the data shown in Fig. 5d, the near-surface layers of the IrO₂/TiO₂ anode co-catalyst can be reduced to metallic iridium (from the surface to the core of the catalyst particles, see Fig. 5c) within a few hours when exposed to the H₂ environment of a PEMFC anode at $\sim 0 \text{ V}$ vs RHE during the conditioning and recording of a polarization curve (see experimental section). This, combined with the fact that metallic iridium surfaces (and their electrochemical oxidation product, E-IrO_x) exhibit very high transient dissolution rates, render it very likely that there might be substantial iridium dissolution from the anode co-catalyst during SUSD cycles; if true, this could lead to an iridium loss from the anode electrode and to iridium re-precipitation in the membrane or in the cathode electrode.

In order to examine whether iridium dissolution during SUSD cycles leads to a diffusion and re-precipitation of iridium in the oxygen (cathode) electrode, the mitigated MEA was harvested after 500 SUSD cycles and examined by XPS. Figure 6b shows the XPS Pt 4f and Ir 4f spectra of the pristine and SUSD cycled anode and cathode electrodes of the mitigated MEA. All the spectra exhibit Pt 4f doublets with Pt 4f_{7/2} peaks at $\sim 71.8 \text{ eV}$ (vertical dashed line in Pt 4f region), indicating that the surface chemistry of the platinum catalyst in both anode and cathode does not change over the 500 SUSD cycles. The Ir 4f spectra of the pristine and the SUSD cycled anodes are very similar to those of the as-received IrO₂/TiO₂ catalyst powder (bottom panel in Fig. 4a), with Ir 4f_{7/2} peaks at ~ 62.2 and $\sim 62.1 \text{ eV}$, respectively. Based on the analysis presented in Table I, the Ir 4f spectra of the as-received IrO₂/TiO₂ catalyst are composed of signals from amorphous (A-IrO_x) and crystalline (C-IrO₂) iridium oxide. Although it is expected that the near-surface layers of the IrO₂/TiO₂ anode co-catalyst will be partially reduced to metallic Ir during the initial conditioning step and recording of a polarization curve, a metallic Ir signal ($\sim 60.9 \text{ eV}$, see Table I) is not detected in the SUSD cycled anode spectrum. This is most likely due to the electrochemical oxidation of metallic Ir and transition to E-IrO_x by potential cycling between ~ 0 – 1.05 V vs RHE during SUSD cycles, where it is reported that E-IrO_x is composed of two different iridium oxide species with Ir4f binding energies comparable to the as-received IrO₂/TiO₂ catalyst in this study.⁶⁶ Therefore, the Ir4f signal in the SUSD cycled anode spectrum should predominantly reflect the contribution of E-IrO_x as well as the contribution from the sub-surface IrO₂ of the IrO₂/TiO₂ catalyst that did not get reduced to metallic Ir during the experiments. Note that a significant fraction of sub-surface IrO₂ was also observed in the XPS spectrum of the TGA-1h-120 $^\circ\text{C}$ sample in Fig. 4a, even though $\sim 50\%$ of the IrO₂ in this sample was reduced to metallic near-surface Ir during the TGA experiment (see blue line in Fig. 3a).

With regards to the XPS spectra of the cathode electrodes, no Ir 4f signal is detected for the pristine cathode, as it only contains the Pt/C catalyst. However, a relatively strong Ir 4f signal could be detected in the XPS spectrum of the cathode electrode after 500 SUSD cycles, indicating iridium dissolution in the anode electrode and subsequent permeation of Irⁿ⁺ species through the membrane to the cathode electrode (often referred to as crossover). The Ir 4f_{7/2} peak energy of $\sim 61.2 \text{ eV}$ observed for the SUSD cycled cathode is between the characteristic binding energy of metallic iridium ($\sim 60.9 \text{ eV}$, see Table I) and that observed for E-IrO_x ($\sim 61.6 \text{ eV}$ for Ir(IV) contribution in E-IrO_x) in our previous study.⁶⁶ The cathode electrode experiences a potential cycling between ~ 0.95 to $>1.4 \text{ V}$ vs RHE during SUSD cycles (more details about potential profile of the cathode electrode during SUSD cycles are provided in the last section). This consequently promotes the oxidation of iridium in cathode during the course of SUSD experiment.⁶¹ On the other hand, during the measurement of H₂/air polarization curves at different SUSD cycling intervals, the cathode electrode potential

remains at values below 0.65 V vs RHE for the course of several minutes during each polarization curve, a potential region in which metallic Ir is thermodynamically stable.⁶⁷ Therefore, the nature of such iridium surface contaminations in the SUSD cycled cathode electrode could be essentially prone to the potential profile experienced by the cathode electrode during the experiments. Hence, the identification of the exact nature of iridium in the SUSD cycled cathode electrode is not trivial. However, the ORR activity loss of the mitigated MEA within the first ~100 SUSD cycles that was observed in Fig. 6a could be explained by assuming that iridium dissolved in the anode is deposited on the platinum surface of the Pt/C cathode catalyst; owing to the ~100-fold lower ORR activity of iridium compared to platinum, this would lead to a loss of ORR activity of the Pt/C cathode catalyst.^{68–70} This phenomenon would be analogous to the observations made in the context of (partial) Ru dissolution from PtRu alloy anode catalysts in direct methanol fuel cells or in PEMFCs operated with reformate, where the dissolved Ru species were shown to permeate through the membrane to the cathode and to deteriorate the ORR performance of the Pt/C cathode catalyst.^{71–74} Based on these considerations, the overall ~40 mV higher potential loss over 500 SUSD cycles for the mitigated MEA (Fig. 6a) can be assigned to the poisoning of the ORR activity of the Pt/C cathode catalyst by re-deposited crossover iridium. It should be noted that iridium dissolution was also observed when using the same IrO₂/TiO₂ catalyst as oxygen evolution catalyst in a PEM water electrolyzer that was cycled between OCV and electrolysis mode.²⁹ During the OCV periods, the oxygen electrode (anode) potential dropped to ~0 V vs RHE due to H₂ permeation through the membrane into the anode compartment, while during operation, the anode potential was above 1.5 V vs RHE. In this case, however, the dissolved iridium was precipitated in the H₂-saturated membrane phase, which prevented iridium crossover to the hydrogen electrode (cathode).

Cell reversal for pristine or SUSD cycled MEAs.—Cell reversal tests (CRTs) were performed on pristine and SUSD cycled mitigated MEAs (Pt/C + IrO₂/TiO₂ anode) to determine the effect of the SUSD induced iridium dissolution on the CRT tolerance of mitigated MEAs; as a reference, a CRT was also performed for the pristine non-mitigated MEA (Pt/C anode). In order to initiate the CRT, the anode gas was switched from H₂ to N₂, while air was continuously fed to the cathode electrode and a current density of 0.2 A cm⁻²_{MEA} was applied. Upon the replacement of H₂ by N₂, the anodic current initially supplied by the hydrogen oxidation reaction (HOR) will have to be provided by a combination of the oxygen evolution reaction (OER; see green line in Fig. 7a) and the carbon oxidation reaction acc. to Eq. 1 (COR; see black line in Fig. 7a), whose relative contribution to the overall current depends on the OER activity of the anode catalyst(s) and on the nature of the carbon support materials (graphitized carbon supports being more stable than non-graphitized ones).⁷⁵ The higher the OER/COR activity ratio at a given potential and at a given overall current density, the lower will be the degradation of the anode carbon support over the course of a CRT, i.e., the higher will be the CRT tolerance of an MEA. As the OER and COR currents are only appreciable above ~1.3–1.4 V vs RHE and as the cathode potential in a PEMFC ranges between ~0.7–0.9 V vs RHE (see pink line in Fig. 7a), the cell voltage during cell reversal becomes negative ($E_{\text{cell}} \equiv E_{\text{cathode}} - E_{\text{anode}}$) and is marked by the horizontal arrows in Fig. 7a. As the anode electrode degrades over the course of a CRT (predominantly due to anode carbon support corrosion), the cell voltage becomes more and more negative; in this work, the time to reach a cell voltage of -1.5 V was set as the end-of-life (EOL) criterion and is further on referred to as *reversal tolerance time* of the MEAs.

Figure 7b shows the CRT for the non-mitigated MEA (turquoise line) as a reference, with a reversal tolerance time of only ~36 s. This very rapid degradation is due to the poor OER activity of a Pt/C

catalyst, so that its OER kinetics are similar or even slower than the COR of the graphitized carbon support.^{4,19,75} In the context of the scheme in Fig. 7a, this means that the green line marking the OER kinetics would be shifted positively and would be located at or to the right of the black line marking the COR. In this case, the overall current will be carried to a comparable fraction by both the OER and the COR, leading to a rapid corrosion of the carbon support, which in turn leads to the collapse of the anode catalyst layer and to cell failure.

In contrast to the non-mitigated MEA, the use of IrO₂/TiO₂ as an anode co-catalyst in the mitigated MEA drastically increases the reversal tolerance time to ~77 min. This is due to the much higher OER activity of IrO₂/TiO₂ compared to Pt/C, illustrated in Fig. 7a by the green line for the OER, resulting in a lower anode potential and, consequently, a much lower fraction of the overall current contributed by the COR. Here it should be noted that the OER activity of the IrO₂/TiO₂ catalyst when used as anode co-catalyst is even higher than the OER activity of the as-received material, due to the enhanced OER activity of the (partially) reduced IrO₂ phase compared to the initially crystalline IrO₂ (compare yellow and black lines in Fig. 5e) that is formed within hours under the conditions of a H₂ anode (see Fig. 5d). As a corollary, a non-reducible IrO₂ based catalyst would exhibit a lower reversal tolerance due to its lower OER activity. While the SUSD cycling induced iridium dissolution in the anode of the mitigated MEA leads to an ORR activity loss of ~120 mV at 1.2 A cm⁻² (see dark purple line/symbols in Fig. 6a) and of ~35 mV at 0.2 A cm⁻² (data not shown), this would not affect the cell reversal tolerance of the mitigated MEA, as this would not affect the anode potential during cell reversal (green line in Fig. 7a) and thus would not affect the rate of the COR, even though the cell voltage during the CRT would be more negative. Therefore, in this case, one would expect identical cell reversal tolerance for the pristine and for the SUSD cycled mitigated MEA. The cell reversal tolerance would only be affected negatively, if i) the OER activity of the IrO₂/TiO₂ anode co-catalyst would decrease over the course of SUSD cycling (illustrated by the yellow line in Fig. 7a), and/or if ii) the anode carbon support would be partially corroded by the SUSD cycling due to the H₂/air front induced anode potential cycles (see above). The latter is highly unlikely, as only minor anode thinning (~10%), indicating little carbon support corrosion was observed after 500 SUSD/voltage cycles at 80 °C for a non-graphitized Vulcan carbon support,²⁸ so that for the here conducted 500 SUSD cycles at 35 °C and graphitized Vulcan carbon support, anode carbon support corrosion can be considered negligible (anode thinning of <10%) due to the high apparent activation energy of the COR.⁷⁵ Whether the SUSD induced iridium dissolution will also affect the OER activity, and thus the cell reversal tolerance of the mitigated MEAs, will be examined in the following.

As shown in Fig. 7b, the cell reversal tolerance time of the mitigated MEA that was subjected to the 500 SUSD cycles (see Fig. 6a) prior to the CRT is ~3-fold shorter (~26 min; see dark purple line in Fig. 7b) than that of the pristine mitigated MEA. In addition, as shown in the inset of Fig. 7b, the initial CRT cell voltage of the SUSD cycled mitigated MEA (dark purple line) is ~88 mV lower compared to the pristine mitigated MEA (red line). Since the cell voltage during a CRT is the difference between the cathode (ORR) and the anode (OER) half-cell potentials, as shown schematically in Fig. 7a, the lower cell voltage of the SUSD cycled mitigated MEA (denoted as ①+② in the inset of Fig. 7a) must originate from a half-cell potential shift of either the ORR (marked by ① in Fig. 7a) and/or the OER (marked by ②). Here it should be noted that with an anode carbon loading of 0.2 mg cm⁻²_{MEA} in this study, if all of the carbon support were to corrode at the end of CRT in the anode electrode through Eq. 1 (4e⁻/CO₂), it would correspond to a maximum COR charge of ~6.4 C cm⁻²_{MEA}. The overall charge that is drawn at the end of CRT is ~924 C cm⁻²_{MEA} and ~312 C cm⁻²_{MEA} for the mitigated MEA (red curve in Fig. 7b) and mitigated MEA after 500 SUSD cycles (dark purple curve in

Fig. 7b), respectively. This would signify that the maximum time averaged COR contribution to the overall drawn charge (OER + COR) during CRT would only be $\sim 0.7\%$ and $\sim 2.1\%$ for the mitigated MEA (red curve in Fig. 7b) and mitigated MEA after 500 SUSD cycles (dark purple curve in Fig. 7b), respectively. Hence, the contribution of the COR to the overall anodic current can be neglected when using a highly active OER anode co-catalyst. Based on the H_2/air performance curves recorded over the course of the SUSD test (data not shown), the increase of the ORR overpotential at 0.2 A cm^{-2} after 500 SUSD cycles is $\sim 35 \text{ mV}$ ($\equiv \textcircled{D}$). Thus, the difference between this value and the $\sim 88 \text{ mV}$ lower initial CRT voltage, equating to $\sim 53 \text{ mV}$, can only be ascribed to a loss in OER activity of the $\text{IrO}_2/\text{TiO}_2$ anode co-catalyst after the 500 SUSD cycles, thereby corresponding to a positive-shift of the OER potential as compared to the pristine mitigated MEA at the beginning of CRT ($\equiv \textcircled{D}$). Such loss in OER activity would increase the anode potential and would thus increase the fractional CRT current that is provided by the COR, leading to the observed decrease of the reversal tolerance time.

There are two possible hypotheses to explain the loss of OER activity of the $\text{IrO}_2/\text{TiO}_2$ anode co-catalyst that is apparently induced by SUSD cycling: i) dissolution of iridium from the anode catalyst during SUSD transients, leading to an overall loss of OER active material in the anode; and/or, ii) dissolution of Pt from the Pt/C anode catalyst due to anode voltage cycling during the SUSD transients and re-deposition of the dissolved Pt^{n+} species on the $\text{Ir}/\text{IrO}_2/\text{TiO}_2$ anode co-catalyst, lowering its OER activity by blocking the OER active iridium surface sites. The former would require a substantial loss of iridium from the anode: at a Tafel slope for the OER of $\sim 50\text{--}60 \text{ mV decade}^{-1}$,³¹ a loss of 90% of the active iridium sites would lead to an OER activity loss of $\sim 50\text{--}60 \text{ mV}$. Considering a $\sim 7.5 \text{ nm}$ thick layer of IrO_2 covering the TiO_2 support in the $\text{IrO}_2/\text{TiO}_2$ catalyst (see Fig. A-1, inset), the dissolution of iridium from the surface of the catalyst would constantly expose the underlying iridium active sites in the IrO_2 layer, which would consequently participate into OER; therefore, no apparent loss of OER activity is expected until the last few mono-layers of IrO_2 covering the TiO_2 support particles start to dissolve. As the ratio between the Pt 4f and the Ir 4f XPS spectra of the pristine and the SUSD cycled anodes in Fig. 6b do not indicate such high losses of iridium after 500 SUSD cycles, a poisoning of OER active iridium sites by re-deposited platinum seems more likely.

Summary of the SUSD induced processes and their effect on the CRT tolerance.—In order to summarize the foregoing analysis

and discussion, a schematic representation of the processes occurring in the mitigated MEA with an $\text{IrO}_2/\text{TiO}_2$ anode co-catalyst during the normal operation of a PEMFC and during the shut-down and the start-up half-cycles of an SUSD test are shown in Fig. 8. When using an IrO_2 based anode co-catalyst for mitigating cell reversal damages in PEMFCs, it was shown above that the near-surface layer(s) of the $\text{IrO}_2/\text{TiO}_2$ catalyst get chemically reduced to metallic Ir by H_2 during the normal operation of the fuel cell, as illustrated in Fig. 8a. Such chemical alteration of the catalyst surface should improve its reversal tolerance time in a CRT, since metallic iridium that converts to electrochemically oxidized (often referred to as E-IrO_x) or hydrous iridium oxide once the potential is increased into the OER region has a higher intrinsic OER activity than the initial heat-treated, highly crystalline IrO_2 .

At the same time, however, metallic Ir is reported to exhibit a ~ 2 orders of magnitude higher dissolution rate than crystalline IrO_2 ,⁶⁴ rendering it more prone to dissolution during the SUSD induced anode potential cycles ($\sim 0\text{--}1.05 \text{ V}$ vs RHE).²⁸ During the fuel cell shut-down step, described in Fig. 8b, the passage of the air-front pushes the H_2 from anode inlet to the anode outlet (from bottom to top in Fig. 8b), whereby the anode potential increases from $\sim 0 \text{ V}$ vs RHE (in the H_2 -filled segment) to $\sim 1.05 \text{ V}$ vs RHE (in the air-filled segment). This leads to platinum and iridium dissolution from the anode catalysts, forming Pt^{n+} and Ir^{n+} ions that are dissolved in the ionomer phase and can diffuse across the anode, the membrane, and the cathode. As the air-front passes through the anode, the cathode segment adjacent to the air-filled anode will be at potentials of $>1.4 \text{ V}$ vs RHE. After the passage of the air-front, the cathode potential will also assume $\sim 1.05 \text{ V}$ vs RHE⁸ (the cell voltage being $\sim 0 \text{ V}$); whether re-deposition of Pt^{n+} and Ir^{n+} (possibly also in form of underpotential deposition on Pt) will occur at such high potential on the Pt/C cathode catalyst is still an open question. In the subsequent start-up step, described in Fig. 8c, a H_2 -front passes from the anode inlet to the anode outlet, displacing air from the anode compartment. In the H_2 -filled anode segment, the potential drops to $\sim 0 \text{ V}$ vs RHE and the dissolved Pt^{n+} and Ir^{n+} species will deposit on the surface of the anode catalysts. As the nucleation of metallic Pt and Ir is expected to be more facile on metal surfaces compared to nucleation of nanoparticles on the carbon support, one would expect that the dissolved metals deposit preferentially on the platinum and iridium phases. Since the HOR activity of iridium is very high and only ~ 3 -fold lower than the that of platinum,³⁶ this would not affect the HOR performance of the anode. On the other hand, since the OER activity of iridium based catalysts is orders of magnitude higher than that of platinum,⁷⁶ a deposition of platinum

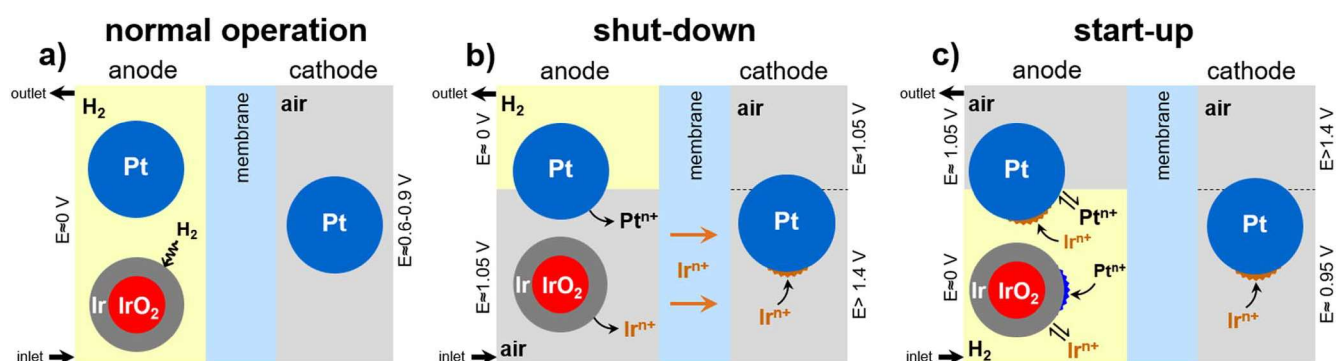


Figure 8. Schematic representation of the processes occurring in a mitigated MEA in the presence with an iridium oxide based anode co-catalyst during normal fuel cell operation, fuel cell shut-down, and fuel cell start-up. (a) *Normal fuel cell operation:* illustrating the chemical reduction of the near-surface layer(s) of the iridium oxide phase of the $\text{IrO}_2/\text{TiO}_2$ anode co-catalyst by H_2 to metallic Ir. (b) *Fuel cell shut-down step:* upon passage of the air-front, the anode potential increases to $\sim 1.05 \text{ V}$ vs RHE,²⁸ leading to platinum and iridium dissolution from the anode catalysts, whereby the resulting Pt^{n+} and Ir^{n+} ions can diffuse within in the ionomer and membrane phase; after passage of the air-front, the cathode potential will assume $\sim 1.05 \text{ V}$,⁸ and re-deposition of crossover iridium on the platinum surface of the Pt/C cathode catalyst could possibly occur. (c) *Fuel cell shut-down step:* upon passage of the H_2 -front, the anode potential decreases from $\sim 1.05 \text{ V}$ to $\sim 0 \text{ V}$ vs RHE, and the re-deposition of Pt^{n+} and Ir^{n+} on the Pt/C and the $\text{IrO}_2/\text{TiO}_2$ catalysts in the anode will occur; after passage of the H_2 -front, the cathode potential is $\sim 0.95 \text{ V}$ (this lower OCV is due to H_2 crossover), and iridium deposition on the Pt/C cathode catalyst becomes more likely.

on the surface of the $\text{IrO}_2/\text{TiO}_2$ anode co-catalyst would be expected to drastically reduce its OER activity. Once the H_2 -front has passed, the open circuit potential of the cathode electrode will be lowered to $\sim 0.90\text{--}0.95$ V vs RHE due to the H_2 permeation through membrane (corresponding to the OCV of a H_2/air cell), at which potential the (underpotential) deposition of iridium ions dissolved in the ionomer phase of the cathode electrode (as well as the deposition of dissolved platinum ions) on the Pt/C cathode catalyst will likely occur. As iridium has a much lower ORR activity than Pt,^{68–70} (underpotential) deposition of iridium on the platinum of the cathode catalyst would lead to the lower ORR activity after SUSD cycles, as deduced from Fig. 6a. In summary, our analysis suggests that the ~ 3 -fold lower reversal tolerance time observed for the mitigated MEA after 500 SUSD cycles is most likely due to a loss of OER activity of the anode co-catalyst caused by the transient dissolution of platinum from the anode Pt/C catalyst and its partial deposition on the surface of the iridium phase of the $\text{IrO}_2/\text{TiO}_2$ anode co-catalyst. It has to be mentioned that during the start-up process, any dissolved Pt or Ir will immediately re-deposit on the parent particle due to the low anode potential in the presence of H_2 (a similar phenomenon was suggested for Pt by Schwämmlein et al.²⁸), so that Ir^{n+} crossover to the cathode can be neglected during the start-up process and should be mainly occurring during the shut-down process. Based on the here proposed mechanisms, the degradation of the ORR activity of the Pt/C cathode catalyst during SUSD cycles could be avoided, if the chemical reduction of the active iridium oxide phase of the $\text{IrO}_2/\text{TiO}_2$ anode co-catalyst could be prevented. Thus, future research towards the development of a more stable anode co-catalyst to mitigate cell reversal degradation would be to focus on stabilization strategies to hinder the chemical reduction of iridium oxide based catalysts by H_2 at the operational temperatures of PEMFCs, along with designing high OER active IrO_2 catalysts. However, whether Pt would deposit on the surface of a non-reducible iridium oxide based anode co-catalyst and equally degrade its OER activity upon SUSD cycling is still an open question, which requires further investigation in future studies.

Conclusions

In this study, it is shown that when using an IrO_2 based anode co-catalyst for mitigating cell reversal damages in PEMFCs, the near-surface layer(s) of the $\text{IrO}_2/\text{TiO}_2$ catalyst get chemically reduced to metallic Ir by H_2 during the normal operation of the fuel cell. Such alteration of the near-surface layer(s) of IrO_2 drastically affects its stability during the anode potential transients during SUSD cycles, where it was shown that the dissolution of metallic Ir and crossover of the dissolved Ir^{n+} species through the membrane to the cathode electrode cause iridium deposition on the Pt/C cathode catalyst, as evidenced by XPS Ir4f spectra of the cathode electrodes after SUSD cycling. Such iridium-based contamination on the cathode catalyst surface deteriorates the ORR activity of Pt and results in a significant performance loss during the normal operation of the fuel cell. At the same time, SUSD transients also cause an OER activity loss of the anode co-catalyst, which was shown to be mainly due to the re-deposition of Pt dissolved from the anode HOR catalyst onto the reduced IrO_2 anode co-catalyst, blocking its OER active sites.

In light of the here made observations, it is clear that the reduction of the near-surface layer(s) of the IrO_2 anode co-catalyst to metallic Ir compromises its stability during the anode potential transients that occur during SUSD cycles. Therefore, it is suggested that the stability of IrO_2 -based anode co-catalysts in H_2 -containing

atmosphere should be carefully evaluated by a here proposed new methodology prior to using the catalysts in a PEMFC anode. It is based on an extended isothermal TGA experiment at operational temperatures of PEMFCs and under a dilute H_2 atmosphere, where the reducibility of the IrO_2 catalyst can be reliably and quantitatively examined. After the isothermal TGA experiment, the catalyst powder can be electrochemically investigated by RDE experiments in order to determine the effect of the exposure of the catalyst to a reducing H_2 atmosphere on its electrochemical properties.

Last but not least, future research towards the development of new anode co-catalysts should focus on stabilization strategies to hinder the chemical reduction of iridium oxide based catalysts by H_2 at the operational temperatures of PEMFCs, along with designing highly OER active IrO_2 catalysts.

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Appendix

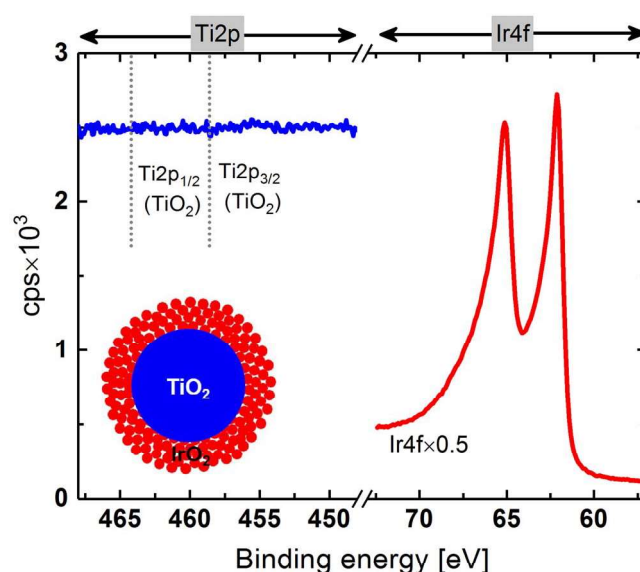


Figure A-1. XPS Ti2p and Ir4f spectra of as-received $\text{IrO}_2/\text{TiO}_2$ catalyst. The vertically dashed lines in Ti2p region represent the positions of $\text{Ti2p}_{3/2}$ and $\text{Ti2p}_{1/2}$ signals in a TiO_2 sample.⁷⁷ The Ir4f signal is multiplied by 0.5 for a better representation of the data. Inset shows schematic representation of a TiO_2 support particle, which is completely covered by IrO_2 particles. If the IrO_2 layer is assumed as a uniform and compact film covering the TiO_2 support particle ($d_{\text{TiO}_2} \approx 28$ nm), an equivalent IrO_2 film thickness of ~ 7.5 nm can be consequently calculated for this structure.

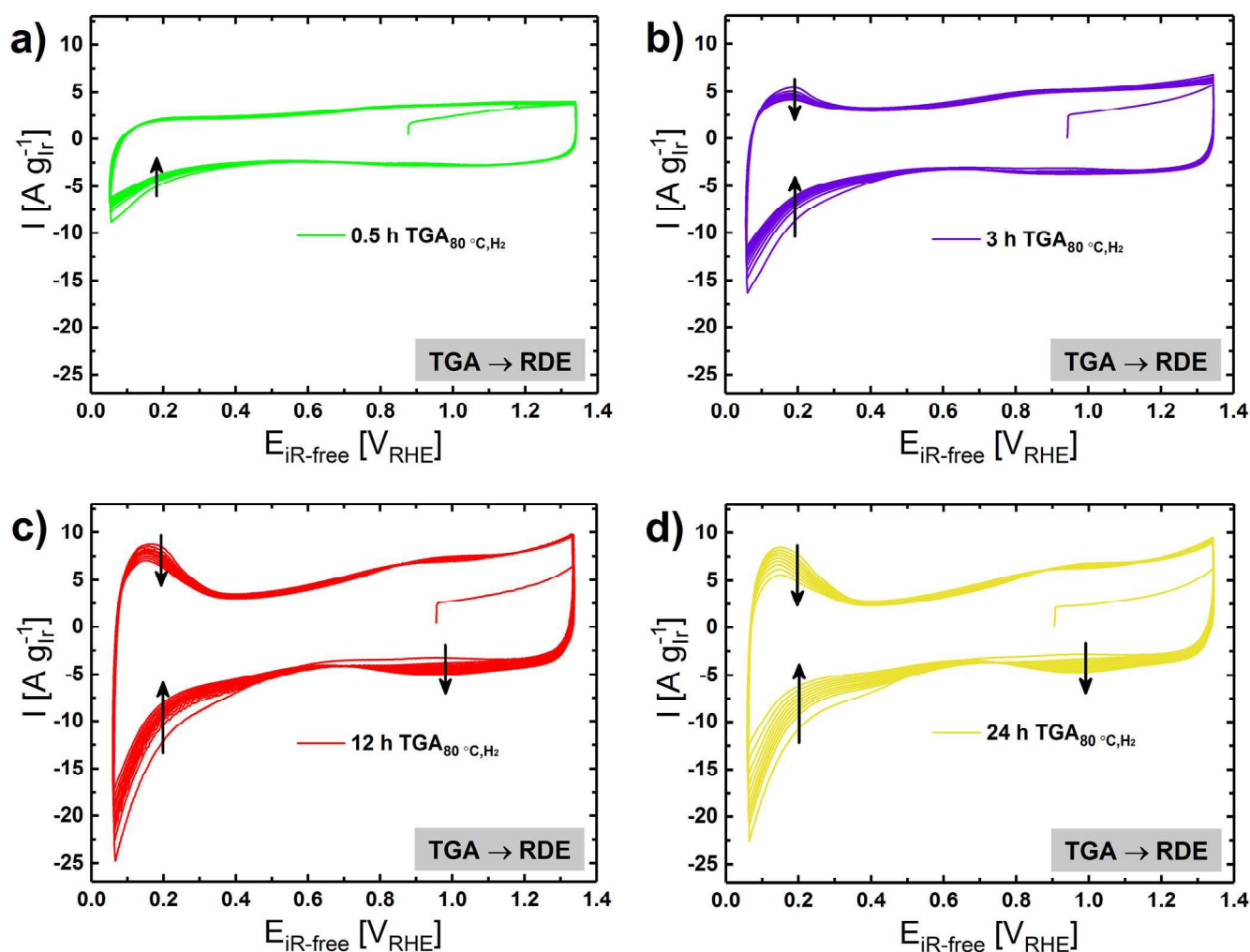


Figure A-2. The initial 10 cyclic voltammograms (CVs) of the partially reduced $\text{IrO}_2/\text{TiO}_2$ samples marked in Fig. 5a, namely after (a) 0.5 h, (b) 3 h, (c) 12 h, and (d) 24 h of the TGA isothermal experiment at 80 °C. In order to plot Fig. 5b, the first voltammetric cycles out of the measured 10 cycles were taken, whereby the initial anodic going sweeps from OCP ($\sim 0.9 \text{ V}_{\text{RHE}}$) to 1.35 V_{RHE} were removed. The arrows show the evolution of the CVs from cycle 1 to 10. The RDE measurements conditions are the same as given in Fig. 5b.

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3.4 Synthesis and Characterization of Reduction Resistant IrO₂ Catalysts

This section presents the manuscript “Irreducible IrO₂ Anode Co-catalysts for PEM Fuel Cell Voltage Reversal Mitigation and Their Stability Under Start-up/Shut-down Conditions” which was published in July 2024 in the *Journal of The Electrochemical Society*.¹²⁰ It is an open access article distributed under the terms of the Creative Commons Attribution 4.0 License (CC BY). The article can be found under the permanent web-link: <https://doi.org/10.1149/1945-7111/ad6211>. Under the discoveries within the scope of research in this section, the rights of development of such irreducible IrO₂ catalysts are protected in form of a published patent application.¹⁵² Additionally, the study was accepted for an oral presentation by Mohammad Fathi Tovini at the 241st Meeting of the Electrochemical Society (May 29-June 2, 2022, Vancouver, Canada, Abstract number: I03-1466). However, the presentation was made by Ana Marija Damjanovic due to the delayed travel Visa issuance to the original presenter.

IrO₂ is the most stable OER catalyst in acidic media, and the addition of IrO₂ as a co-catalyst to the anode electrode of PEMFCs would seem to be the simplest strategy to mitigate cell reversal damages.^{34, 36, 37} It was shown in section 3.3 that despite the high OER activity of an IrO₂ anode co-catalyst, its stability under the normal and transient operating conditions of a PEMFC must be considered. The near-surface layer(s) of IrO₂ can be completely reduced to metallic Ir upon exposure to H₂, e.g., under the normal operating conditions of a PEMFC anode.⁵⁶ Such alteration of the near-surface layer(s) of IrO₂ drastically affects its stability over the course of the anode potential transients which occur during SUSDC cycles, leading to: i) iridium dissolution and cross-over through the membrane to the cathode electrode, followed by iridium deposition on the Pt/C cathode catalyst, which deteriorates its ORR activity; ii) an OER activity loss of the IrO₂ anode co-catalyst due to the re-deposition of Pt dissolved from the anode HOR catalyst onto the reduced IrO₂ anode co-catalyst.⁵⁶

The origin of this degradation mechanism is the chemical reduction of typically synthesized IrO₂ catalysts in a PEMFC anode, which implies that a reduction-resistance IrO₂ catalyst would be required. In this study, an unprecedented approach is introduced to prepare IrO₂ catalysts which are not reduced in the PEMFC anode environment. The preparation of such irreducible IrO₂ (“irr-IrO₂”) catalysts is based on an industrially scalable procedure consisting of a high-temperature (650-1000 °C) heat treatment step, followed by a ball-milling and a post-annealing step to prepare catalyst powders with specific surface areas of > 20 m² g⁻¹. TGA experiments in 3.3% H₂/Ar showed that the formation of metallic Ir is hindered in the near-surface layer(s) of such irr-IrO₂ catalysts due to their intrinsic structural distinctions from the typically synthesized IrO₂ reported in the literature and from the commercial IrO₂ catalysts. Finally, it is shown that anode potential transients, caused by SUSD cycles, do not lead to the dissolution of iridium from this new class of reduction resistant IrO₂-based anode co-catalysts. The advantages of using this new class of anode co-catalysts on the long-term PEMFC performance will be discussed.

Author contributions

M.F.T. proposed the idea of IrO₂ stabilization by heat treatment and prepared all the catalysts and fabricated the MEAs. M.F.T. and A.M.D. performed the electrochemical testing in a PEMFC, and M.F.T. analyzed the experimental test results of the MEAs. M.F.T. performed the XPD measurements and M.F.T. and B.S. performed the XPD data analysis. M.F.T. performed all the other physical/chemical and electrochemical measurements and analyzed the data. M.F.T. wrote the manuscript and H.A.G., A.M.D., and B.S. edited it. All authors discussed the experimental results and revised the manuscript.



Irreducible IrO₂ Anode Co-Catalysts for PEM Fuel Cell Voltage Reversal Mitigation and Their Stability Under Start-Up/Shut-Down Conditions

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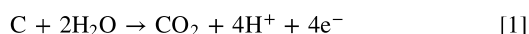
IrO₂ has been widely used as the anode co-catalyst for mitigating cell voltage reversal damages in proton exchange membrane fuel cells (PEMFCs). However, under the PEMFC anode operation conditions, conventionally prepared IrO₂ catalysts are reduced by H₂, forming metallic Ir on their surface, which is prone to dissolution during start-up/shut-down (SUSD) cycles. The dissolved Irⁿ⁺ ions can permeate through the membrane to the cathode electrode, poisoning the oxygen reduction reaction (ORR) activity of the Pt/C cathode catalyst. In this study, we introduce an unprecedented approach to synthesize IrO₂ catalysts (irr-IrO₂) which are not reduced in the PEMFC anode environment at 80 °C over extended time. Their preparation is based on an industrially scalable procedure, consisting of a high-temperature (650 °C–1000 °C) heat treatment step, a subsequent ball milling step, and a final post-annealing step, thereby attaining catalysts with specific surface areas of ~25 m² g⁻¹. The high reduction resistance of the irr-IrO₂ catalysts, attributed to their highly ordered crystalline structure compared to that of typically synthesized IrO₂ catalysts, is reflected by the observation that SUSD cycling of MEAs with the irr-IrO₂ as anode co-catalysts does not result in iridium dissolution and the associated iridium poisoning of the Pt/C cathode catalyst.

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One of the major hurdles for the widespread commercialization of proton exchange membrane fuel cell (PEMFC) electric vehicles is meeting their long-term durability targets.^{1–3} Particularly the degradation of membrane electrode assemblies (MEAs) during cell voltage reversal events which can occur during the transient operation of a PEMFC stack has recently received much attention.^{4–7} During cell reversal events, the anode potential increases to >>1 V vs the reversible hydrogen electrode potential (RHE), causing severe oxidation of the anode catalyst carbon support:



This carbon oxidation reaction (COR) is kinetically fast at potentials >1.0 V_{RHE}, such that cell reversal events lead to a collapse of the anode catalyst layer and to cell failure.^{8–10} A common strategy to mitigate cell reversal damages is the addition of a co-catalyst to the anode electrode, which catalyzes the oxygen evolution reaction (OER), so that the non-damaging OER rather than the damaging COR takes place. A commonly used anode co-catalyst to favor the OER over the COR during cell reversal events is iridium oxide (IrO₂).^{4,6,11–13}

The OER activity of an IrO₂ catalyst has been considered to be the most important figure-of-merit when evaluating different IrO₂ anode co-catalysts, because a higher OER activity results in a lower contribution of the COR to the current drawn during a cell reversal event, and thus in a higher cell reversal tolerance of the MEA.¹⁴ For this reason, numerous studies in the literature investigated possible approaches to attain highly OER-active IrO₂ anode co-catalysts, namely by examining different synthesis routes or by modifying the anode catalyst layer design.^{14–18} However, our recent findings showed that in addition to a high OER activity, the stability of an IrO₂-based anode co-catalyst under the normal operation conditions of a PEMFC anode (~80 °C and ~100 kPa H₂) is another critical criterion.¹⁹ This is related to the fact that the near-surface layer(s) of

IrO₂ can be reduced to metallic Ir upon exposure to H₂ under the operating conditions of a PEMFC anode, which has two consequences: On one hand, the formation of metallic Ir on the catalyst surface increases its OER activity, thereby improving the cell reversal tolerance of an MEA with an anode co-catalyst.¹⁹ On the other hand, the reduction of the near-surface layer(s) of an IrO₂ catalyst drastically compromises its stability during the anode potential transients which occur during start-up/shut-down (SUSD) events,²⁰ where the anode potential cycles between ~0 and ~1 V_{RHE}, promoting the dissolution of metallic Ir; the permeation of the thus produced dissolved Irⁿ⁺ species through the membrane to the cathode electrode then leads to iridium deposition on the Pt/C cathode catalyst and a concomitant poisoning of its oxygen reduction reaction (ORR) activity. At the same time, SUSD transients also cause an OER activity loss of the anode co-catalyst, which was shown to be mainly due to the redeposition of Pt dissolved from the anode hydrogen oxidation reaction (HOR) catalyst onto the reduced IrO₂ anode co-catalyst, blocking its OER active sites.¹⁹ As the origin of these degradation mechanisms is the chemical reduction of the typically employed IrO₂ anode co-catalysts in the PEMFC anode, we proposed that a reduction-resistant IrO₂ anode co-catalyst would be required, a material which we subsequently developed.²¹ Later on, this idea was also investigated by Marić et al., demonstrating a better long-term stability of a rutile type IrO₂ anode co-catalyst compared to hydrous iridium oxide or metallic iridium.²²

In this study, we present a novel approach to synthesize IrO₂ catalysts that are not reduced in the PEMFC anode environment at 80 °C over extended time. The preparation of such irreducible IrO₂ (irr-IrO₂) catalysts is based on an industrially scalable procedure, consisting of a high-temperature (650–1000 °C) heat treatment step, followed by a ball-milling step, and a final post-annealing step, resulting in catalyst powders with specific surface areas of ~25 m² g⁻¹. Thermogravimetric analysis (TGA) in reductive atmosphere (3.3 vol% H₂/Ar), previously shown to be a reliable method to simulate the reductive environment of PEMFC anode,¹⁹ is used to investigate the stability of the prepared IrO₂ catalysts towards reduction. The TGA results show that the chemical reduction of irr-IrO₂ catalysts by H₂ is kinetically hindered, reflected by a higher activation energy for the reduction reaction of irr-IrO₂ (~155 kJ mol⁻¹) compared to that of typically synthesized IrO₂ (~115 kJ mol⁻¹). X-ray

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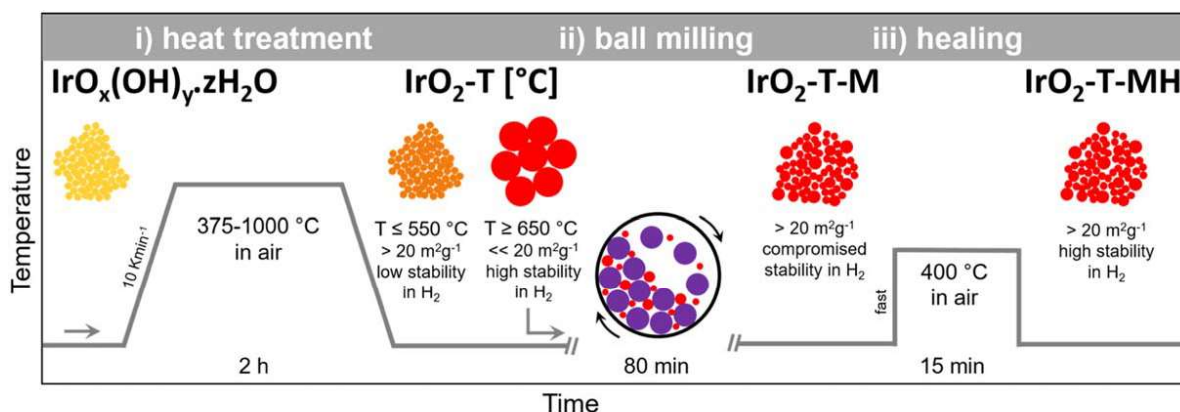


Figure 1. Synthesis procedure of the various IrO_2 catalysts, comprised of three steps: (i) *Heat treatment*: heat treatment in a tube furnace under synthetic air (1 L min^{-1}) at different temperatures ($375, 500, 550, 650, 750$, or $1000\text{ }^\circ\text{C}$) for 2 h (set via a heating rate of 10 K min^{-1}), yielding the heat-treated IrO_2 samples denoted as “ $\text{IrO}_2\text{-T}$ ” (T being the heat treatment temperature in $^\circ\text{C}$). (ii) *Ball milling*: ball milling of the $\text{IrO}_2\text{-T}$ ($T \geq 650\text{ }^\circ\text{C}$) samples which have a high resistance towards reduction in H_2 but a low specific surface area ($< 20\text{ m}^2\text{g}^{-1}$); after 80 ball milling cycles (consisting of 1 min at 1000 RPM and 4 min at 0 RPM), specific surface areas of $> 20\text{ m}^2\text{g}^{-1}$ are obtained, and the samples are denoted as “ $\text{IrO}_2\text{-T-M}$ ” (M indicating the ball milling process). (iii) *Healing*: post-annealing of the $\text{IrO}_2\text{-T-M}$ samples under synthetic air to recover their partially compromised reduction resistance, caused by the ball milling step. The healing step was performed by pushing a catalyst-containing crucible into a tube furnace that was pre-heated at $400\text{ }^\circ\text{C}$, waiting for 15 min, and then pulling the crucible out of the furnace to cool down to room temperature under ambient air. The $\text{IrO}_2\text{-T-M}$ catalysts after the healing step are denoted as “ $\text{IrO}_2\text{-T-MH}$ ” (with H standing for healing).

powder diffraction (XPD) data show that such reductive stability improvement of the irr- IrO_2 catalysts can be ascribed to their intrinsic structural distinction from the typically synthesized IrO_2 catalysts. To determine the effect of these differences on MEA stability, MEAs using anode co-catalysts based on either irr- IrO_2 or a typically synthesized IrO_2 are subjected to SUSD cycling in 5 cm^2 active area single-cell PEMFCs. After 500 cycles, cyclic voltammetry and X-ray photoelectron spectroscopy (XPS) reveal the deposition of iridium in the cathode electrode for the conventional IrO_2 anode co-catalyst (via iridium dissolution and crossover), which is absent for the irr- IrO_2 catalyst.

Experimental

Synthesis of the various IrO_2 catalysts.—A hydrated iridium oxyhydroxide with a general chemical formula of $\text{IrO}_x(\text{OH})_y \cdot z\text{H}_2\text{O}$ based on the literature²³ was used as a precursor for the following synthesis of IrO_2 catalysts. The synthesis and the subsequent stabilization procedure is comprised of three steps, as schematically shown in Fig. 1. In step i, $\sim 12\text{ g}$ $\text{IrO}_x(\text{OH})_y \cdot z\text{H}_2\text{O}$ were weighed into an alumina crucible, placed in a tube furnace (HST 12/400, Carbolite Gero GmbH & Co. KG) purged with synthetic air (1 L min^{-1}), and heated at 10 K min^{-1} to a final temperature between $375\text{ }^\circ\text{C}$ – $1000\text{ }^\circ\text{C}$ (viz., to either $375, 500, 550, 650, 750$, or $1000\text{ }^\circ\text{C}$), where it was held for 2 h; the thus obtained heat-treated samples are denoted as “ $\text{IrO}_2\text{-T}$,” where T stands for the heat treatment temperature in $^\circ\text{C}$ (e.g., $\text{IrO}_2\text{-375}$ is a sample that was heat-treated for 2 h at $375\text{ }^\circ\text{C}$). As will be shown later, although the samples which are heat-treated at $T \geq 650\text{ }^\circ\text{C}$ acquire a high stability towards reduction under H_2 , they have specific surface areas that are too low for a sufficiently active anode co-catalyst ($< 20\text{ m}^2\text{g}^{-1}$), due to the agglomeration/growth of IrO_2 particles during the heat treatment at high temperatures.

Therefore, a subsequent ball milling step is required to increase the specific surface area of these samples, as described by step ii: $\sim 30\text{ g}$ ZrO_2 beads (1 mm diameter; FRITSCH GmbH, Germany) were placed in a grinding bowl (a 20 ml ZrO_2 vessel, encased in stainless steel; FRITSCH GmbH, Germany), together with $\sim 10\text{ g}$ of a given $\text{IrO}_2\text{-T}$ sample ($T \geq 650\text{ }^\circ\text{C}$) and $\sim 2.5\text{ ml}$ DI water. Subsequently, the grinding bowl was sealed with a cap and was placed in a planetary milling machine (Planetary Micro Mill PULVERISETTE 7 premium line, FRITSCH GmbH, Germany) to apply 80 cycles of ball milling, each comprised of 1 min of milling at 1000 revolutions per minute (RPM) and 4 min of pause (0 RPM) to maintain the temperature of the vessel near room temperature; after every 10 cycles, $\sim 0.25\text{ ml}$ DI water was added to the sample in order

to maintain a suitable viscosity of the suspension, as the best results for a wet-milling process is reported to be achieved when the suspension has the “same consistency as motor oil.”²⁴ In the case of the $\text{IrO}_2\text{-1000}$ sample, ball milling was also performed for 160 cycles in order to investigate the effect of ball milling time on the specific surface area of the sample and the amount of zirconium contamination in the sample due to the abrasion of ZrO_2 beads. After ball milling, the sample was separated from the beads by washing it through a sieve (mesh number 20) by DI water. Then, the resulting suspension was centrifuged at 10000 RPM (5810 R, Eppendorf) to separate the sample from the water, and the resulting paste was dried in an oven at $70\text{ }^\circ\text{C}$ for 12 h under air. After drying, the sample was ground by mortar and pestle and stored in a glass vial; these samples are denoted as “ $\text{IrO}_2\text{-T-M}$,” with T standing for the heat treatment temperature in step i, and M for the ball milling process in step ii (80 cycles).

As will be shown later, the ball milling process partially compromises the reduction resistance of the heat-treated samples, so that a post-annealing step had to be performed with the $\text{IrO}_2\text{-T-M}$ samples in order to recover their resistance towards reduction under H_2 (see step iii in Fig. 1). To do this, a certain amount of the $\text{IrO}_2\text{-T-M}$ sample was placed into an alumina crucible and pushed into the hot zone of a tube furnace pre-heated at $400\text{ }^\circ\text{C}$ and flushed with synthetic air (1 L min^{-1}). After 15 min, the sample was pulled out of the furnace to cool down to room temperature under ambient air. Since the reduction resistance of the samples is recovered after this post-annealing step, it is referred to as “healing step” and the $\text{IrO}_2\text{-T-M}$ samples after the healing step are denoted as “ $\text{IrO}_2\text{-T-MH}$.” After the healing step, the samples were thoroughly ground using mortar and pestle and stored in glass vials for further characterization.

As a reference material, a commercial OER catalyst consisting of IrO_2 supported on high-structure TiO_2 particles ($\text{IrO}_2/\text{TiO}_2$ with 75 wt% iridium, Elyst Ir75 0480 from Umicore, Germany) was selected, serving as a benchmark to compare the OER activity as well as the resistance towards the reduction under H_2 with that of the catalysts prepared in this study. According to the patent,²⁵ the commercial $\text{IrO}_2/\text{TiO}_2$ catalyst was heat-treated at $400\text{ }^\circ\text{C}$ in an air atmosphere. This catalyst is referred to as “ $\text{IrO}_2/\text{TiO}_2$ (Umicore)” throughout this study.

Thin-film rotating disk electrode (RDE) measurements.—Thin-film RDE measurements were carried out in a three-electrode cell,

using an Au mesh (6.3 cm², 82 mesh, 99.99%, Advent Research Materials, UK) fused together with a 0.5 mm Au wire (99.999%, Alfa Aesar, Germany) as counter electrode (CE) and a 5 mm diameter polycrystalline Au disk as working electrode (WE) substrate, assembled in an interchangeable rotating ring-disk electrode (RRDE) shaft made of polyether ketone (Pine Research Instrumentation, USA). Furthermore, a static H₂ reference electrode (RE) was used, consisting of a Pt wire sealed into one end of a glass tube which was drawn to a capillary and filled with electrolyte; prior to each experiment, a bubble of H₂ was produced electrolytically in the RE tube and then the RE was calibrated in a H₂ saturated electrolyte using the Pt ring of the RRDE (the WE potentials of RDE experiments throughout this work are referenced to this reversible hydrogen electrode potential (V_{RHE})).²⁶ A 0.05 M H₂SO₄ aqueous solution was used as electrolyte, which was prepared by mixing high purity H₂SO₄ (Ultrapur, 96%, Merck Millipore KGaA, Germany) and ultra-pure water (18.2 MΩ cm at 20 °C, Merck Millipore KGaA, Germany). High-purity Ar, H₂, and O₂ (6.0-grade, Westfalen AG) were used to purge the electrolyte.

Before each measurement, the Au working electrode disk was removed from the RRDE shaft, polished with 0.3 μm alumina polishing suspension (Buhler AG), and then sonicated in ultra-pure water for several times. A catalyst ink suspension was prepared using a given catalyst powder, a pH = 3 solution of the high purity H₂SO₄ in ultra-pure water, and a Nafion[®] ionomer solution (5 wt% ionomer in mixture of lower aliphatic alcohols and water, Sigma Aldrich). The ink composition was adjusted to achieve 0.98 mg_{Ir} ml⁻¹_{ink} and 2 wt% ionomer in the final dried coating consisting of catalyst and ionomer. The suspension was sonicated for 30 min in a sonication bath (Elmasonic S 30 H, Elma Schmidbauer GmbH) in order to achieve a homogenous ink, with the bath temperature being maintained below 35 °C in order to prevent solvent evaporation. Finally, 20 μl of the thus prepared ink was drop-casted onto the polished and cleaned Au WE substrate, yielding a thin-film RDE catalyst loading of 0.10 mg_{Ir} cm⁻²_{disk}.

All RDE measurements (using the RRDE assembly) were performed at room temperature, using an Autolab potentiostat (PGSTAT302N, Metrohm AG) and a rotator (Pine Research Instrumentation). Freshly coated working electrodes were first dipped in Ar-saturated electrolyte, and the uncompensated solution resistance between the reference and the working electrodes was determined by electrochemical impedance spectroscopy (EIS; from 0.1–100 kHz) at open circuit voltage (OCV). Subsequently, cyclic voltammetry (CV) was performed at 100 mV s⁻¹ and 2500 RPM between 0.05–1.35 V_{RHE} for 10 cycles in order to record the characteristic voltammetric behavior of the catalyst powders as well as to ensure the mechanical stability of the catalyst coating on the Au WE disk. After that, the electrolyte was fully saturated with O₂, and an OER polarization curve at 20 mV s⁻¹ was recorded at 2500 RPM by collecting a CV between 1.3–1.6 V_{RHE} , whereby only the very first positive-going scan is used for the evaluation of the OER activity.

Membrane electrode assembly (MEA) preparation and cell assembly.—All fuel cell tests were conducted using 5 cm² active area single-cells with in-house designed flow fields,²⁷ operated with a G60 fuel cell test station (Greenlight Innovation Corp., Canada). The MEAs were composed of an IrO₂ catalyst at the anode electrode and a cathode electrode with a Vulcan carbon supported platinum catalyst (50 wt% Pt/C) at a loading of 0.3 mg_{Pt} cm⁻²_{MEA}. The cathode catalyst layers were provided by Greenerity GmbH and were prepared by using a high-equivalent weight ionomer at an ionomer: carbon mass ratio of 0.65:1. Three different IrO₂ catalysts were used for the preparation of the anode catalyst layers, namely a catalyst with a high reduction resistance (IrO₂–750-MH), a catalyst with an intermediate reduction resistance (IrO₂–550), and the commercial IrO₂/TiO₂ (Umicore) reference catalyst. The ionomer content of the anode electrodes was adjusted to 12 wt%, using a Nafion ionomer solution (20 wt% ionomer, D2021 from IonPower, USA); the anode

catalyst loadings were 2.5, 2.2, and 1.6 mg_{Ir} cm⁻²_{MEA} for the IrO₂–750-MH, the IrO₂–550, and the IrO₂/TiO₂ (Umicore) catalyst, respectively. The MEAs were laminated onto a 15 μm thick membrane (low EW, mitigated GORE-SELECT[®] Membrane, from W. L. Gore & Associates) by the decal transfer method. More details on the IrO₂ ink composition and the decal transfer to produce the catalyst coated membranes (CCMs) can be found in our previous study.²⁸ For cell assembly, a CCM was sandwiched between gas diffusion layers (GDL; H14C7 from Freudenberg & Co. KG, Germany), and the cell was sealed with PTFE coated fiberglass (Fiberflon, Fiberflon GmbH & Co. KG, Germany) to achieve 15% GDL compression.

Prior to recording cathode CVs of the SUSD-cycled MEAs (see next section), the cells were disassembled and the anode GDLs were replaced by gas diffusion electrodes (GDEs); subsequently, the cells were reassembled to record the cathode CVs. The GDEs were prepared by coating an H14C10 GDL (Freudenberg & Co. KG, Germany) with a catalyst layer based on a Vulcan carbon supported Pt catalyst (50% Pt/C, TEC10V50E, TKK) at a loading of 0.4 mg_{Pt} cm⁻²_{GDE} and an ionomer:carbon mass ratio of 0.65:1 (20 wt% ionomer, D2021 from IonPower, USA), using the Mayer rod technique. The preparation of the Pt/C ink to make the GDEs was similar to the preparation of Pt/C inks in our previous study,²⁹ except that the ink's solid content was adjusted to 0.04 g_{carbon} ml⁻¹_{ink}.

OCV-hold, cyclic voltammetry, and SUSD measurements with the MEAs.—The stability of the 5 cm² MEAs based on IrO₂ (anode) and Pt/C (cathode) catalysts under open circuit voltage (OCV) conditions was investigated using 2000 nccm flow of fully humidified H₂ (anode) and 5000 nccm flow of fully humidified air (cathode) at 80 °C and in inlet-controlled cell pressure of 170 kPa_{abs} (nccm here refers to a volumetric flow rate in units of cm³ min⁻¹, referenced to a pressure of 101.3 kPa and a temperature of 0 °C). The cell was kept under these conditions at OCV for an overall duration of 12 h. At different OCV holding time intervals, CVs of the anode (serving as working electrode) at ambient pressure and 40 °C were recorded using a Gamry potentiostat (Reference3000, Gamry Instruments, USA), applying a scan rate of 300 mV s⁻¹ in the potential range of 0.07–1.00 V_{RHE} . For this, fully humidified N₂ was fed to the anode (5 nccm) and fully humidified 5 vol% H₂/Ar to the cathode electrode (500 nccm; serving as the counter and reference electrode) at ambient pressure; an extended N₂ purge of the anode humidifier was conducted before recording the CVs. After an overall OCV hold of 12 h, only the MEAs with the IrO₂–550 and the IrO₂–750-MH anode catalysts were subjected to the following SUSD cycling experiment.

SUSD cycling was performed at 35 °C, ambient cell pressure, and a fully humidified air flow (500 nccm) through the cathode. A single SUSD cycle consisted of five steps: (i) operating the cell under OCV conditions at 100% RH for 60 s, with an anode H₂ flow rate of 500 nccm; (ii) setting the anode gas flow to 0, and holding the resulting OCV for 10 s; (iii) introducing air with 56% RH to the anode compartment at a flow rate of 500 nccm, corresponding to an H₂/air-front residence time of ~0.02 s (shutdown step); (iv) keeping the air flow rate in the anode at 500 nccm and 56% RH for 60 s; and, finally, (v) introducing fully humidified H₂ to the anode compartment at 500 nccm flow rate, corresponding to an H₂/air-front residence time of ~0.02 s (start-up step). Note that before feeding it into the anode, the air stream was passed through an anode secondary humidifier, whose water temperature was set to 25 °C, resulting in a relative humidity of the anode air-feed of 56% RH when referenced to the cell temperature of 35 °C.

After performing 500 SUSD cycles, anode CVs were recorded again at the above-mentioned conditions. Then, the cell was disassembled and the anode GDL was replaced by the Pt/C based GDE, after which the cell was reassembled and CVs of the cathode (serving as working electrode) were recorded at ambient pressure and 40 °C by applying a scan rate of 50 mV s⁻¹ in the potential range of 0.07–1.00 V_{RHE} . For this, fully humidified N₂ was fed to

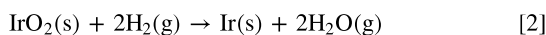
the cathode (5 nccm) and fully humidified 5 vol% H₂/Ar to the anode electrode (500 nccm; serving as the counter and reference electrode). All the potentials referred to in the CVs are referenced to the reversible hydrogen electrode (RHE) potential at a nominal hydrogen pressure of 100 kPa_{abs}. This was obtained by correcting for the Nernstian shift of the hydrogen reference/counter electrode.

Thermogravimetric analysis (TGA).—Thermogravimetric analysis (TGA) of the prepared IrO₂ catalyst samples and the as-received IrO₂/TiO₂ (Umicore) catalyst was performed with a Mettler Toledo TGA/DSC 1 instrument. ~3 mg of the catalyst powder were weighed into a sapphire crucible (volume 70 μl) closed with a perforated sapphire lid and directly inserted into the TGA furnace. All the gases used in the TGA experiments were 5.0-grade (Westfalen AG). Ar (20 ml min⁻¹) was always used as the cell carrier gas in addition to the reactive gases.

In order to investigate the mass loss behavior of the as-received IrO_x(OH)_y·zH₂O precursor upon calcination in an oxidative atmosphere, mimicking the conditions of step i conducted in the tube furnace (see Fig. 1, a TGA temperature ramp experiment was performed in an oxidative atmosphere. During this experiment, the temperature was ramped from 25 to 1150 °C at 2.5 K min⁻¹ while supplying synthetic air (20.5 vol% O₂/N₂, 40 ml min⁻¹) to the TGA furnace. It should be noted that during this experiment, the effective O₂ concentration was 13.7 vol% O₂/(Ar+N₂) due to the additional cell carrier gas stream of Ar.

TGA experiments to investigate the reduction resistance of the catalysts in a H₂-containing atmosphere were composed of two main steps: (i) an initial in situ drying/cleaning step in oxidative atmosphere (mass profiles of this step are not shown in the figures) and (ii) a subsequent metal oxide reduction step in reductive atmosphere. The former was performed at 200 °C in an oxygen-containing atmosphere; further details regarding this step can be found in our previous study.¹⁹ After this initial drying/cleaning step, the metal oxide reduction step was carried out in two different modes: (i) a temperature ramp mode and (ii) an isothermal mode. For the former, the temperature was ramped from 25 to 300 °C with different heating rates (1, 2.5, 5, and 10 K min⁻¹) while supplying 5 vol% H₂/Ar at 40 ml min⁻¹. On the other hand, the isothermal reduction experiment was carried out by heating the TGA furnace from 25 °C to a target temperature of 80 or 120 °C at 5 K min⁻¹ in Ar (100 ml min⁻¹), followed by switching the gas supply from Ar to 5 vol% H₂/Ar (40 ml min⁻¹) and keeping the furnace at the target temperature for a certain amount of time (24 h for the experiments performed at 80 °C and 16 h for the experiment performed at 120 °C). In both cases, when considering the cell carrier Ar stream, the effective H₂ concentration is 3.3 vol%.

During the TGA experiments under the diluted H₂ atmosphere, IrO₂ can be reduced according to the following reaction:



A stoichiometric IrO₂ (iridium(IV) oxide) consists of 85.7 wt% Ir and 14.3 wt% O, so that the total mass loss of an IrO₂ catalyst upon its complete reduction to Ir would be accompanied by a mass loss of 14.3 wt%, a value that will be used to quantify the extent of the IrO₂ reduction for the later shown TGA data. Assuming that the TiO₂ support material cannot be reduced within the temperature range of the TGA experiments in this study, the total mass loss of the IrO₂/TiO₂ (Umicore) catalyst upon the complete reduction of the IrO₂ phase to Ir would amount to a mass loss of 12.5 wt%, as was estimated in our previous study.¹⁹

The kinetic analysis of the TGA data was performed based on an isoconversional method to determine the Arrhenius activation energy of the IrO₂ reduction reaction, as explained in detail in our previous study.¹⁹ In short, we used the Flynn-Wall-Ozawa (FWO) integral method, based on the procedure described in ASTM E1641-16.^{30,31} This method is based on the general rate equation derived from an Arrhenius equation, which can then be solved for a

given extent of the reaction, α (i.e., the fraction of IrO₂ reduced to Ir) to determine the activation energy:

$$\ln(\beta) = \ln\left(\frac{A \cdot E_a}{R \cdot g(\alpha)}\right) - 5.523 - 1.053 \cdot \frac{E_a}{RT} \quad [3]$$

Here, β is the heating rate (in K min⁻¹), A is the pre-exponential factor in the Arrhenius term, E_a is the activation energy (in J mol⁻¹), R is the gas constant (8.314 J mol⁻¹ K⁻¹), $g(\alpha)$ is the integral form of the reaction kinetic model, and T is the absolute temperature (in K). According to Eq. 3, the activation energy at $\alpha = \text{constant}$ can be calculated by a linear regression of $\ln(\beta)$ vs $1/T$, where T are the temperatures at which the chosen constant α value is reached for different heating rates β (here, at 1, 2.5, 5, and 10 K min⁻¹). This analysis can be performed for different constant α values, yielding the corresponding activation energies E_a vs α .

X-ray powder diffraction (XPD).—X-ray powder diffraction (XPD) was performed using a Stadi P instrument (Stoe & Cie GmbH, Germany) with Cu-K α_1 radiation ($\lambda = 1.54059$ Å, 50 kV, 30 mA, Ge(111) monochromatized) and a Mythen 1 K position-sensitive detector (Dectris Ltd, Switzerland) in transmission mode. About 5 mg of a catalyst powder sample was smoothly spread onto a scotch tape and placed into the central hole of the sample holder. The XPD patterns were recorded in the 2θ range of 20–90° with one data point every 0.015°/ 2θ , amounting to an acquisition time of 2 h per diffractogram. The XPD data were analyzed with the software package Topas,³² following the same approach used in our previous study.³³ The IrO₂ samples were treated with the structure-independent Pawley method using the tetragonal $P4_2/mnm$ symmetry (space group no. 136).³⁴ This analysis method was chosen as it does not require any structural model (in contrast to the Rietveld method), so that it focuses primarily on fitting and optimizing the reflection broadening.

We refined the background (Chebyshev polynomial with 10 coefficients), the instrumental parameters (zero error and axial divergence), the two lattice parameters a and c as well as the intensity of each individual reflection (according to the Pawley method). However, we are particularly interested in the line broadening of the reflections, β_{hkl} :

$$\beta_{\text{hkl}} = \beta_{\text{instrument}} + \beta_{\text{size}} + \beta_{\text{strain}} \quad [4]$$

where $\beta_{\text{instrument}}$ is the instrumental contribution to the line broadening, and β_{size} and β_{strain} are the contributions of the measured sample to the line broadening. Initially, the instrumental broadening ($\beta_{\text{instrument}}$) was determined with a silicon standard material using the Thompson-Cox-Hastings pseudo-Voigt function (Topas command *TCHZ_Peak_Type*, parameters U , W , Y , and X activated).³⁵ However, it was observed that the total line broadening measured for the IrO₂-1000 sample falls into the $\beta_{\text{instrument}}$ broadening determined by the silicon standard material (which however might also involve some broadening of silicon itself). This means that in this experimental setup, no additional line broadening except $\beta_{\text{instrument}}$ could be determined for the IrO₂-1000 sample and that the contribution of β_{size} and β_{strain} to the total line broadening of this sample is negligible. Therefore, the total line broadening of the IrO₂-1000 sample was defined as $\beta_{\text{instrument}}$ for the evaluation of the data for the other samples (using the same function/parameters as above).

The crystallite size of the sample leads to line broadening according to the well-known Scherrer equation:

$$\beta_{\text{size}} = \frac{K \cdot \lambda}{L_{\text{vol}} \cdot \cos(\theta)} \quad [5]$$

Here, K is a shape factor (on the order of 1), λ is the X-ray wavelength, θ is the Bragg angle, and L_{vol} is the volume-weighted mean column length of the crystallites. Assuming spherical

crystallites, their average diameter corresponds to $d_{\text{sphere}} = 4/3 \cdot L_{\text{vol}}$,³⁵ whereby d_{sphere} will be referred to as d_{XPD} throughout this study. Note that the Scherrer equation is only applicable to sub- μm crystallites (for our setup, for L_{vol} being less than ~ 200 nm). Finally, there is a microstrain contribution of the sample to the line broadening:

$$\beta_{\text{strain}} = 4 \cdot \varepsilon_0 \cdot \tan(\theta) \quad [6]$$

Here, $\varepsilon_0 = \Delta d/d$ is the mean lattice spacing deviation. This is caused by the displacement of atoms from their ideal positions, e.g., due to point defects such as vacancies and interstitials. The strain and size contributions to the line broadening can be separated by their θ -dependence, $\beta_{\text{size}} \sim 1/\cos(\theta)$ vs $\beta_{\text{strain}} \sim \tan(\theta)$.

Another important aspect of the size/strain analysis addresses the calculation method of the peak broadening. The Topas Technical Reference recommends to extract L_{vol} from the integral breadth-based $\beta_{\text{size(IB)}}$ value, while ε_0 should depend on the full width at half maximum based $\beta_{\text{strain(FWHM)}}$ value.³⁵ The integral breadth of a peak is obtained from dividing the line profile area by its height, and the thereof determined crystallite size is fairly independent of the size distribution and shape (with K set to 1). Following this suggestion, we used the `LVol_FWHM_CS_G_L` and the `e0_from_Strain` commands in Topas, which both comprise Lorentzian and Gaussian component convolutions. Thus, there is a total number of four parameters to describe the IrO_2 line profile, but we deactivated the parameters with a limit-warning of the program (individually for each IrO_2 sample). This could happen when the crystallite size is too large or the microstrain is too small to be quantifiable. Overall, however, the Lorentzian components never reached the limit-warning of the program and they were always activated for the evaluation of crystallite size and microstrain of the samples. On the other hand, the Gaussian component of the microstrain always reached the limit-warning of the program and was thus deactivated in the data evaluation for all the samples, while no specific trend in the Gaussian component of the crystallite size was observed for any of the samples.

X-ray photoelectron spectroscopy (XPS) measurements.—XPS data were acquired with a Kratos Axis Supra spectrometer using monochromatic Al K_{α} radiation at an energy of 1486.6 eV. The spectra were recorded at a total X-ray source power of 225 W (15 kV and 15 mA). For XPS measurements on the cathode electrodes of the as-prepared and the SUSD-cycled MEAs, the MEA samples were cut into small pieces ($\sim 5 \times 5$ mm) and attached to a self-adhesive copper tape (the cathode electrode facing up) that in turn was attached to a stainless steel sample holder (in floating mode, where the sample holder was electrically insulated from the copper tape). Prior to inserting the MEA samples into the ultrahigh vacuum (UHV) sample-introduction chamber, they were outgassed for 24 h in a vacuum oven at 80 °C. Then, the samples were additionally outgassed overnight in the UHV sample-introduction chamber to further remove moisture and contaminants, so that the pressure in the analysis chamber during the XPS data acquisition remained below $1.0 \cdot 10^{-8}$ Torr. High-resolution spectra were collected between 58–81 eV to acquire the Ir 4f (~ 60 –68 eV) and Pt 4f (~ 70 –79 eV) signals, using a step size of 0.05 eV, a measurement time of 0.6 s/step, and a pass energy of 20 eV; the shown spectra represent the average of 10 individual spectra. All binding energy values are corrected using the adventitious carbon signal (C 1s = 284.8 eV) of the Pt/C cathode catalyst. A Shirley function was used to subtract the background from the spectra using the Casa XPS software.

Specific surface area measurements of the catalyst samples.—The specific surface area of the samples was measured by N_2 physisorption at 77 K, using an Autosorb iQ gas sorption analyzer (Quantachrome Instruments, USA). All samples were evacuated at 120 °C for 12 h prior to the measurements. The sample mass was chosen to achieve a minimum absolute surface area of ~ 2.5 m² in the sample vial. Adsorption isotherms were measured with 11 data

points in the relative pressure range of $0.05 \leq p/p_0 \leq 0.30$, where p represents the gas pressure and p_0 the saturation pressure of N_2 . The specific surface area was calculated according to the Brunauer-Emmet-Teller (BET) theory, whereby the ideal linear range was selected by the Micropore BET Assistant of the ASiQwin software (typically 7 out of the 11 points). The determined specific surface areas (A_{BET}) in this study are in units of m² g⁻¹_{IrO₂} unless otherwise is stated. The A_{BET} values were then used to estimate the average IrO_2 particle size, assuming a spherical particle geometry:

$$d_{\text{BET}}[\text{nm}] = \frac{6000}{\rho_{\text{IrO}_2} \cdot A_{\text{BET}}} \quad [7]$$

Here, d_{BET} is the estimated average particle size (in nm), ρ_{IrO_2} is the density of IrO_2 (11.66 g cm⁻³), and A_{BET} is the specific surface area of the sample (in m² g⁻¹).

Transmission electron microscopy (TEM) measurements.—TEM was further used for particle size analysis. A very small amount of sample was ultrasonically dispersed in DI water and then deposited onto a carbon-coated copper grid (Cu, 400 mesh, Formvar carbon film, Science Services). The obtained samples were then analyzed using a Philips CM100 electron microscope with an acceleration voltage of 100 kV.

Elemental analysis.—For elemental analysis, inductively coupled plasma atomic emission spectroscopy (ICP-AES) was performed at the Mikroanalytisches Labor Pascher (Remagen, Germany), for which the IrO_2 powder samples were dissolved by pressurized acid digestion in HCl/HF.

Results and Discussion

In our previous study, we have shown that the origin of the degradation of an IrO_2 anode co-catalyst during the intermittent operation of a PEMFC is the reduction of IrO_2 to metallic Ir upon its exposure to H_2 under the normal operating conditions of the anode.¹⁹ Therefore, it was suggested that such degradation could be avoided, if the chemical reduction of IrO_2 under the normal anode operating conditions is kinetically hindered. In the following, a novel approach is introduced to prepare IrO_2 -based catalysts which are irreducible under the operating conditions of a PEMFC anode.²¹ In order to explain the stability improvement of such irreducible IrO_2 (irr- IrO_2) samples, we will perform a detailed analysis of the IrO_2 reduction kinetics under H_2 in combination with structural investigations. Lastly, we will implement IrO_2 catalyst samples with different reduction resistances in MEAs and investigate the effect of the reduction resistance on the long-term stability of IrO_2 catalysts in a PEMFC anode.

Three-step procedure to prepare reduction resistant IrO_2 catalysts.—Temperature programmed reduction (TPR) of IrO_2 in a H_2 -containing atmosphere has occasionally been used to probe the temperature induced transformation of different IrO_2 species and to correlate these changes to the catalytic properties of the resulting materials towards the OER. There, it has generally been observed that heat treatment of an IrO_2 sample at intermediate temperatures (~ 250 °C–600 °C) in an O_2 -containing atmosphere can improve its reduction resistance measured by TPR, and that increasing the heat treatment temperature results in a higher stability of IrO_2 in a reductive atmosphere.^{36–39} Such stability improvement is believed to be due to the higher reduction resistance of a highly-crystalline IrO_2 phase (further on referred to as “c- IrO_2 ”) that is formed during heat treatment at higher temperatures, in contrast to the lower reduction resistance of a highly-disordered, amorphous IrO_2 phase (further on referred to as “a- IrO_x ”) that is the dominating species after the heat treatment at lower temperatures.^{37,38} Furthermore, our previous study suggested that the activation energy for the reduction of c- IrO_2 is higher than that of a- IrO_x ,¹⁹ so that a perfectly crystalline

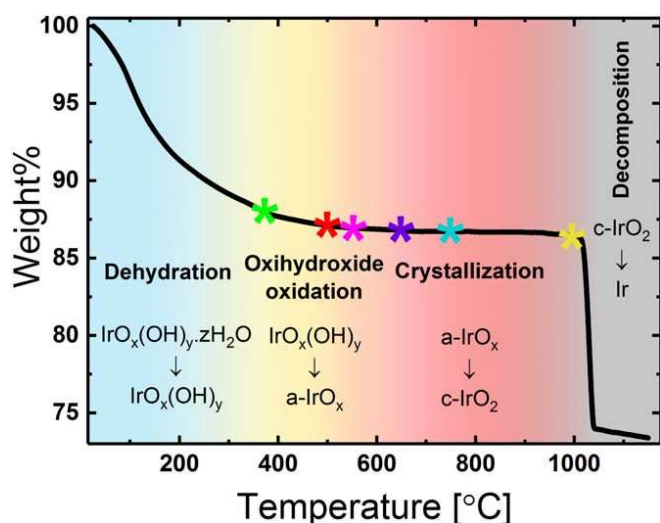


Figure 2. TGA temperature ramp experiment with the as-received hydrated iridium oxy-hydroxide precursor powder ($\text{IrO}_x(\text{OH})_y \cdot z\text{H}_2\text{O}$), acquired under 13.7 vol% $\text{O}_2/(\text{Ar}+\text{N}_2)$ at a heating rate of 2.5 K min^{-1} from 25°C – 1150°C . The areas shaded in different colors mark the approximate temperature ranges where the indicated chemical/structural transitions occur (see the text for further details). The differently colored asterisks mark the different here examined heat treatment temperatures for step I (see Fig. 1), viz., 375°C (green), 500°C (red), 550°C (purple), 650°C (violet), 750°C (light blue), and 1000°C (yellow).

IrO_2 should be more reduction resistant. However, as the preparation of a phase-pure c- IrO_2 sample requires a heat treatment at high temperatures, the concomitant particle sintering leads to materials with a specific surface area that is too low for their practical application as OER catalysts. Thus, the preparation of application-relevant irr- IrO_2 catalysts requires additional processing steps.

Figure 1 shows a schematic representation of the here pursued preparation of an irr- IrO_2 catalyst with a high specific surface area. The procedure is composed of three main steps: (i) an initial heat treatment, (ii) a subsequent ball milling, and (iii) a final “healing.” In step I, a heat treatment of the $\text{IrO}_x(\text{OH})_y \cdot z\text{H}_2\text{O}$ precursor is performed at different temperatures between 375°C – 1000°C in a tube furnace under synthetic air. This temperature range not only covers the temperatures at which the commonly synthesized IrO_2 catalysts are treated in the literature (typically up to 600°C),^{37,40,41} but also investigates the heat treatment up to 1000°C . In order to get better insights into the thermally induced transformations of the $\text{IrO}_x(\text{OH})_y \cdot z\text{H}_2\text{O}$ precursor during the initial heat treatment step, a TGA temperature ramp experiment with the precursor was performed in an O_2 -containing atmosphere between 25°C – 1150°C . The TGA curve in Fig. 2 shows a continuous mass loss up to a temperature of $\sim 600^\circ\text{C}$, where the curve reaches a plateau at $\sim 86.7 \text{ wt}\%$. This plateau continues up to a temperature of $\sim 1015^\circ\text{C}$, where a sudden mass loss of $\sim 12.7 \text{ wt}\%$ occurs (see gray shaded area in Fig. 2). When normalized to the weight of c- IrO_2 of $\sim 86.7 \text{ wt}\%$ at 600°C – 1015°C , this mass loss reasonably closely corresponds to that expected for the thermal decomposition of IrO_2 to metallic Ir ($14.3 \text{ wt}\%$), which is reported to occur slightly above 1000°C .^{23,42} This is the reason for the selection of 1000°C as the upper limit temperature for the heat treatment step in Fig. 1 (step i). The initial mass loss at $T < 600^\circ\text{C}$ is mainly attributed to the dehydration of the hydrated oxy-hydroxide precursor to iridium oxy-hydroxide (blue shaded area in Fig. 2) and its subsequent oxidation to an iridium oxide (yellow shaded area in Fig. 2).^{23,39,43,44} Bestaoui et al. reported that the dehydration step occurs at $T < 440^\circ\text{C}$, followed by the oxy-hydroxide oxidation step at $T > 440^\circ\text{C}$.²³ However, the mass loss curve in Fig. 2 does not show any clearly distinguishable temperature regimes for these two reactions, which appear to overlap in our study. It has been reported that the crystallization of the thermal decomposition products of the precursor to form a rutile-type,

Table I. Specific surface area (A_{BET} ; in units of $\text{m}^2 \text{ g}^{-1} \text{IrO}_2$) and zirconium contamination of the IrO_2 -750 and IrO_2 -1000 samples in their as-prepared state and after different numbers of ball milling cycles (each cycle consisting of 1 min milling at 1000 RPM and 4 min of rest). The errors represent the mean absolute deviations of two measurements.

Sample	Ball milling cycles [#]	A_{BET} [$\text{m}^2 \text{ g}^{-1} \text{IrO}_2$]	Zirconium contamination [wt.%]
IrO_2 -1000	0	0.9	< 0.05
	80	27.0	1.51 ± 0.01
	160	29.6	3.41 ± 0.02
IrO_2 -750	0	3.8	not measured
	40	22.5	not measured
	80	25.9	0.72 ± 0.01

crystalline IrO_2 starts to take place at $T \approx 400^\circ\text{C}$.^{39,44,45} However, since Fig. 2 shows a continued mass loss between 400°C up to $\sim 600^\circ\text{C}$, the oxidation of the oxy-hydroxide (accompanied by a mass loss) must also overlap with the crystallization step. Therefore, if the precursor is heat treated between $\sim 300^\circ\text{C}$ – 600°C , the resulting product might be a mixture of an oxy-hydroxide species and a somewhat crystalline IrO_2 species; in order to simplify the denomination of such a mixed products, we will refer to it as “a- IrO_x ” (see Fig. 2). There is no further mass loss observed in the TGA curve between 600 and 1015°C , indicating that the decomposition of the precursor is completed once the temperature has reached 600°C , so that it can be assumed that only the crystallization of a- IrO_x to a highly crystalline IrO_2 (referred to as c- IrO_2 in Fig. 2) occurs in this temperature range. In summary, by selecting this wide temperature range for the synthesis of IrO_2 , catalyst materials ranging from a highly disordered a- IrO_x to a highly crystalline c- IrO_2 can be produced and will be investigated in this study. The chosen temperatures for the initial heat treatment (step i in Fig. 1) are marked by the colored asterisks shown in Fig. 2.

After the heat treatment step in the tube furnace, the samples are denominated as IrO_2 -T (T standing for the heat treatment temperature in $^\circ\text{C}$). As shown later on in Table II, the specific surface area (A_{BET}) of the IrO_2 -T samples decreases with increasing heat treatment temperature, due to the temperature-induced particle agglomeration and growth. Since the A_{BET} values of the IrO_2 -T samples which are heat treated at $T \geq 650^\circ\text{C}$ is substantially compromised ($A_{\text{BET}} \ll 20 \text{ m}^2 \text{ g}^{-1}$), these samples were subjected to a ball milling process (see step ii in Fig. 1) in order to deagglomerate the catalyst particles and to increase their A_{BET} values. In order to get better insights into the effect of ball milling time on the A_{BET} values of these samples, the A_{BET} values of the IrO_2 -750 and IrO_2 -1000 samples were measured after 80 and 160 ball milling cycles (one cycle consisting of 1 min of milling and 4 min of rest). As shown in Table I, the A_{BET} values of the samples increase drastically after the first set of ball milling cycles, but do not increase substantially with further ball milling. However, as shown in the last column of Table I, the amount of zirconium contamination of the samples increases significantly with increasing ball milling cycles (e.g., ~ 2 -fold for the IrO_2 -1000 sample between 80 and 160 cycles), caused by the abrasion of the ZrO_2 beads during milling. Therefore, 80 cycles were chosen for the ball milling step to get a high A_{BET} and to minimize the amount of zirconium contamination. The IrO_2 -T ($T \geq 650^\circ\text{C}$) samples after 80 ball milling cycles will be denominated as “ IrO_2 -T-M” (M standing for ball milling).

The last step of the three-step synthesis to produce reduction resistant- IrO_2 will be referred to as healing step (step iii in Fig. 1), which is a short heat treatment of the IrO_2 -T-M samples at 400°C in air, thought to remove defects introduced during the prior ball milling step. The resulting materials will be denoted as IrO_2 -T-MH samples (with H standing for healing of the milled samples). In order to better understand the significance of the healing step, a TGA temperature

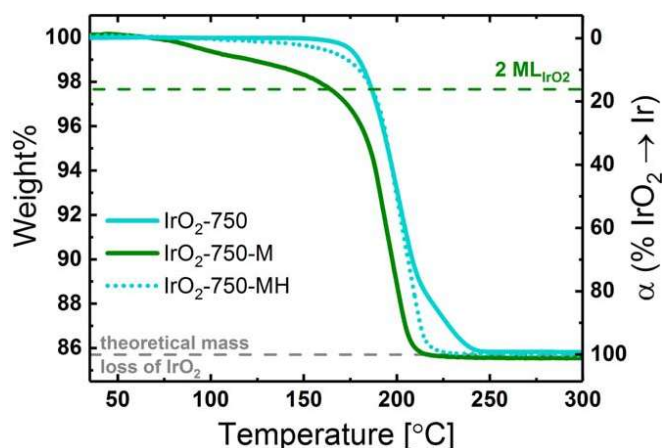


Figure 3. TGA temperature ramp experiments with the IrO₂-750, the IrO₂-750-M, and the IrO₂-750-MH samples under 3.3 vol% H₂/Ar at 5 K min⁻¹ (following the drying/cleaning step; see Experimental section). The left y-axis represents the wt% mass loss of the IrO₂ samples vs temperature, while the right y-axis depicts the fraction of the IrO₂ that is reduced to metallic Ir (α). The horizontal dashed green line represents the reduction of the two outermost monolayers of IrO₂ (i.e., 2 ML_{IrO₂}) of the IrO₂-750-M particles; this was estimated from the sample's A_{BET} value in combination with a spherical particle model (see Eqs. 3 and 4 in reference 19), which projects that the reduction of 2 ML_{IrO₂} on the particle surface of this sample corresponds to a mass loss of ~2.34 wt% or to a reaction extent of $\alpha \approx 16.4\%$. The horizontal dashed gray line marks the theoretical mass loss (14.3 wt%) of IrO₂ upon its full reduction to Ir.

ramp experiment in 3.3 vol% H₂/Ar was carried out with the IrO₂-750, the IrO₂-750-M, and the IrO₂-750-MH samples. As shown in Fig. 3, as the temperature reaches 300 °C, all the TGA curves approach the mass loss of 14.3 wt% that is expected for the full reduction of IrO₂ to metallic Ir. However, it is clear that unlike the IrO₂-750 sample (light blue line), the reduction of the IrO₂-750-M sample (green line) can be separated into two distinct steps: a gradual reduction reaction occurring at lower temperatures, with an onset of the mass loss at ~80 °C, followed by a fast mass loss at higher temperatures, similar to what is observed for the IrO₂-750 sample. This apparently compromised reduction resistance of the IrO₂-750-M sample must originate from structural defects induced by the ball milling process. The generation of

defects in crystalline materials by ball milling has often been reported in the literature, where it has been shown that it can lead to the formation of an amorphous, few atomic monolayer (ML) thick shell covering the crystalline core materials.^{46–48} Therefore, the much lower onset temperature for the reduction of the IrO₂-750-M compared to the IrO₂-750 sample could be caused by the reduction of a several ML thick amorphous shell, followed by the reduction of the crystalline core. In order to evaluate the thickness of the amorphous shell, one can estimate the mass loss corresponding to the reduction of 1 ML_{IrO₂} on the surface of the IrO₂-750-M sample from its A_{BET} value (25.9 m² g⁻¹, see Table I), using the estimation method based on a spherical particle model introduced in our previous study (Eqs. 3 and 4 in reference 19). For the IrO₂-750-M sample, this model predicts that the outermost monolayer of the particles contain ~8.2% of the total IrO₂ contained in the particle, so that the complete reduction of the outermost monolayer would result in a mass loss of ~1.17 wt% (i.e., 8.2% of 14.3 wt%); when viewed in terms of the overall reaction extent α (i.e., the fraction of the entire IrO₂ material that is being reduced to Ir), the complete reduction of the outermost monolayer thus corresponds to a reaction extent of $\alpha \approx 8.2\%$. The horizontal dashed green line in Fig. 3 represents the estimated mass loss for the reduction of 2 ML_{IrO₂} on the surface of the IrO₂-750-M sample (i.e., ~2.34 wt%), suggesting that the mass loss of the IrO₂-750-M sample between ~80 °C–165 °C closely corresponds to the reduction of its outermost 2 ML_{IrO₂}. This is in line with the hypothesis that structural defects are generated during the ball milling process and that such defects are mainly located on the catalyst surface as an amorphous layer. Since amorphous iridium oxide (a-IrO_x) is less stable than c-IrO₂ in a H₂-containing atmosphere,^{36–39} the reduction of this amorphous layer on the catalyst surface occurs at lower temperatures.

In order to recrystallize such an a-IrO_x shell and retrieve the higher reduction resistance of the IrO₂-750 material, the IrO₂-750-M material was heat-treated for 15 min in a post-annealing step under air at T = 400 °C (step iii in Fig. 1, a temperature at which the crystallization of a-IrO_x is reported to take place.^{39,45} The large impact of this “healing” step on the recovery of the reduction resistance of the ball milled catalysts can be seen in Fig. 3, where the mass loss curve clearly shows that the reduction resistance of the IrO₂-750-MH material (dotted light blue line) can be improved substantially. It actually reaches that of the IrO₂-750 sample that does not get reduced up to ~170 °C, despite the ~6 times larger A_{BET} value of the IrO₂-750-MH material (see Table II). It should be

Table II. Comparison of the IrO₂-T and the IrO₂-T-MH samples with respect to their specific surface area measured by the BET method (A_{BET}; in units of m² g⁻¹_{IrO₂}) and their average A_{BET}-deduced particle size (d_{BET}) based on assuming a spherical particle geometry. Note that for the IrO₂/TiO₂ (Umicore) catalyst it is assumed that N₂ sorption only reflects the surface area of the IrO₂ particles which completely cover the TiO₂ support particles; therefore, the measured A_{BET} value of this catalyst (27.2 m² g⁻¹_{IrO₂/TiO₂}) is normalized to its IrO₂ mass (87.5 wt% IrO₂; see Reference 19 for details). Further shown are the relevant parameters from the XPD data fits, viz., the fit quality factors (R_{wp} and χ^2), the determined crystallite diameters (d_{XPD}) based on assuming a spherical crystallite shape (d_{XPD} = 4/3·L_{vol}), and the microstrain values (ϵ_0). Due to the artefacts in the evaluation of the d_{XPD} and ϵ_0 values of the IrO₂-T-MH samples on account of their inhomogeneous and very broad particle size distribution, these likely unreliable values are placed in square brackets. The reported errors of the XPD data are the standard deviation estimated from a single measurement by the refinement program. The last column shows the d_{XPD}/d_{BET} ratio for each sample to check the quality of XPD data fitting.

Sample	N ₂ sorption		XPD				
	A _{BET} [m ² g ⁻¹ _{IrO₂}]	d _{BET} [nm]	R _{wp} [%]	χ^2	d _{XPD} [nm]	ϵ_0 [%]	d _{XPD} /d _{BET}
IrO ₂ /TiO ₂ (Umicore)	31.1	—	—	—	—	—	—
IrO ₂ -375	55.2	9.3	—	—	—	—	—
IrO ₂ -500	26.4	19.5	2.52	0.65	10.7 ± 0.2	0.115 ± 0.005	0.5
IrO ₂ -550	22.6	22.9	2.89	0.89	16.1 ± 0.2	0.06 ± 0.002	0.7
IrO ₂ -650	9.7	53.3	3.71	1.65	54.0 ± 0.6	0.020 ± 0.001	1.0
IrO ₂ -750	3.8	136	6.30	4.34	224.8 ± 8.2	0.007 ± 0.001	1.6
IrO ₂ -1000	0.9	575	8.57	2.19	too large	—	—
IrO ₂ -650-MH	30.7	16.8	3.36	1.02	[43.9 ± 0.9]	[0.123 ± 0.002]	2.6
IrO ₂ -750-MH	23.7	21.8	3.92	1.56	[84.9 ± 10.7]	[0.124 ± 0.008]	3.9
IrO ₂ -1000-MH	24.8	20.9	4.48	2.44	[125.0 ± 9.6]	[0.168 ± 0.003]	6.0

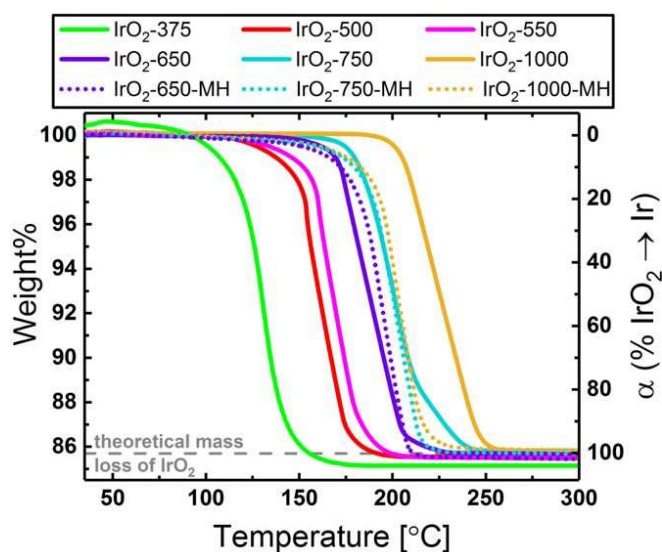


Figure 4. TGA temperature ramp experiments with the IrO₂-T (solid lines) and the IrO₂-T-MH (dashed lines) samples under 3.3 vol% H₂/Ar at 5 K min⁻¹ (following the drying/cleaning step; see Experimental section). The left y-axis represents the wt% mass loss of the IrO₂ samples vs temperature, while the right y-axis depicts the fraction of the IrO₂ that is reduced to metallic Ir (α). The horizontal dashed gray line marks the theoretical mass loss (14.3 wt%) of IrO₂ upon the full reduction to Ir (see experimental section).

noted that the A_{BET} values are not significantly compromised during the healing process due to the short heat treatment time at this step (compare A_{BET} values in Tables I and II).

Figure 4 shows the TGA temperature ramp experiments of the various IrO₂-T and the IrO₂-T-MH samples in 3.3 vol% H₂/Ar at 5 K min⁻¹. All the TGA curves reach the theoretical mass loss of 14.3 wt% that is expected for the full reduction of IrO₂ to metallic Ir, with the exception of the IrO₂-375 sample (green line) that still contains oxy-hydroxide species (see the discussion of Fig. 2) and therefore has a slightly higher mass loss. Based on the TGA curves of the IrO₂-T samples in Fig. 4, the reduction resistance of the samples increases with increasing heat treatment temperature, which is in line with the literature reports that c-IrO₂ is being formed by heat treatment at higher temperatures and that c-IrO₂ species are more stable in H₂-containing atmospheres.^{37,38} Here, however, it must be considered that the A_{BET} values of the IrO₂-T samples also drastically decrease with increasing heat treatment temperature, corresponding to an increase of their average particle size (d_{BET} ; see Table II), which might also contribute to the observed increased reduction resistance with temperature.⁴⁹ The contribution of the particle size can be estimated by comparing the reduction resistance of the samples before and after the milling+healing steps: even though the d_{BET} values are ~3-fold larger for the IrO₂-650 vs the IrO₂-650-MH sample (see Table II), they have essentially the same reduction resistance (violet solid and dashed lines in Fig. 4); similarly, the d_{BET} values are ~6-fold larger for the IrO₂-750 vs the IrO₂-750-MH sample (see Table II), but their reduction resistance again is essentially identical (light blue solid and dashed lines). Only in the extreme case of the samples heat-treated at 1000 °C, where the average particle size is ~28-fold higher for the IrO₂-1000 vs the IrO₂-1000-MH, the latter has indeed a lower reduction resistance (yellow solid and dashed lines). The reduction resistance is clearly affected by the average particle size for the IrO₂-1000 sample, indicating the impact of bulk oxygen diffusion resistances for the very large IrO₂-1000 particles ($d_{\text{BET}} \approx 575$ nm). Based on these considerations, it can be concluded that the improvement of the reduction resistance upon heat treatment at $T \leq 750$ °C is mainly due to the formation of highly crystalline c-IrO₂, and that the particle size growth upon heat treatment in this temperature range has a

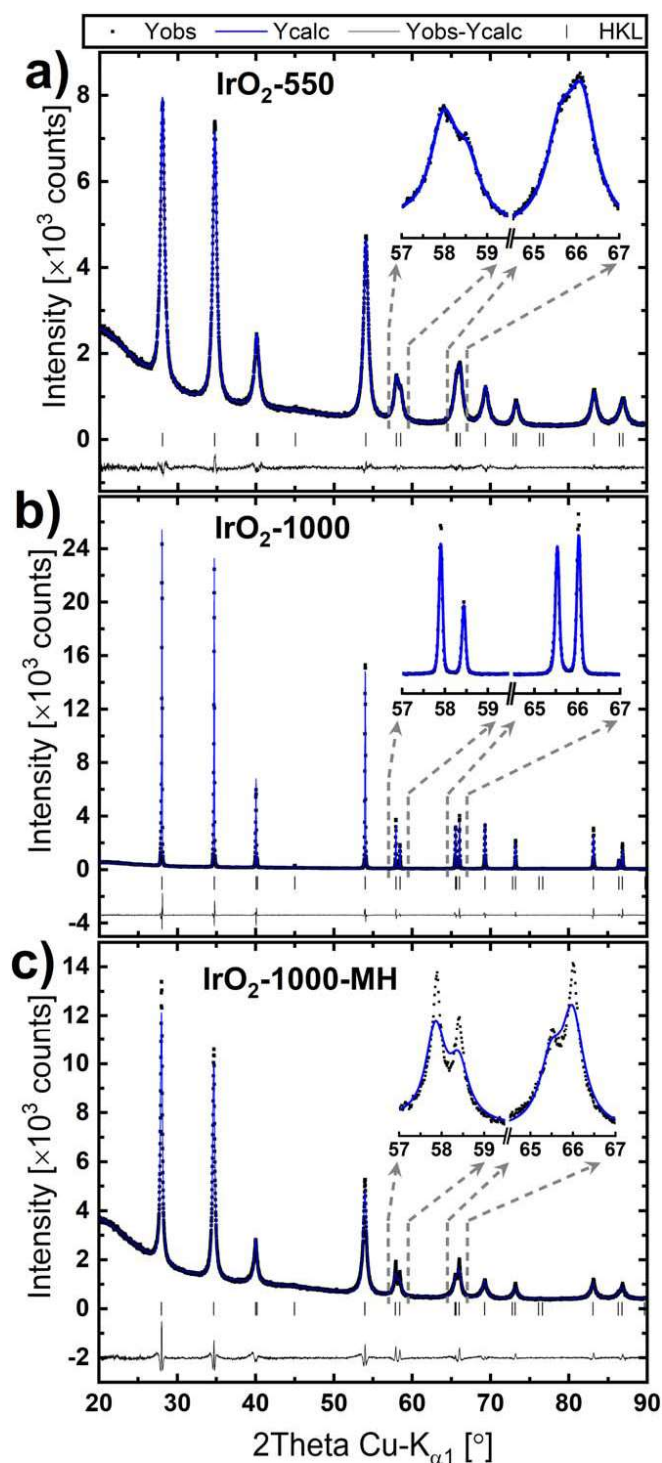


Figure 5. Exemplary X-ray powder diffraction (XPD) data and analysis results for: (a) IrO₂-550, (b) IrO₂-1000, and (c) IrO₂-1000-MH. The data were collected with our in-house Cu-diffractometer ($\lambda = 1.54059$ Å) and then refined with a structure-independent fit of the $P42/mnm$ space group according to the Pawley method, putting a special emphasis on the size/strain analysis of the peak broadening (see Experimental section). The detailed fitting parameters can be found in Table II. The observed (black points) and the calculated (blue lines) diffraction profiles as well as the residual difference (black lines) are shown together with the position of the Bragg peaks (black ticks). The insets show a subset of peaks as a guide-to-the-eye to check the quality of the fits.

minor impact on the observed reduction resistance improvement. However, when an IrO₂ sample is heat treated at 1000 °C, its major reduction resistance improvement compared to a sample heat treated

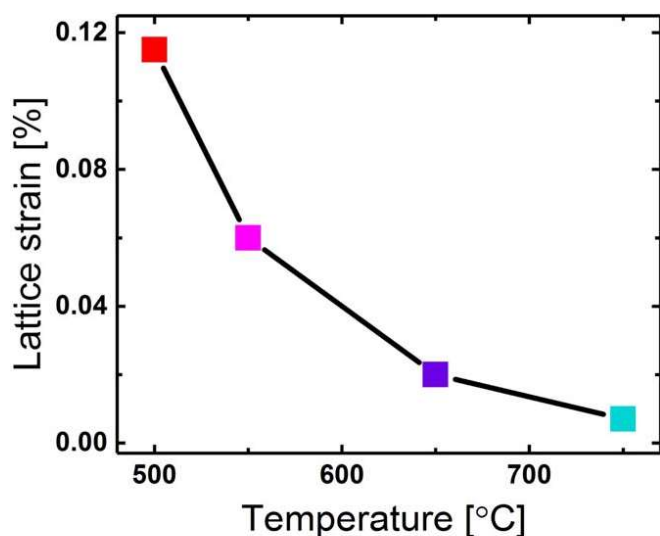


Figure 6. Relationship between lattice strain and the heat treatment temperature for the IrO₂-T materials, namely IrO₂-500 (red square), IrO₂-550 (purple square), IrO₂-650 (violet square), and IrO₂-750 (light blue square). The lattice strain values were estimated by the size/strain analysis of the peak broadening in the XPD data (see Table II and the Experimental section for further details).

at 750 °C is due to particle size growth, as demonstrated by the fact that the IrO₂-750-MH (light blue dashed line) and the IrO₂-1000-MH (yellow dashed line) samples with essentially identical d_{BET} values (see Table II) have similar reduction resistances. This implies that the crystallization of IrO₂ and the formation of a long-range structural order mainly occurs up to a temperature of ~750 °C. This phenomenon will be investigated more quantitatively in the following.

Fundamental aspects of the reduction resistance of IrO₂ materials under H₂.—The structural transformation from a highly disordered amorphous to a highly ordered crystalline structure during the crystallization step should be accompanied by the annihilation of any lattice imperfection such as dislocations and vacancies. This phenomenon can be described by the analysis of crystal lattice strain, a quantity that shows the deviation of a lattice structure from a “perfect” model structure that is caused by lattice imperfection.^{50–52} For this purpose, a size/strain analysis of the XPD data of the here prepared materials was performed. Figure 5 shows a few examples of the XPD patterns recorded in this study, namely the diffractograms of the IrO₂-550 (Fig. 5a), the IrO₂-1000 (Fig. 5b), and the IrO₂-1000-MH (Fig. 5c) materials. Based on Fig. 5, these materials exhibit a well-defined crystalline structure that can be indexed according to the tetragonal rutile IrO₂ structure with the *P42/mnm* symmetry. It can be clearly seen that by increasing the heat treatment temperature from 550 °C (Fig. 5a) to 1000 °C (Fig. 5b), the diffractogram peaks become narrower, which is expected due to the increase in crystallite size (d_{BET} increasing from ~19.5 to ~575 nm, see Table II) and a likely reduction in microstrain with heat treatment temperature. To further examine this, an XPD-based size/strain analysis was performed (the detailed fitting procedure is described in the Experimental section), the results of which are summarized in Table II.

Due to the narrow reflections in the XPD pattern of the IrO₂-1000 material (Fig. 5b), the total line broadening of this sample was estimated to be similar to the instrumental line broadening that was determined by a silicon standard material in our measurement setup (see Experimental section). This implies that the contributions of strain and particle size to the total line broadening (see Eq. 4) of the IrO₂-1000 material is negligible, which is reasonable in view of its large particle size ($d_{\text{BET}} \approx 575$ nm, see Table II) and the high heat treatment temperature that should result

in highly crystalline IrO₂. Therefore, the line broadening observed in the diffractogram of the IrO₂-1000 material (Fig. 5b) is considered as the instrumental line broadening for the evaluation of the XPD data of the other materials. Since we are primarily interested in the trend of the size/strain values amongst the investigated materials and not in the absolute size/strain values, the here used normalization approach for determining the instrumental line broadening is still expected to correctly capture the relevant trends. However, in order to determine whether the parameter values obtained by the XPD analysis are reasonable, we compared for each sample the average crystallite diameter values obtained by the XPD analysis (d_{XPD} , see Experimental section for further details) with that estimated from the BET surface area (d_{BET}). This comparison is given in terms of the $d_{\text{XPD}}/d_{\text{BET}}$ ratios in Table II, showing that for the IrO₂-T materials the d_{XPD} and d_{BET} values only differ by at most a factor of 2, which is a good indication of the reliability of the XPD analysis for the IrO₂-T materials.

The lattice strain values (ϵ_0 , see Eq. 6) of the various IrO₂-T materials obtained from the XPD fits are plotted in Fig. 6, clearly showing that the lattice strain decreases with increasing heat treatment temperature (T). Such a decrease in the lattice strain values suggests an annihilation of lattice imperfections and the formation of a long-range crystalline order upon heat treatment at higher temperatures, which is in line with the conclusions drawn from the TGA data in Fig. 4. A similar decrease of the lattice strain values vs heat treatment temperature was observed in the literature when studying the relationship between the OER activity of IrO₂ and its structural changes upon heat treatment.⁵² While Sharma et al. excluded the presence of a significant amount of oxygen vacancies as the origin of lattice imperfections,⁵⁰ Pfeifer et al. showed by a combination of theoretical calculations and an analysis of the near-surface region of different iridium oxide samples that the presence of iridium cationic (Ir⁴⁺) vacancies in the IrO₂ crystal structure is the likely origin of such lattice imperfections, and that such Ir⁴⁺ vacancies can be annihilated by heat treatment at high temperatures, yielding a highly ordered IrO₂ crystal structure.³⁹

When evaluating the XPD data of the IrO₂-T-MH materials, it was noticed that there was a rather large difference between the d_{XPD} and the d_{BET} values compared to what was obtained for the IrO₂-T samples (see $d_{\text{XPD}}/d_{\text{BET}}$ ratios in Table II). The origin of such a deviation can be found when comparing the XPD diffractograms of the IrO₂-550 and the IrO₂-1000-MH materials. This reveals that the peak profiles in the IrO₂-1000-MH diffractogram (Fig. 5c) are unusually broad at the base and sharp at the tip (best seen by comparing the peaks at 54°), having a so-called super-Lorentzian line shape. The latter is usually caused by the superposition of more than one Lorentzian function and is often an indication of a very broad or multi modal crystallite size distribution.⁵³ In order to investigate this possibility, the particle size distributions of the IrO₂-550 and the IrO₂-1000-MH materials were analyzed by TEM (see Fig. A-1). Although these samples have very similar A_{BET} and d_{BET} values (see Table II), it can be seen that the IrO₂-1000-MH material (Fig. A-1b) exhibits an inhomogeneous and very broad particle size distribution, clearly distinct from the much more narrow size distribution of the IrO₂-550 material (Fig. A-1a). Since the XPD line broadening is inversely proportional to the crystallite size of a material (see Eq. 5), smaller crystallites will result in a broader line shape and vice versa. That being said, when a material is composed of particles that are widely distributed in size, it causes an inhomogeneous broadening of a line that cannot be fully described by the single crystallite size parameter that is obtained from the measurement of the integral breadth of the line. On the other hand, the lattice strain also contributes to the peak broadening based on Eq. 6, and the total line broadening based on Eq. 4 is composed of lattice strain and crystallite size contributions. Therefore, any significant artefact in the determination of crystallite size of a material with a broad particle size distribution will result in artefacts in the determination of the lattice strain of such a material, which can affect the quality of the XPD data fitting. This can be seen by

comparing the XPD data fit quality in the insets of Figs. 5a and 5c, where unlike for the IrO₂-550 material (inset of Fig. 5a), the fitted data (blue curve) for the IrO₂-1000-MH material (inset of Fig. 5c) do not give a good fit of the XPD data (black dotted curve). Therefore, it is expected that the high lattice strain values reported for the IrO₂-T-MH materials in Table II do not accurately represent their actual lattice strain values, as these are significantly affected by the artefacts due to the broad particle size distribution of these materials. Nevertheless, based on the analysis of the reduction resistance of the samples in Figs. 3 and 4, it can be assumed that most of the structural changes induced by the ball milling process are recovered during the healing step and that there are no significant structural differences between a given IrO₂-T-MH material and its IrO₂-T counterpart.

Based on the above analyses, it is clear that the structural transformation upon the heat treatment at high temperatures leads to the crystallization of a-IrO_x to c-IrO₂ as well as to the formation of a long-range crystalline order of the c-IrO₂. Therefore, a high-temperature heat-treated material like, e.g., the IrO₂-750-MH material, would mainly contain a highly-ordered c-IrO₂ species. If this were true, the reduction kinetics of the IrO₂-750-MH material would have to be clearly distinguishable from those of the materials heat-treated at lower temperatures. In order to evaluate the IrO₂ reduction kinetics, the Flynn-Wall-Ozawa (FWO) method, described in the Experimental section and in our previous study,¹⁹ was used to perform a kinetic analysis and to calculate the activation energy for the reduction of the various IrO₂ materials.^{19,30,31} It was shown in our previous study that the a-IrO_x species can be more easily reduced by H₂, and we suggested that the activation energy for the reduction of a-IrO_x species would be lower than that of c-IrO₂ species.¹⁹ With this in mind and considering the trend in the reduction resistance observed for the different materials in Fig. 4, three materials were chosen for the reduction kinetics analysis by the FWO method: (i) the IrO₂-375 sample with a low reduction resistance; (ii) the IrO₂-500 sample with an intermediate reduction resistance; and, (iii) the IrO₂-750-MH sample with a high reduction resistance.

Figures A.2a–A.2c show the TGA temperature ramp curves of these samples in 3.3 vol% H₂/Ar at four different heating rates ($\beta = 1, 2.5, 5, \text{ and } 10 \text{ K min}^{-1}$). The analysis of these data is shown in Figs. A.2d–A.2f, depicting the linear regressions of the $\text{Ln}(\beta)$ vs $1/T$ points which were collected from the TGA curves at different constant reaction extents α (selected between $\alpha = 10\%$ – 90%). The activation energy at each α value was then calculated based on Eq. 3, using the slopes of the fitted lines in Figs. A.2d–A.2f. The thus determined activation energies (E_a) vs α for the three different materials are plotted in Fig. 7; for comparison, the α -dependent activation energies for the reduction of the IrO₂ phase of the IrO₂/TiO₂ (Umicore) catalyst, taken from our previous study,¹⁹ are also plotted in Fig. 7. It can be seen in Fig. 7 that the IrO₂-375 material (green squares) has the lowest activation energies for reduction under H₂ among the materials prepared in this study, with an average activation energy of $\sim 113 \text{ kJ mol}^{-1}$ for α values between 10% – 90% . This may be compared to the activation energy for reduction of the IrO₂/TiO₂ (Umicore) catalyst (violet squares) that is in a similar range for $\alpha \approx 10\%$ and substantially higher for larger α values. Based on our previous analysis of the reduction of the IrO₂ phase in the IrO₂/TiO₂ (Umicore) catalyst,¹⁹ its low activation energy up to $\alpha \approx 10\%$ reflects the reduction of the outermost monolayer of the IrO₂/TiO₂ (Umicore) particles, which was ascribed to the amorphous nature of its outermost monolayer, while the higher activation energies at higher α values were ascribed to the reduction of the more crystalline layers underneath. Therefore, the similar values for the average activation energy for reduction of the IrO₂-375 material and that of the IrO₂/TiO₂ (Umicore) catalyst at $\alpha = 10\%$ suggest that the former is mainly composed of a-IrO_x species, consistent with what we had concluded from Fig. 2.

Moving to the IrO₂-500 material that has an intermediate reduction resistance based on Fig. 4 (red line), Fig. 7 shows that its activation energies for reduction (red squares) are significantly

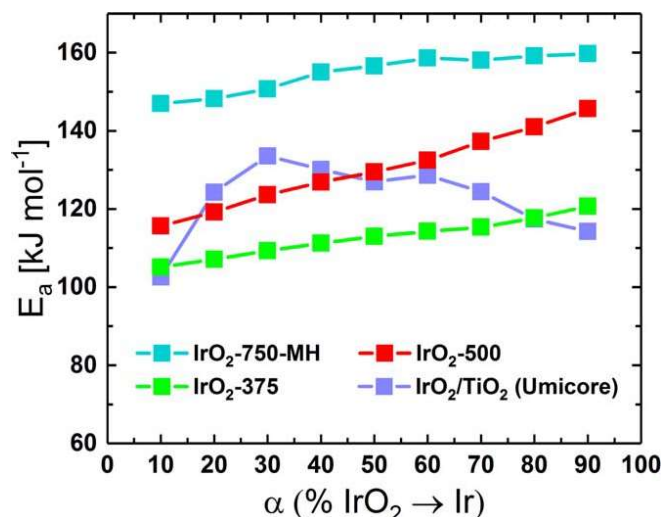


Figure 7. Plots of activation energy vs α for the reduction of the IrO₂-375, the IrO₂-500, and the IrO₂-750-MH materials, calculated based on the FWO method (see Eq. 3 in the Experimental section). The data are derived from TGA temperature ramp experiments conducted at different heating rates (see Fig. A.2a–A.2c in the appendix), using the regression line slopes in Fig. A.2d–A.2f in combination with Eq. 3. The activation energy values for the reduction of the IrO₂ phase of the IrO₂/TiO₂ (Umicore) catalyst is taken from our previous study.¹⁹

higher at any α value than those of the IrO₂-375 material. The average activation energy for reduction of $\sim 130 \text{ kJ mol}^{-1}$ for the IrO₂-500 material is similar to the activation energy for the reduction of the IrO₂ phase in the IrO₂/TiO₂ (Umicore) catalyst at $20\% \leq \alpha \leq 70\%$ ($\sim 130 \text{ kJ mol}^{-1}$), which was assigned to the reduction of a mixture of a-IrO_x and c-IrO₂ in our previous study.¹⁹ Therefore, based on this similarity and in view of the analysis of Fig. 2, it can be assumed that the IrO₂-500 material is composed of a mixture of a-IrO_x and c-IrO₂ species.

Finally, the highest activation energies for reduction are obtained for the IrO₂-750-MH material (light blue squares in Fig. 7), with an average value of $\sim 155 \text{ kJ mol}^{-1}$ between α values of 10% – 90% . Based on the analyses of Figs. 2, 4, and 6, such a high activation energy must be due to the predominance of c-IrO₂ species in the IrO₂-750-MH material. Therefore, this material meets all the requirements for being an irr-IrO₂ OER catalyst, namely having both a high specific surface area ($\sim 24 \text{ m}^2 \text{ g}^{-1}$, see Table II) and a high reduction resistance in H₂-containing atmospheres (stable up to $\sim 120^\circ \text{C}$ based on Fig. 4). In the following, the latter quality will be investigated at conditions that more closely reflect those in an actual PEMFC.

Stability of IrO₂ catalysts in a simulated PEMFC anode environment.

—It was shown in our previous study that long-term (up to 24 h) isothermal TGA experiments in 3.3 vol% H₂/Ar at 80°C can reliably estimate the reduction resistance of a catalyst under the reducing environment of a PEMFC H₂ anode.¹⁹ This approach will be utilized here for screening the reduction resistance of the different materials prepared in this study, and the results are shown in Fig. 8, whereby the mass losses over the course of this experiment are given in terms of the fraction of IrO₂ reduced to metallic Ir (α). It should be noted that any mass loss observed during this isothermal TGA experiment correspond to the reduction of IrO₂ by H₂ according to Eq. 2, since the in situ drying/cleaning step prior to the TGA measurement in 3.3 vol% H₂/Ar (see Experimental section) quantitatively removes adsorbed water or any organic residues from the catalysts surface. It can be seen at first glance from Fig. 8 that the reduction resistance of the IrO₂-T materials increases in the order of IrO₂-375 < IrO₂-500 < IrO₂-550, following the same order that was observed in Fig. 4. Since all of the samples which are heat-treated at

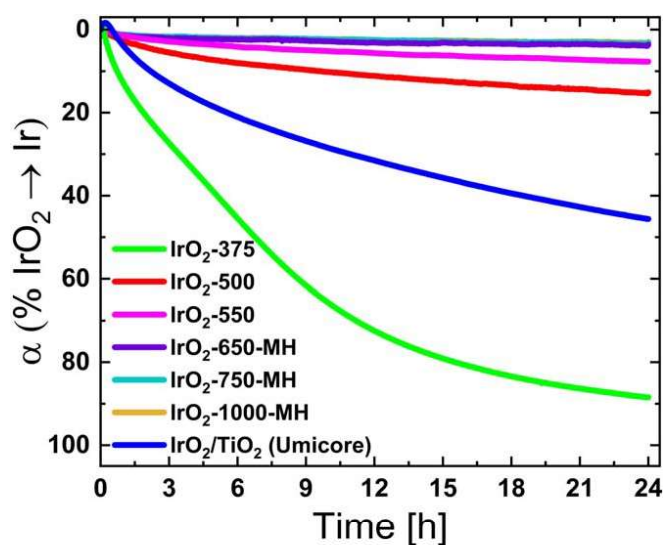


Figure 8. Long-term isothermal TGA experiments on the reduction of different IrO₂ samples in 3.3 vol% H₂/Ar at 80 °C (following the drying/cleaning step; see Experimental section), aiming to simulate the PEMFC hydrogen anode environment. The y-axis represents the fraction of IrO₂ that is reduced to metallic Ir (α).

T ≤ 550 °C get noticeably reduced over the 24 h of the isothermal experiment in Fig. 8, none of them qualify as an irr-IrO₂ catalyst for use as anode co-catalyst in a PEMFC anode. On the other hand, the materials annealed at ≥ 650 °C and subsequently milled+heated to obtain A_{BET} values of >20 m² g⁻¹, i.e., the IrO₂-T-MH materials, do not show any significant IrO₂ reduction within the error of the measurement, considering that α values of <4% after 24 h of the isothermal experiment cannot be reliably assigned to be exclusively due to the reduction of IrO₂. This is due to the fact that the very small mass loss corresponding to such low α values is within the measurement error of such long-term isothermal experiment (the main errors being due to the compensation of a blank curve recorded with an empty crucible, the microbalance drift, etc.).

To circumvent this issue and to obtain an order of magnitude estimate of the reduction resistance of the IrO₂-T-MH materials in the PEMFC anode environment, the stability of the IrO₂-750-MH material was further investigated by an isothermal TGA experiment in 3.3 vol% H₂/Ar at the higher temperature of 120 °C for 16 h (see Fig. A-3). Then, the reduction rate of the IrO₂-750-MH material at 80 °C was estimated using the rate observed at 120 °C and the Arrhenius equation in combination with the activation energy for reduction of the IrO₂-750-MH material (light blue squares in Fig. 7):

$$r_1 = r_2 \exp \left[\frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \right] \quad [8]$$

Here, r_1 and r_2 are the rates of IrO₂ reduction (in %IrO₂ h⁻¹) at the temperatures of $T_1 = 353$ K (≡80 °C) and $T_2 = 393$ K (≡120 °C), respectively, E_a is the activation energy of IrO₂ reduction (in J mol⁻¹), and R is the gas constant (8.314 J mol⁻¹ K⁻¹). The measured reduction rate of the IrO₂-750-MH material at 120 °C was $r_2 \approx 0.74\%_{\text{IrO}_2} \text{ h}^{-1}$ (reduction of 11.8%IrO₂ to metallic Ir after 16 h; see Fig. A-3). Since the reduction of only a few ML_{IrO2} on the surface of an IrO₂ catalyst is sufficient to completely change its electrochemical properties (its OER activity and its stability during SUSD events),¹⁹ a reduction extent α of only 20% of the IrO₂-750-MH material (corresponding to ~2.7 ML_{IrO2}) was considered for the projection based on Eq. 8. Therefore, the activation energy for reduction of this catalyst was averaged for the α values of 10 and 20% shown in Fig. 7, yielding $E_a \approx 148$ kJ mol⁻¹. Using these values in Eq. 8, a reduction rate of $r_1 \approx 0.004\%_{\text{IrO}_2} \text{ h}^{-1}$ can be estimated for the IrO₂-750-MH material at 80 °C. This would mean

that a reduction extent of $\alpha = 20\%$ of the IrO₂-750-MH material is projected to occur after ~5000 h of operation at 80 °C. While this represents a rather rough estimate, the projected long-term reduction stability of the IrO₂-750-MH material at 80 °C in H₂ is on the same order as the durability target of 8000 h for PEM fuel cell systems for light-duty automotive applications and perhaps even as the ~25000 h target for heavy-duty applications.^{1,3} In order to ultimately determine whether the IrO₂-750-MH material is a viable irr-IrO₂ anode co-catalyst, long-term PEMFC tests would be required. In the next section, the OER activity of the irr-IrO₂ catalysts (i.e., the IrO₂-T-MH materials) will be compared with the conventional IrO₂ catalysts by using the RDE technique.

OER activity of the various IrO₂ catalysts measured by the RDE technique.—In our previous study, we have shown that the RDE-based OER activity of an IrO₂ catalyst does not always reflect its activity in the anode of an MEA during cell reversal tests in a PEMFC.¹⁹ This is due to the fact that when an IrO₂ catalyst is reducible in the environment of a PEMFC H₂ anode, metallic Ir forms in the near-surface region of the catalyst, which drastically increases its OER activity due to the higher intrinsic OER activity of metallic Ir compared to heat-treated IrO₂ surfaces.¹⁹ The fact that this initial reduction of the OER catalyst surface to metallic Ir does not happen with an irr-IrO₂ catalyst (due to its high reduction resistance in H₂-containing atmospheres) explains the differences in OER activity obtained by RDE vs MEA measurements. Nevertheless, since the RDE technique is a quick and straightforward screening tool for the investigation of the OER activity of catalysts synthesized by different routes,^{54,55} it can still provide a valuable initial screening of the OER activity of as-synthesized catalysts, as long as one keeps in mind that the OER activity of reducible OER catalysts could be higher when being used as anode co-catalyst.

Figure 9a shows the RDE-based OER polarization curves for the different here synthesized materials as well as for the IrO₂/TiO₂ (Umicore) catalyst, allowing for an initial OER activity ranking. As the iridium loading is the same for all catalysts (0.1 mg_{Ir} cm⁻²_{disk}), their OER activity can be evaluated by the frequently used metric of the potential at which a geometric current of $i_{\text{geo.}} = 10 \text{ mA cm}^{-2}_{\text{disk}}$ is obtained.⁵⁶ Based on this, Fig. 9a (see right-hand y-axis) clearly shows that the OER mass activity of the IrO₂-T-MH catalysts (with T = 650, 750, and 1000 °C) is lower than that of the other catalysts which had been heat-treated at lower temperatures (i.e., the IrO₂-375, IrO₂-500, and IrO₂/TiO₂ (Umicore) catalysts). Since the difference in the OER mass activities can in part originate from differences in electrochemically active surface area, most closely represented by a catalyst's A_{BET} value (see Table II), a comparison of the intrinsic OER activity of different catalysts must be done in terms of their specific OER activity (i_s ; i.e., the OER activity referenced to the catalyst's A_{BET} value). Therefore, the specific OER activities were calculated using the mass activities (i_m) recorded at 1.54 V_{RHE} in Fig. 9a and normalizing them by the respective A_{BET} values (see Table II; note that a conversion of Ir loading to IrO₂ loading is required before this normalization, as the A_{BET} values are in units of m² g⁻¹_{IrO2}).

Figure 9b shows the resulting specific OER activities (i_s) of the catalysts at 1.54 V_{RHE}, which are up to ~2.5-fold lower for the IrO₂-T-MH catalysts heat-treated at ≥ 650 °C compared to the catalysts heat-treated at lower temperatures, viz., the IrO₂-375, IrO₂-500, and IrO₂/TiO₂ (Umicore) catalysts (note that according to the patent, the latter was heat-treated at ~400 °C²⁵). This may be compared to a very similar factor reported by Geiger et al., who found a ~2-fold lower specific OER activity for IrO₂ catalysts heat-treated at high temperatures (~600 °C) compared to those heat-treated at lower temperatures (~400 °C).⁴⁰ This was ascribed to the difference in the active surface species of the catalysts, whereby amorphous, hydrous IrO(OH)_x species with an intrinsically higher OER activity are present in the catalysts heat-treated at lower temperatures, while intrinsically less active crystalline IrO₂ species

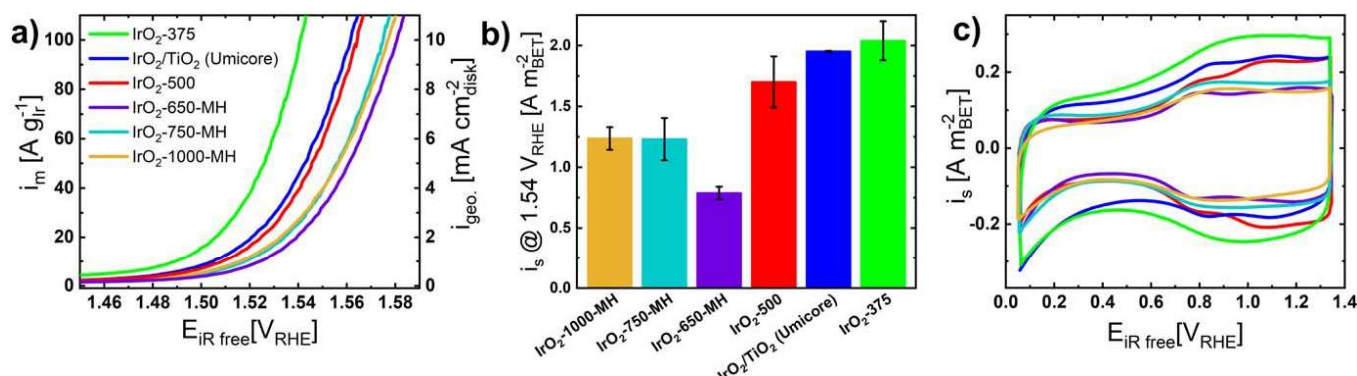


Figure 9. RDE measurements of some of the here prepared catalysts and of the IrO₂/TiO₂ (Umicore) catalyst, conducted at room temperature and 2500 RPM in 0.05 M H₂SO₄ electrolyte, using identical loadings of 0.1 mg_{Ir} cm⁻²_{disk}. (a) OER polarization curves at 20 mV s⁻¹ in O₂-saturated electrolyte (first positive-going scan after the initial CVs described in c). (b) Specific OER activity (i_s) of the catalysts at 1.54 V_{RHE}, obtained by dividing the mass activities (i_m) in panel a by the catalyst's specific A_{BET} value (see Table II; Ir loadings are converted to IrO₂ loadings prior to this normalization, as the A_{BET} values are in units of m² g⁻¹_{IrO₂}). The error bars indicate the standard deviation of at least two independent measurements. (c) Cyclic voltammograms (CVs) recorded between 0.05–1.35 V_{RHE} at 100 mV s⁻¹ in Ar-saturated electrolyte; the currents are also normalized by the respective A_{BET} values. The color-coding of the samples is maintained the same for all the panels.

are present at the surface of catalysts heat-treated at higher temperature.⁴⁰ Thus, the higher intrinsic OER activity of the IrO₂-T-MH catalysts must be due to the predominant presence of c-IrO₂ species, which is consistent with the conclusions drawn from Fig. 2.

In order to get better insights into the surface chemistry of the various catalysts, cyclic voltammograms (CVs) were recorded; these are depicted in terms of A_{BET}-normalized currents in Fig. 9c. It is known that the amorphous, hydrous IrO(OH)_x species can be distinguished based on its strong redox features between 0.7–1.3 V_{RHE} from c-IrO₂ species that typically do not show well-defined redox features in this potential range.^{40,57} It is obvious in Fig. 9c that the IrO₂-375 (green line), the IrO₂-500 (red line), and the IrO₂/TiO₂ (Umicore) (blue line) catalysts have rather pronounced redox features between 0.7–1.3 V_{RHE}, indicating the clear presence of amorphous, hydrous IrO(OH)_x species; these typical redox features are only very weakly visible for the IrO₂-T-MH samples, explaining their lower specific OER activity. In the next section, some of the IrO₂ catalysts will be implemented in an MEA to investigate their stability in a PEMFC anode under normal operating conditions.

IrO₂ catalysts stability in a PEMFC anode under normal operating conditions.—Based on the above gained insights, it is now clear that the IrO₂-T-MH catalysts are mainly composed of c-IrO₂ species and that they are therefore expected to have a high reduction

resistance in a PEMFC H₂ anode under normal operating conditions, i.e., that they might indeed represent a class of irr-IrO₂ catalysts. To further examine this, three IrO₂ catalysts were selected based on their different reduction resistances observed in Fig. 8, and were implemented in an MEA for evaluating their reduction resistance under the normal operation conditions of a PEMFC anode: (i) the IrO₂-750-MH catalyst (high reduction resistance); (ii) the IrO₂-550 catalyst (intermediate reduction resistance); and, (iii) the IrO₂/TiO₂ (Umicore) catalyst (low reduction resistance). For the 5 cm² MEAs, the IrO₂ catalysts were used for the anode electrode and a Pt/C catalyst (0.3 mg_{Pt} cm⁻²_{MEA}) was used for the cathode electrode. It should be noted that the high iridium loading of ≥1.6 mg_{Ir} cm⁻²_{MEA} used in these MEAs is not relevant for the application of IrO₂ as an anode co-catalyst in a PEMFC (there, typically used iridium loadings are on the order of ~0.05 mg_{Ir} cm⁻²_{MEA}^{17,58}), and that these high loadings were only used to better compare the reduction resistance of the different IrO₂ catalysts. The MEAs were held at OCV at 80 °C, supplying a constant flow of fully-humidified H₂ (2000 nccm) through the anode compartment pressurized at 170 kPa_{abs}. Anode CVs were recorded after different time intervals at 40 °C, and were compared to the CVs of the IrO₂ catalysts at the beginning-of-test (BOT), i.e., before ever flowing H₂ through the anode compartment. These anode CVs are shown in Fig. 10 for the IrO₂/TiO₂ (Umicore) catalyst (panel a), the IrO₂-550 catalyst (panel b), and the IrO₂-750-MH catalyst (panel c). The voltammetric currents of the catalysts at BOT (black curves in Fig. 10) are rather

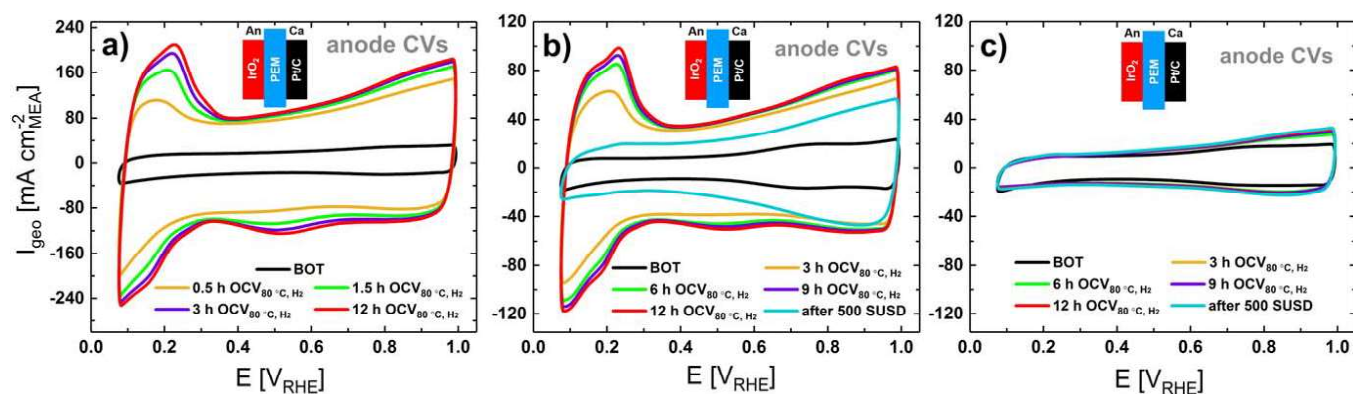


Figure 10. CVs at 300 mV s⁻¹ acquired between 0.07–1.00 V_{RHE} at 40 °C and ambient pressure with fully-humidified N₂ (anode) and 5 vol% H₂/Ar (cathode) for 5 cm² MEAs with different IrO₂ catalysts on the anode: (a) IrO₂/TiO₂ (Umicore) at 1.6 mg_{Ir} cm⁻²_{MEA}; (b) IrO₂-550 catalyst at 2.2 mg_{Ir} cm⁻²_{MEA}; and, (c) IrO₂-750-MH at 2.2 mg_{Ir} cm⁻²_{MEA}. The CVs were taken at beginning-of-test (BOT; black lines), i.e., prior to any exposure to H₂, as well as after a series of OCV hold times at 80 °C/100% RH and 170 kPa_{abs}, with flows of 2000 nccm H₂ at the anode and 5000 nccm air at the cathode. Panels b and c also show CVs taken after 500 start-up/shut-down (SUSD) cycles at 35 °C (see Experimental section), which were conducted after 12 h of hold time at OCV. The cathode of the MEAs had a Pt/C catalyst at 0.3 mg_{Pt} cm⁻²_{MEA}.

small, with not very strongly pronounced redox features between 0.07–1.0 V_{RHE} , similar to the RDE-based BOT CVs (see Fig. 9a). However, after the exposure to H_2 under the OCV conditions at 80 °C/100% RH, the voltammetric features develop differently for the different catalysts: The CVs of the IrO_2/TiO_2 (Umicore) catalyst (Fig. 10a) and the IrO_2 -550 catalyst (Fig. 10b) show a gradual formation of hydrogen under-potential deposition (H_{UPD}) features between 0.07–0.35 V_{RHE} , which are characteristic of metallic iridium or carbon-supported iridium nanoparticles.^{59,60} This implies that these IrO_2 catalysts are being reduced to metallic Ir upon exposure of the anode electrodes of the MEA to H_2 in a PEMFC (clearly apparent after already 0.5 h, see the orange line in Fig. 10a), consistent with the observed reduction of these catalysts in the isothermal TGA experiments (see blue and pink lines in Fig. 8). On the other hand, the voltammetric features of the IrO_2 -750-MH catalyst (see Fig. 10c) even after 12 h of exposure to H_2 remain very similar to those at BOT and show no distinct H_{UPD} features, suggesting that the surface state of this catalyst still resembles that of a heat-treated IrO_2 , i.e., that the IrO_2 -750-MH catalyst represents an irr- IrO_2 catalyst, at least within the timeframe of this experiment.

Another interesting question that can be examined based on the data in Fig. 10 is whether the mechanism of the IrO_2 reduction reaction differs between the IrO_2/TiO_2 (Umicore) and the IrO_2 -550 catalysts. At the first glance, Figs. 10a and 10b suggest that the CVs reach a steady-state after 12 h of the OCV experiment, indicating that the reduction of the IrO_2 surface is fully completed by that time and is possibly proceeding into the sub-surface layers of the catalyst particles. In order to get better insights into this phenomenon, the average of the anodic and cathodic charges of the CVs in Fig. 10 between 0.07–1.0 V_{RHE} were determined and normalized to the A_{BET} values of the catalysts (see Table II); the resulting specific charges vs the hold time in H_2 at OCV are plotted in Fig. 11. It can be seen that at BOT (hold time = 0 h in Fig. 11), the specific charge of the IrO_2/TiO_2 (Umicore) catalyst ($\sim 110 \mu C cm^{-2}_{IrO_2}$) is ~ 2 -fold higher than that of the IrO_2 -550 ($\sim 65 \mu C cm^{-2}_{IrO_2}$) and of the IrO_2 -750-MH ($\sim 50 \mu C cm^{-2}_{IrO_2}$) catalysts. This is likely related to the presence of some hydrous $IrO(OH)_x$ surface species on the IrO_2/TiO_2 (Umicore) catalyst that was heat-treated at a lower temperature (~ 400 °C, based on the patent²⁵) than the other two catalysts, based on the observation that hydrous $IrO(OH)_x$ yields a higher specific charge than crystalline IrO_2 .^{19,40}

Since, according to Fig. 10c, the IrO_2 -750-MH catalyst is not being reduced to metallic Ir after 12 h hold time in H_2 (consistent with Fig. 8, light blue line), its specific charge is relatively constant over the course of the OCV experiment. On the other hand, the surfaces of the IrO_2/TiO_2 (Umicore) and the IrO_2 -550 catalysts are being (partially) reduced to metallic Ir, and since the metallic Ir surfaces have higher specific charge values than heat-treated IrO_2 surfaces,¹⁹ the specific charges of these catalysts increase substantially and appear to reach a nearly constant value at the end of the OCV experiments, indicating that the reduction reaction of the surface is nearly completed and might further proceed into the sub-surface layers of the catalyst particles. Under this assumption, one would expect that the surface of these catalysts is nearly completely reduced to metallic Ir, so that one would expect also similar specific charge values for the IrO_2/TiO_2 (Umicore) and the IrO_2 -550 after the 12 h OCV hold in H_2 , contrary to what is shown in Fig. 11: the specific charge of the IrO_2/TiO_2 (Umicore) catalyst ($\sim 670 \mu C cm^{-2}_{IrO_2}$) is ~ 2.3 -fold higher than that of the IrO_2 -550 catalyst ($\sim 285 \mu C cm^{-2}_{IrO_2}$), implying that the IrO_2 reduction reaction mechanism is fundamentally different for these two catalysts. This could be rationalized by two different mechanistic models:

1) For the IrO_2/TiO_2 (Umicore) catalyst, the reduction reaction might initiate homogeneously at a large number of nucleation sites on its surface, converting the outermost surface layer to metallic Ir. Since the metallic Ir surfaces have higher specific charge values than heat-treated IrO_2 surfaces,¹⁹ this would result in the observed higher specific charge values for this catalyst

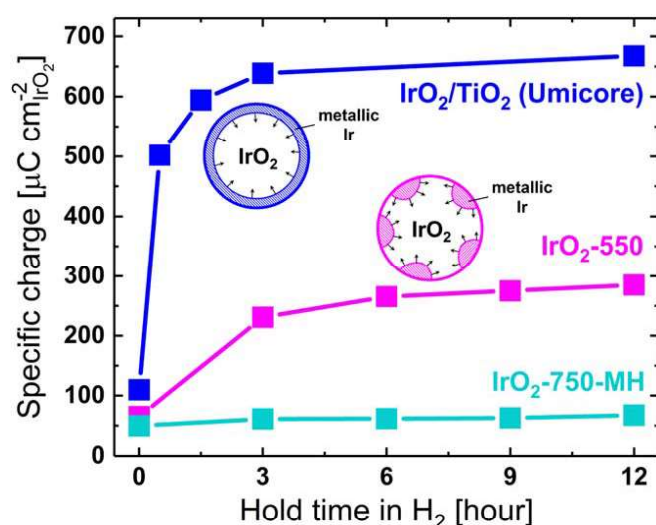


Figure 11. Specific charge values for the IrO_2/TiO_2 (Umicore), the IrO_2 -550, and the IrO_2 -750-MH catalysts vs the hold time in H_2 at OCV (at 80 °C/100% RH), estimated using the average of the anodic and the cathodic charge under the CVs recorded in Fig. 10 between 0.07–1.00 V_{RHE} , and normalizing them to the A_{BET} values of the catalysts (see Table II). The schemes represent the hypothesized, dominating reduction reaction mechanisms for the different catalysts: a *contracting sphere model* for the reduction of the IrO_2 phase in the IrO_2/TiO_2 (Umicore) catalyst (upper-blue scheme) in contrast to a *nucleation model* for the reduction of the IrO_2 -550 catalyst (lower-magenta scheme).

over the course of the OCV hold experiment (blue symbols in Fig. 11). While over time the reaction-front may proceed into the sub-surface layers of the catalyst particles, leading to a bulk reduction of the IrO_2 , this would no longer be traceable by voltammetry. This mechanism, which is referred to as the *contracting sphere model* in studies of the reduction kinetics of metal oxides in the literature,^{61–63} is depicted by the blue-colored scheme in Fig. 11.

2) On the other hand, for the IrO_2 -550 catalyst heat-treated at a higher temperature (thus forming a more crystalline surface phase), the reduction reaction might take place non-homogeneously at a lower number of nucleation sites on the catalyst surface, leading to the formation of metallic Ir grains, which then might grow into the sub-surface layers of the particle. As a result, the surface of the catalyst would be composed of both metallic Ir and non-reduced, crystalline IrO_2 domains. Since the crystalline IrO_2 surfaces have lower specific charge values than the metallic Ir surfaces,¹⁹ a smaller specific charge is expected at the initial stages of the reduction of this catalyst. In the literature, this mechanism is referred to as the *nucleation model*, and is depicted by the pink-colored scheme in Fig. 11.^{61–63}

One plausible explanation for the different reduction reaction mechanisms could be the structural differences between the two catalysts. As it was shown in the previous sections, a higher amount of a- IrO_x species is expected in the structure of an IrO_2 catalyst which is heat-treated at a lower temperature. Due to the lower heat treatment temperature of the IrO_2/TiO_2 (Umicore) catalyst (~ 400 °C, based on the patent²⁵) compared to that of the IrO_2 -550 catalyst, a higher amount of a- IrO_x species is expected for the former. Since a- IrO_x species is easily reducible by H_2 , it provides a high number of nucleation sites, thereby allowing for a homogeneous reduction of the IrO_2 phase on the surface of IrO_2/TiO_2 (Umicore) catalyst, which is described by the contracting sphere model. On the other hand, the lower amount of a- IrO_x species in the IrO_2 -550 catalyst that was heat-treated at a higher temperature provides a lower number of nucleation sites for the onset of the reduction reaction on the catalyst surface, which would favor the nucleation model as the dominating mechanism.

IrO₂ catalyst stability in a PEMFC anode upon SUSD-cycling.—Next, we investigate the stability of different IrO₂-based catalysts when a PEMFC is subjected to SUSD events, where the anode potential cycles between ~ 0 V_{RHE} and ~ 1.05 V_{RHE} due to the passage of H₂/air-fronts through the anode compartment, which in the case of Pt/C anode catalysts leads to an accelerated Pt dissolution during these voltage transients.²⁰ The observation that potential cycling between ~ 0 and ~ 1 V_{RHE} leads to a ~ 100 -fold higher transient dissolution rate of metallic Ir compared to heat-treated IrO₂ catalysts⁶⁴ therefore explains why the formation of metallic Ir in the near-surface layers of an IrO₂ anode co-catalyst in a PEMFC H₂ anode substantially compromises its stability during SUSD cycles.¹⁹ The concomitant dissolution of metallic Ir surfaces and the crossover of the dissolved Ir³⁺ species through the membrane to the cathode electrode was shown to lead to iridium deposition on the Pt/C cathode catalyst.¹⁹ Since the ORR activity of iridium is ~ 2 orders of magnitude less than that of platinum,^{65–68} the re-deposited crossover iridium can cause a substantial poisoning of the ORR activity of the Pt/C cathode catalyst.¹⁹ This phenomenon is analogous to the observations made in the context of Ru dissolution from PtRu alloy anode catalysts in direct methanol fuel cells or in PEMFCs operated with reformate, where the dissolved Ru species were shown to permeate through the membrane to the cathode and to deteriorate the ORR performance of the Pt/C cathode catalyst.^{69–72} As a proof-of-concept experiment to demonstrate that the transient dissolution of iridium during SUSD-cycling is indeed substantially suppressed when an irr-IrO₂ catalyst is used as anode co-catalysts, even after prolonged exposure to H₂ in a PEMFC anode, 500 SUSD cycles (at 35 °C, with H₂/air-front residence times of 0.02 s, see Experimental section) were performed after 12 h of the OCV experiment with the MEA with the IrO₂-750-MH catalyst (i.e., after the experiment shown in Fig. 10c). For comparison, the MEA with the IrO₂-550 catalyst was also subjected to the same SUSD test after the 12 h OCV experiment (Fig. 10b). It should be noted that these experiments only examine the stability of an irr-IrO₂ anode co-catalyst and that its effectiveness to mitigate cell reversal damages in a PEMFC must still be investigated by combining the reduction-resistant IrO₂-750-MH catalyst with a Pt/C HOR catalyst and performing cell reversal tests, which will be the focus of our future studies.

After the 500 SUSD cycles, anode CVs were recorded for the IrO₂-550 and the IrO₂-750-MH catalysts (light blue lines in Figs. 10b and 10c, respectively). A comparison of the CV of the IrO₂-550 catalyst after the 12 h OCV hold (i.e., just prior to the SUSD test) with that after 500 SUSD cycles (red vs light blue lines in Fig. 10b) clearly shows that the H_{UPD} features of metallic Ir between 0.07–0.35 V_{RHE} vanish after 500 SUSD cycles, which is due to the transformation of metallic Ir to an electrochemically-grown, highly-porous iridium oxy-hydroxide (further on referred to as e-IrO_x) upon the SUSD-induced anode potential cycles (between ~ 0 and ~ 1 V_{RHE}).^{20, 73, 74} On the other hand, the voltammetric features of the IrO₂-750-MH anode catalyst after 500 SUSD cycles are essentially identical with those after the preceding 12 h OCV hold (light blue vs red lines in Fig. 10c), indicating no substantial SUSD-induced changes of the catalyst surface.

Based on these findings, one would expect significant iridium dissolution and iridium cross-over to the cathode electrode for the IrO₂-550 catalyst upon SUSD-cycling, which could be probed by conducting cathode CVs of the SUSD-cycled MEAs. However, in order to record artefact-free CVs of the cathode electrodes, the anode electrodes which in this case serve as both counter electrode (CE) and reference electrode (RE) must be sufficiently active for the hydrogen oxidation/evolution reaction (HOR/HER), which is not the case for IrO₂ surfaces.^{75, 76} As this would result in undefined shifts of the CE and thus the RE potential while recording the cathode CVs, it was necessary to introduce an HOR/HER-active catalyst layer to the anode electrodes before recording the cathode CVs. To do this, the cells were disassembled prior to recording the cathode CVs, and the anode gas diffusion layers (GDLs) were replaced with gas diffusion

electrodes (GDEs). The latter contained a Pt/C catalyst layer that upon re-assembly faced the IrO₂ anode electrodes and thus served as highly HOR/HER-active CE and RE for recording the cathode CVs, as schematically shown in Fig. 12a.

Prior to discussing the cathode CVs of the aged MEAs, it is instrumental to briefly discuss the CV of the pristine Pt/C cathodes, using a freshly prepared MEA with the same cathode electrode (0.3 mg_{Pt} cm⁻²_{MEA}) and a Pt/C-based anode (0.05 mg_{Pt} cm⁻²_{MEA}), which is depicted by the black CVs shown in Figs. 12a and 12b. For the pristine Pt/C cathode, three distinct voltammetric features can be distinguished: (i) the H_{UPD} features of the metallic Pt surface between 0.07–0.35 V_{RHE}; (ii) the charge corresponding to the

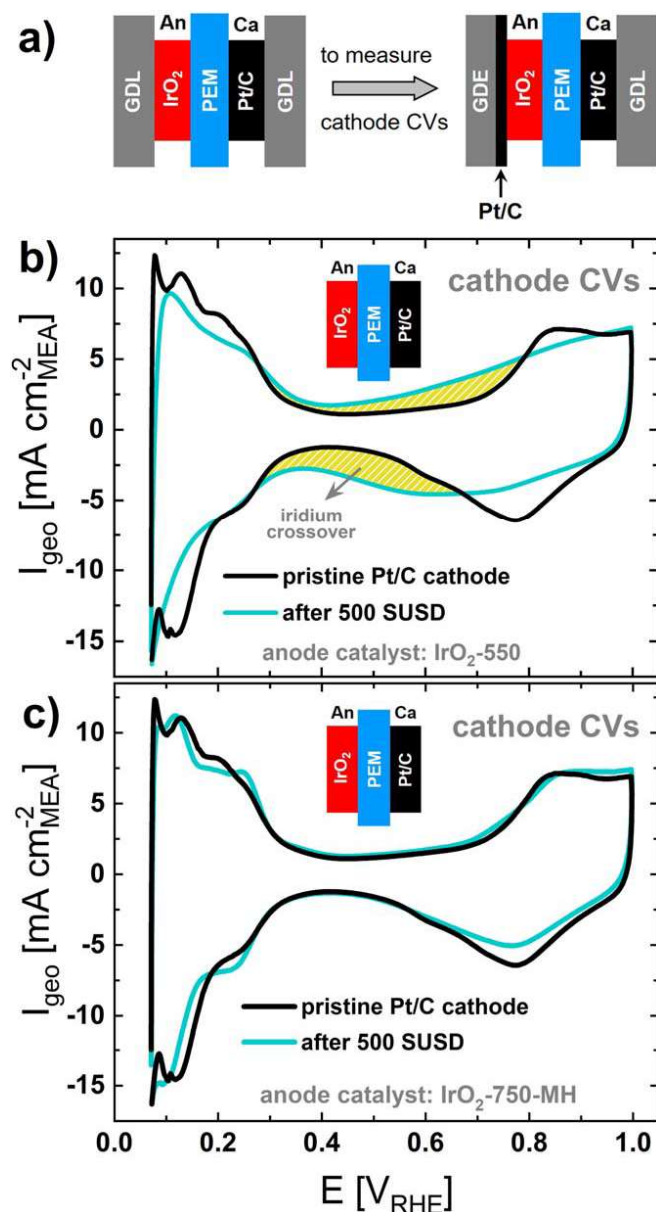


Figure 12. (a) Illustration of the replacement of the anode GDL with a Pt/C coated GDE (with 0.4 mg_{Pt} cm⁻²_{GDE}), which was done prior to recording the cathode CVs of the SUSD-cycled MEAs. The light blue CVs in panels b and c show cathode CVs after the 12 h OCV hold and the 500 SUSD cycles described in Fig. 10 for MEAs with a Pt/C cathode (0.3 mg_{Pt} cm⁻²_{MEA}) and with the following anode catalysts: (b) IrO₂-550 (2.2 mg_{Ir} cm⁻²_{MEA}); (c) IrO₂-750-MH (2.5 mg_{Ir} cm⁻²_{MEA}). As a reference, the black CVs show the cathode CV of a pristine Pt/C cathode (0.3 mg_{Pt} cm⁻²_{MEA}) in an MEA with a Pt/C anode (0.05 mg_{Pt} cm⁻²_{MEA}). The CVs were acquired between 0.07–1.00 V_{RHE} at 40 °C and ambient pressure with fully-humidified N₂ (anode) and 5 vol% H₂/Ar (cathode).

double-layer capacitance of the Pt and the carbon support particle surfaces between 0.35–0.55 V_{RHE} ; and, iii) the redox peaks associated with the formation and reduction of PtO between 0.55–1 V_{RHE} .⁷⁷ When comparing this to the cathode CV of the MEA with the IrO₂–550 anode catalyst after 500 SUSD cycles (light blue CV in Fig. 12b), there is a striking difference in the double-layer region, which exhibits a substantially larger charge for the SUSD-cycled MEA with the IrO₂–550 anode catalyst (highlighted by the yellow area in Fig. 12b). In view of the strong redox features of iridium surfaces in this potential region,^{59,78} such excess charge can only be ascribed to the deposition of iridium species on the Pt/C cathode catalyst, caused by the dissolution of metallic Ir from the IrO₂–550 anode catalyst surface during SUSD cycles and the concomitant cross-over of the dissolved Irⁿ⁺ species to the cathode electrode.

Contrary to the apparent iridium dissolution and cross-over to the cathode observed for the SUSD-cycled MEA with the IrO₂–550 anode catalyst, the cathode CV of the MEA with the IrO₂–750-MH anode catalyst after 500 SUSD cycles (light blue CV in Fig. 12c) is fairly similar to the CV of the pristine Pt/C cathode (black CV) and does not show any increase of the capacitive currents in the double-layer region, indicating that there is no significant amount of iridium cross-over to the cathode electrode after 500 SUSD cycles. This is a direct evidence that iridium dissolution from a highly reduction-resistant IrO₂ anode co-catalyst upon SUSD cycling in a PEMFC anode is significantly lower than that of a more reducible IrO₂ catalyst, where metallic Ir is formed on the catalyst surface under the conditions of a PEMFC H₂ anode. As a last note on the cathode CVs, one needs to mention that the H_{UPD} and the platinum oxide redox features change only very little over the 500 SUSD cycles (Fig. 12), indicating a surprisingly small extent of platinum dissolution and carbon support oxidation. This is due to the low ORR activity of the iridium-based anode catalysts in these MEAs, which significantly suppresses the excursion to high potentials in the cathode electrode during the SUSD cycles, minimizing the SUSD-induced degradation of the Pt/C cathode catalyst.⁶⁸

To further examine the extent of the SUSD-induced iridium cross-over and the chemical nature of the iridium deposited on the Pt/C cathode catalyst, the MEAs were harvested after 500 SUSD cycles and examined by XPS. Figure 13 shows the Pt 4f and the Ir 4f spectra of the pristine and SUSD-cycled cathode electrodes. All the spectra exhibit Pt 4f doublets with the Pt 4f 7/2 peaks centering at ~71.7 eV, close to the binding energy of metallic Pt (~71.2 eV⁷⁹). No Ir 4f signal is detected in the spectrum of the pristine Pt/C cathode electrode in Fig. 13a, consistent with the fact that the MEA only contains Pt/C catalysts. However, as shown in Fig. 13b, a strong Ir 4f signal is detected for the cathode electrode of the SUSD-cycled MEA with the IrO₂–550 anode catalyst, indicating iridium dissolution from the anode electrode during the SUSD experiment and iridium cross-over to the cathode electrode. Such a strong Ir 4f signal in the cathode electrode is consistent with the large capacitive currents in the double-layer region observed in the cathode CV taken from this MEA compared to those of the pristine Pt/C cathode (the area marked with yellow color in Fig. 12b).

Under the following simplifying assumptions and considerations, the amount of crossed-over iridium can be estimated from the integrated areas of the 4f peaks of Pt and Ir in Fig. 13b: (i) Owing to the small Pt particle size of the Vulcan carbon-supported Pt catalyst at the cathode (~3 nm²⁹) and the similar value of the inelastic mean free path of the Pt and Ir 4f photoelectrons of ~3 nm (based on a kinetic photoelectron energy of ~1.4 keV and the tabulation by Seah and Dench⁸⁰), all Pt atoms of a sampled Pt nanoparticle will be measured at roughly equal intensity. (ii) Iridium deposition on the cathode will likely occur on the Pt nanoparticle surface due to the likely preferential nucleation/adsorption on a metal surface. (iii) The film thickness of iridium deposited on the Pt particles will be not more than 1 nm, so that there is no significant shielding of the Pt 4f photoelectrons. (iv) The Pt and Ir 4f signals are very similar in binding energy, so that their detection efficiency in the analyzer is essentially identical. For these assumptions/considerations, the atomic ratio of Pt

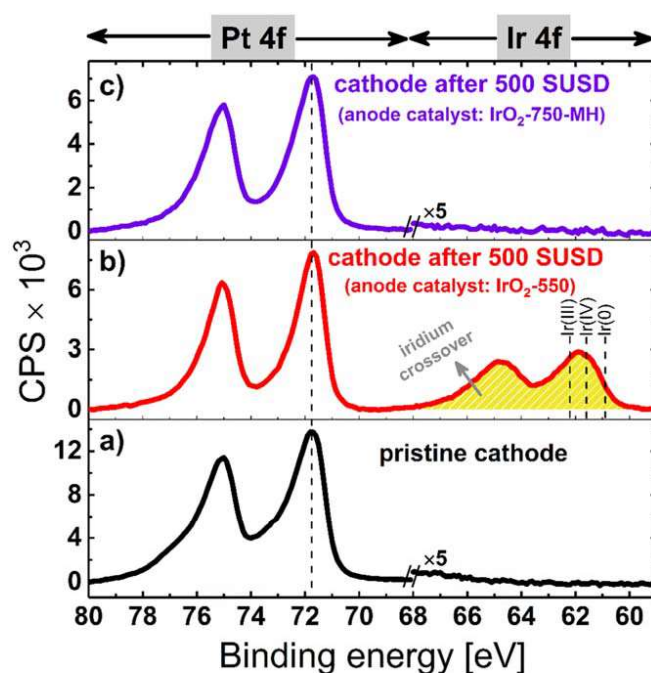


Figure 13. Shirley background-corrected XPS Pt 4f and Ir 4f spectra of different cathode electrodes (see Fig. 12) acquired for: (a) the pristine MEA; (b) the MEA with the IrO₂–550 anode catalyst after 500 SUSD cycles; and, (c) the MEA with the IrO₂–750-MH anode catalyst after 500 SUSD cycles. The vertical dashed line in the Pt 4f region marks the position of the Pt 4f 7/2 binding energy in all the spectra. The vertical dashed lines in the Ir 4f region in panel b mark the binding energies of Ir(0), Ir(IV), and Ir(III) at 60.9, 61.6, and 62.2 eV, respectively.^{74,82} The counts per second (CPS) values in the Ir 4f regions in panels a and c are multiplied by a factor of 5 in order to more clearly demonstrate the absence of Ir 4f signals in the cathode electrodes of the pristine MEA and of the SUSD-cycled MEA with the IrO₂–750-MH anode catalyst.

to Ir ($n_{\text{Pt}}/n_{\text{Ir}}$) can be estimated from the ratio of the integrated Pt and Ir 4f 7/2 + 5/2 areas ($A_{\text{Pt}}/A_{\text{Ir}}$) divided by the ratio of the Scofield factors for the 4f 7/2 + 5/2 photoelectrons ($s_{\text{Pt}}/s_{\text{Ir}} = 15.5/13.9 = 1.12$ ⁸¹). Using the value of $A_{\text{Pt}}/A_{\text{Ir}} = 2$ determined from Fig. 13b, this yields a value of $n_{\text{Pt}}/n_{\text{Ir}} \approx 1.8/1$ for the cathode electrode of the MEA with the IrO₂–550 anode catalyst after 500 SUSD cycles. Based on the cathode Pt loading of 0.3 mg_{Pt} cm⁻²_{MEA}, this would correspond to an amount of crossed-over iridium of ~0.17 mg_{Ir} cm⁻²_{MEA}, which is ~55% of the Pt loading (if deposited only on the Pt nanoparticles, this would correspond to an iridium coverage of ~2 ML or a film thickness of <1 nm), so that assumption iii) above should be satisfied. When referenced to the iridium loading of the IrO₂–550 anode of 2.2 mg_{Ir} cm⁻²_{MEA}, this would correspond to a total cross-over of ~7.7% of the iridium in the anode electrode to the cathode electrode over the 500 SUSD cycles. Regarding the chemical state of the crossed-over iridium, the ex situ XPS data in Fig. 13b suggest the predominant presence of Ir(IV) and perhaps Ir(III) species (see vertical dashed lines in Fig. 13b), likely corresponding to the deposition of hydrous iridium oxide, which is a reasonable assumption considering the air cathode is at potentials of roughly >0.9 V during SUSD events.

On the other hand, for the SUSD-cycled cathode electrode of the MEA with the IrO₂–750-MH anode catalyst no Ir 4f signals can be detected by XPS (see Fig. 13c), from which it can be concluded that the amount of crossed-over iridium is lower by at least a factor of 25 compared to that for the MEA with the IrO₂–550 anode catalyst (based on comparing the Ir 4f signals in Figs. 13b and 13c, considering the high signal-to-noise ratio even at the 5-fold magnification of the Ir 4f signals in Fig. 13c), which would correspond to a rather negligible total cross-over of <0.3% of the iridium in the anode electrode to the cathode electrode over the 500 SUSD cycles. This is in line with the observation of the perfect

overlap of the cathode CV of the MEA with the IrO₂-750-MH anode catalyst in the double-layer region with that of the pristine Pt/C cathode (see Fig. 12c), concluding that iridium dissolution from the surface of the IrO₂-750-MH anode catalyst is very low or zero even after 500 SUSD cycles, so that it can be considered to be an irr-IrO₂ anode co-catalyst.

It should be noted that the anode iridium loadings used in this proof-of-concept SUSD experiment ($\sim 2 \text{ mg}_{\text{Ir}} \text{ cm}^{-2}_{\text{MEA}}$) is ~ 40 times higher than the conventionally used iridium loadings for an anode co-catalyst ($\sim 0.05 \text{ mg}_{\text{Ir}} \text{ cm}^{-2}_{\text{MEA}}$)^{17,58}. This was done to magnify the effect of iridium dissolution from the surface of even an irr-IrO₂ catalyst during SUSD-cycling and to enable a more accurate detection of crossed-over iridium in the cathode electrode. Based on the results of this section, it can be safely concluded that when using an irr-IrO₂ as an anode co-catalyst at a conventional loading of $\sim 0.05 \text{ mg}_{\text{Ir}} \text{ cm}^{-2}_{\text{MEA}}$ in combination with a Pt/C-based HOR catalyst in a PEMFC, the dissolution of iridium during SUSD-cycling as well as other undesired conditions (e.g., cell reversal events, with anode potential transients between ~ 0 and $\sim 1.5 \text{ V}_{\text{RHE}}$) should be negligible. This is particularly true for the effect of crossed-over iridium on the ORR activity of the cathode, since for an expected similar cross-over rate, the absolute amount of crossed-over iridium would scale with the loading of the anode co-catalyst. However, the effectiveness of an irr-IrO₂ catalyst on mitigating cell reversal damages in a PEMFC must still be investigated by combining the reduction-resistant IrO₂-750-MH catalyst with a Pt/C HOR catalyst and performing cell reversal tests, which will be the focus of our future studies.

Conclusions

In this study, a novel procedure for the preparation of irreducible IrO₂ (irr-IrO₂) anode co-catalysts for mitigating cell voltage reversal damages in PEMFCs is introduced. It consists of three industrially scalable steps: (i) a heat treatment step at high temperatures ($650^\circ\text{C} \leq T \leq 1000^\circ\text{C}$) under air to achieve a fully crystalline IrO₂ structure; (ii) a subsequent ball milling step to attain a specific surface area of $\sim 25 \text{ m}^2 \text{ g}^{-1}$; and, (iii) a final short heat treatment step at 400°C under air to retrieve its reduction resistance under hydrogen that is partially compromised during the ball milling step, without compromising the high specific surface area obtained in the same step.

Thermogravimetric analysis (TGA) under a flow of 3.3 vol% H₂/Ar is used to probe the reduction resistance of a variety of IrO₂-based catalysts, showing that conventionally prepared IrO₂ catalysts with heat-treatments up to only $\sim 400^\circ\text{C}$ are being reduced at substantially lower temperatures than the catalysts heat-treated at $\geq 650^\circ\text{C}$ (at comparable specific surface areas). The latter catalysts show essentially no reduction in isothermal TGA experiments with 3.3 vol% H₂/Ar at 80°C over 12 h; estimates based on isothermal TGA experiments at 120°C suggest a reduction stability over the order of 5000 h at 80°C for an IrO₂ catalyst heat-treated at 750°C ,

suggesting that it might be an irreducible IrO₂ catalyst (“irr-IrO₂”) that could serve as anode co-catalyst in PEM fuel cell (PEMFC).

The observed reduction resistance improvement of IrO₂ catalysts heat-treated at $\geq 650^\circ\text{C}$ is due to the dominance of highly crystalline IrO₂ species (“c-IrO₂”) in their structure, indicated by a very low crystal micro-strain as determined by X-ray powder diffraction (XPD) analysis. This is corroborated by an evaluation of the activation energy for reduction under hydrogen (via TGA analysis), which is ~ 1.5 -fold higher for a catalyst heat-treated at 750°C compared to catalysts heat-treated at the conventional temperature of 400°C .

Based on rotating disk electrode (RDE) measurements, the mass activity of the irr-IrO₂ catalysts towards the oxygen evolution reaction (OER) is ~ 4 -fold lower than that of conventionally prepared IrO₂ catalysts heat-treated at $\leq 400^\circ\text{C}$, as the latter contain hydrous iridium oxide surface species that have a higher OER activity than crystalline IrO₂.

It could also be demonstrated that the here prepared irr-IrO₂ catalysts do not get reduced in a PEMFC H₂ anode at $80^\circ\text{C}/100\%$ RH over extended time, and that their high reduction resistance is reflected by the observation that start-up/shut-down (SUSD) cycling of MEAs with the irr-IrO₂ anode catalysts does not result in iridium dissolution and the associated iridium cross-over to the cathode electrode, contrary to what is observed for conventionally prepared IrO₂ catalysts.

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Appendix

This section provides supplementary data regarding the IrO₂ particles size distribution of two differently prepared IrO₂ materials that have very similar A_{BET} values, investigated by TEM (see Fig. A-1). Furthermore, the TGA temperature ramp experiments at varying heating rates are shown for the samples for which the activation energy for their reduction under H₂ atmosphere was determined (see Fig. A-2). The long-term TGA isothermal experiment for the reduction of IrO₂-750-MH at 120°C is also shown to estimate the rate of the reduction of this material at 80°C using the Arrhenius equation and the rate of its reduction at 120°C (see Fig. A-3).

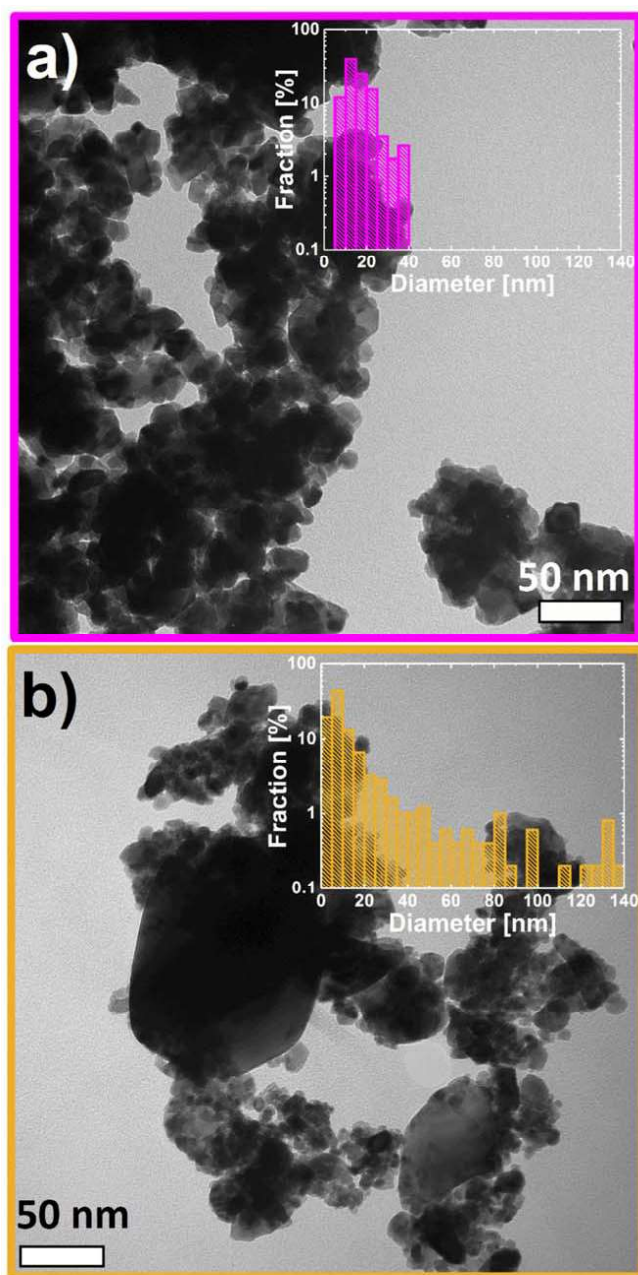


Figure A.1. Exemplary TEM micrographs for: (a) IrO₂-550 and (b) IrO₂-1000-MH. The insets show the respective particle size distributions, which were constructed from counting individual particles (~ 120 and ~ 500 particles for the data in panel a and b, respectively). Although both samples have similar A_{BET} and d_{BET} values of $\sim 23 \text{ m}^2 \text{ g}^{-1}$ and $\sim 22 \text{ nm}$, respectively (see Table II), the IrO₂-1000-MH material (panel b) clearly has a more inhomogeneous and broader particle size distribution than the IrO₂-550 material (panel a).

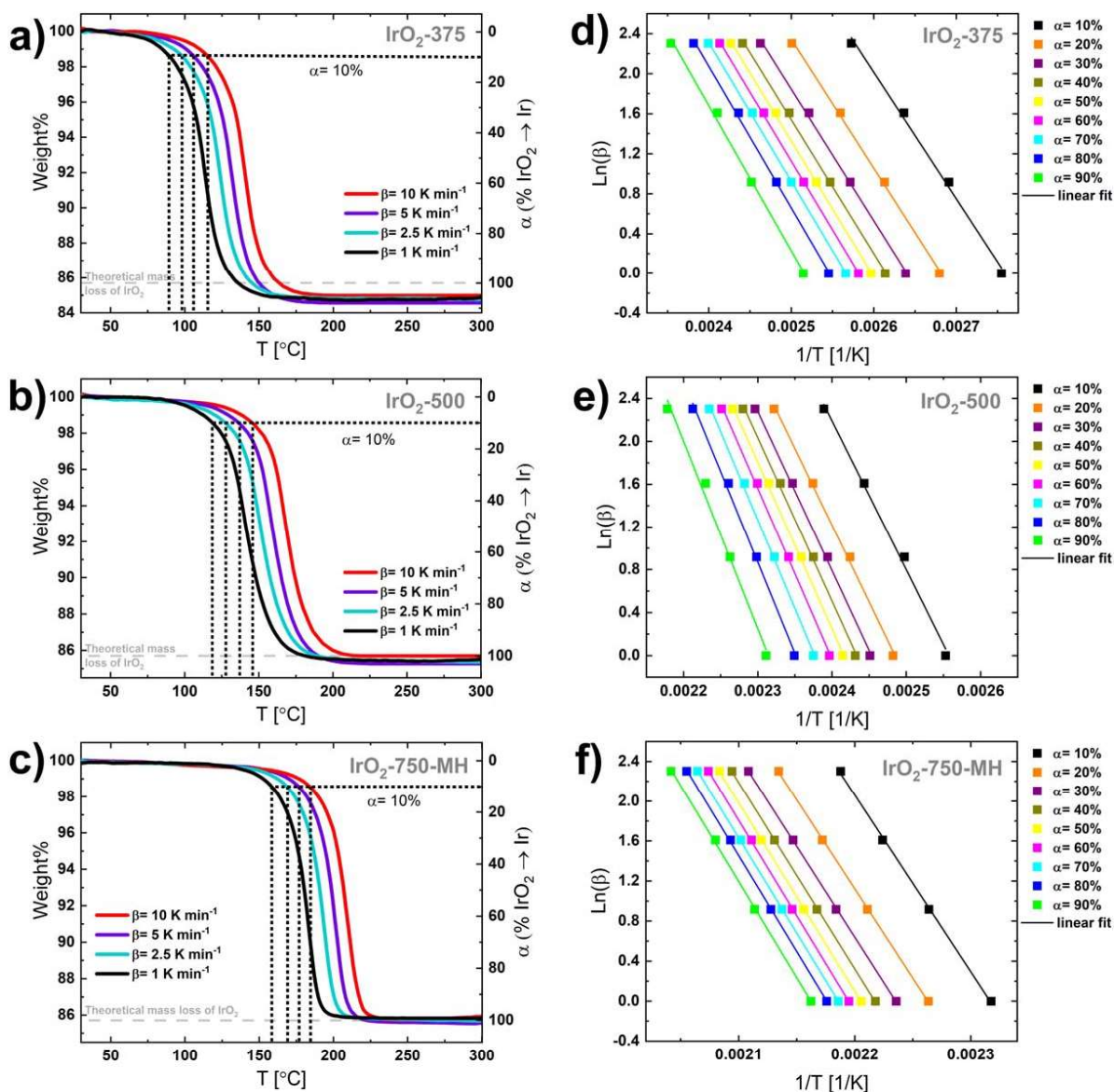


Figure A-2. TGA temperature ramp experiments under 3.3 vol% H₂/Ar at 1, 2.5, 5, and 10 K min⁻¹ (following the drying/cleaning step; see experimental section) with: (a) IrO₂-375, (b) IrO₂-500, and (c) IrO₂-750-MH. The left y-axes represent the weight% mass loss of the samples vs temperature, while the right y-axes depict the fraction of the IrO₂ that is reduced to metallic Ir (α). The gray horizontal dashed lines mark the theoretical mass loss (14.3 wt%) of the samples upon the complete reduction of IrO₂ to metallic Ir by H₂ (see Eq. 2 in the Experimental section). The horizontal and vertical dotted black lines exemplarily mark the data that are used for the analysis in panels (d)–(f) for a reaction extent of $\alpha = 10\%$. (d)–(f) Linear regression of $\ln(\beta)$ vs $1/T$ for a given α value (ranging between 10%–90%) extracted from panels (a)–(c). The differently colored squares represent the data at different α values, and the solid lines are the linear regression fits of the data for a given α value.

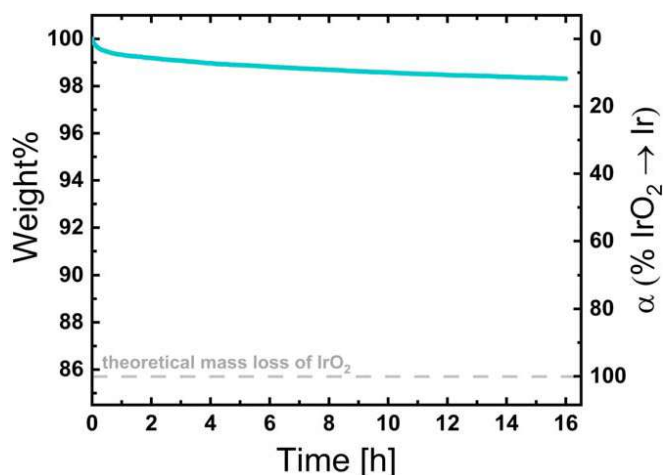


Figure A-3. Long-term isothermal TGA experiment on the reduction of the IrO₂-750-MH catalyst in 3.3 vol% H₂/Ar at 120 °C (following the drying/cleaning step; see Experimental section). The left y-axis represents the weight% mass loss of the catalyst vs temperature, while the right y-axis depicts the fraction of the IrO₂ that is reduced to metallic Ir (α). The gray horizontal dashed line marks the theoretical mass loss (14.3 wt%) of the catalyst upon the complete reduction of IrO₂ to metallic Ir by H₂ (see Eq. 2 in the Experimental section).

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3.5 Synthesis of Reduction Resistant IrO₂- and RuO₂-based Solid-Solution Phases

This section presents the manuscript “A Solid Solution Route to Prepare Irreducible IrO₂ and RuO₂ Anode OER Co-catalysts for PEM Fuel Cell Voltage Reversal Mitigation” that will be submitted to the *Journal of The Electrochemical Society* in the near future.¹²¹ Under the discoveries within the scope of research in this section, the rights of development of such reduction resistant IrO₂- and RuO₂-based catalysts are protected in form of a published patent application.¹⁵³

Addition of an OER co-catalyst such as IrO₂ and RuO₂ to the anode electrode of PEMFCs is one of the strategies to mitigate cell reversal damages.^{34, 36, 37} It was shown for an IrO₂ anode co-catalyst in section 3.3 that despite the high OER activity, the stability of the co-catalyst under the normal and transient operating conditions of a PEMFC must be considered.⁵⁶ The near-surface layer(s) of IrO₂ can be reduced to metallic Ir upon exposure to H₂ in a PEMFC anode. Metallic Ir formed on the catalyst surface was shown to dissolve during SUSDC cycles and to cause degradation of both the Pt/C cathode catalyst and the IrO₂ anode co-catalyst. In this study, it is shown that similar to IrO₂ catalysts, the surface of RuO₂ catalysts is also reduced to metallic Ru upon exposure to H₂ at the operational temperatures of PEMFCs. Since the dissolution rate of metallic Ru surfaces during potential transients is reported to be significantly higher than that of heat-treated RuO₂,⁵⁷ it is expected that the metallic Ru formed on the RuO₂ co-catalyst surface would even more readily dissolve during anode potential transients caused by SUSDC cycles. Again, this would lead to the degradation of both the Pt/C cathode catalyst and the RuO₂ anode co-catalyst, analogous to the mechanism shown for IrO₂ in section 3.3.

These degradation mechanisms can be prevented if RuO₂ and IrO₂ anode co-catalysts are irreducible in the PEMFC anode environment. In this study, an unprecedented stabilization strategy is introduced to prepare IrO₂ and RuO₂ catalysts which are irreducible in the PEMFC anode environment. Such irreducible IrO₂- and RuO₂-based catalysts are prepared by forming a

solid-solution phase of these PGM-oxides with other transition metal oxides, namely TiO₂ or Nb₂O₅. The preparation of the solid-solution phase catalysts is based on a high-temperature heat treatment step to form the solid-solution phase, followed by a ball-milling and a post-annealing step to prepare catalyst powders with specific surface areas of > 25 m² g⁻¹. TGA experiments in 3.3% H₂/Ar demonstrated the higher reduction stability of the solid-solution phase catalysts compared to the pure RuO₂ or IrO₂ catalysts prepared by the same route. Such reduction stability improvement is attributed to the stabilizing effect of TiO₂ and Nb₂O₅ in the solid-solution phases, as these transition metal oxides are not easily reduced by H₂ at temperatures < 800 °C.^{142, 143, 154}

As mentioned in section 1.3.2.2, due to the low thermodynamic stability of Ru at the high potentials during oxygen evolution, the rate of ruthenium dissolution and corrosion is unacceptably high and Ru or RuO₂ is typically not considered as a viable OER catalyst in a PEMWE. In order to investigate if the RuO₂-based solid-solution phase catalysts prepared in this study have a higher stability than RuO₂ during oxygen evolution, the catalysts were incorporated into MEAs and stability measurements were performed in a PEMWE. However, these measurements showed that the RuO₂-TiO₂ solid solution catalyst does not have an improved long-term stability compared to RuO₂ catalyst in a PEMWE anode, and further strategies are required to stabilize RuO₂ catalysts for practical OER applications.

Author contributions

M.F.T. proposed the idea of IrO₂ and RuO₂ stabilization by synthesizing solid-solution phases and prepared all the catalysts. M.F.T. and C.S. fabricated the MEAs and performed the electrochemical testing in a PEMWE; M.F.T. analyzed the experimental test results of the MEAs. M.F.T. performed the XPD measurements and F.F. performed the XPD data analysis. M.F.T. performed all the other physical/chemical and electrochemical measurements and analyzed the data. M.F.T. wrote the manuscript and H.A.G., F.F., H.E., and C.S. edited it. All authors discussed the experimental results and revised the manuscript.

A Solid Solution Route to Prepare Irreducible RuO₂ and IrO₂ Anode OER Co-catalysts for PEM Fuel Cell Voltage Reversal Mitigation

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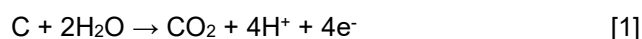
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Abstract

RuO₂ and IrO₂ have been commonly used as anode co-catalysts for mitigating cell voltage reversal damages in proton exchange membrane fuel cells (PEMFCs). We have shown in our previous study that conventionally prepared IrO₂ catalysts are chemically reduced by H₂ to metallic Ir in the normal operation conditions of PEMFC H₂ anodes. The metallic Ir formed on the surface of IrO₂ catalyst can dissolve during start-up/shut-down (SUSD) cycles, and the dissolved Irⁿ⁺ can permeate through the membrane from the anode electrode to the cathode electrode, poisoning the oxygen reduction reaction (ORR) activity of the Pt/C cathode catalyst. In this study, it is shown that similar to IrO₂ catalysts, the surface of RuO₂ catalysts is also reduced to metallic Ru upon exposure to H₂ at operational temperatures of PEMFCs. Since the reduction of RuO₂ anode co-catalysts to metallic Ru would lead to the same degradation mechanism as the one for IrO₂ anode co-catalysts, an unprecedented approach is introduced for the preparation of reduction resistant RuO₂- and IrO₂-based anode co-catalysts by forming a solid solution phase between RuO₂ or IrO₂ and Nb₂O₅ or TiO₂. The advantages and limitations of using this new class of anode co-catalysts is discussed.

Introduction

One of the major challenges for the widespread commercialization of proton exchange membrane fuel cell (PEMFC) electric vehicles is achieving the long-term durability targets.¹⁻³ The cell voltage reversal that can occur during the transient operation of a PEMFC on account of a temporary H₂ under-supply to one or several cells in a fuel cell stack has recently received a great attention among several degradation phenomena of membrane electrode assemblies (MEAs).⁴⁻⁷ During cell reversal events, the anode potential increases (>> 1 V vs. the reversible hydrogen electrode (RHE) potential) causing a severe oxidation of the carbon support of the Pt/C anode catalyst:



The carbon oxidation reaction (COR) based on Eq. 1 is kinetically fast at potentials > 0.9 V_{RHE}; such high

anode potentials occur during cell reversal events and lead to the collapse of the anode catalyst layer and to cell failure.⁸⁻¹⁰ A common strategy to mitigate the damages of cell reversal is the addition of a co-catalyst to the anode catalyst layer, which catalyzes the oxygen evolution reaction (OER), so that the non-destructive OER rather than the destructive COR takes place. IrO₂ and RuO₂ are widely investigated as OER catalysts in acidic media and they are commonly used as anode OER co-catalysts to mitigate cell reversal damages in PEMFCs.¹¹⁻¹⁵

The OER activity of an anode co-catalyst is a major criterion in screening different anode co-catalysts in the literature. The high OER activity of an anode co-catalyst lowers the onset potential of OER and prevents the anode potential from reaching high values during cell reversal, and thus substantially reduces the extent of COR at the anode electrode.¹⁴ However, we have recently shown that the stability of

an IrO₂ anode co-catalyst under the normal operation conditions of a PEMFC anode is another major criterion concerning the long-term durability of MEAs.¹⁶ Our findings showed that the near-surface layer(s) of heat treated IrO₂ anode co-catalysts can be completely reduced to metallic Ir upon exposure to H₂ under the normal operating conditions of a PEMFC anode. The formation of metallic Ir on the surface of the catalyst can improve its OER activity due to the higher intrinsic OER activity of metallic Ir surfaces than the heat treated IrO₂ surfaces. Nevertheless, such alteration of the near surface layer(s) of IrO₂ anode co-catalyst compromises its stability during anode potential cycling between ~ 0 and ~ 1 V_{RHE} caused by H₂/air_{anode} front passage during start-up/shut-down (SUSD) events. It was shown that the dissolution of metallic Ir and crossover of the dissolved Irⁿ⁺ species through membrane to the cathode electrode during SUSD events cause iridium contamination of the Pt/C cathode catalyst, which deteriorate the oxygen reduction reaction (ORR) activity of Pt and results in a significant performance loss during the normal operation of the fuel cell. SUSD transients also cause an OER activity loss of the anode co-catalyst, which was shown to be due to: i) iridium dissolution and loss from the anode electrode; and ii) redeposition of Pt dissolved from the anode hydrogen oxidation reaction (HOR) catalyst onto the reduced IrO₂ anode co-catalyst, blocking its OER active sites. Since the origin of such degradation mechanism is the chemical reduction of typically synthesized IrO₂ anode co-catalysts in a PEMFC anode, development of an IrO₂ anode co-catalyst which is not reduced in PEMFC anode conditions is required.

In a following study, we introduced an unprecedented approach to prepare such irreducible IrO₂ (irr-IrO₂) catalysts based on an industrially scalable procedure consisting of a high-temperature (650-1000 °C) heat treatment step followed by a ball-milling and a post annealing steps.¹⁷ Thermogravimetric analysis (TGA) data in 3.3% H₂/Ar showed that the formation of metallic Ir is hindered in the near-surface layer(s) of such irr-IrO₂ catalysts due to their intrinsic structural

distinctions from the typically synthesized IrO₂ reported in the literature. This higher reduction resistance was reflected by the observation that SUSD cycling of MEAs with the irr-IrO₂ as anode catalyst did not result in iridium dissolution and the associated iridium crossover to the cathode electrode. In this study, it is shown that similar to the typically employed IrO₂ catalysts, the surface of heat treated RuO₂ catalysts is also reduced to metallic Ru upon exposure to H₂ at operational temperatures of PEMFCs. As the dissolution rate of metallic Ru surfaces during potential transients is reported to be significantly higher than that of heat treated RuO₂ surfaces,¹⁸ it is expected that the metallic Ru formed on the RuO₂ anode co-catalyst surface would dissolve during anode potential transients caused by SUSD cycles, causing the same degradation phenomena as the one mentioned above for the IrO₂ anode co-catalysts. We introduce an unprecedented stabilization strategy to improve reduction resistance of RuO₂ and IrO₂ catalysts in PEMFC anode environment. Such reduction-resistant IrO₂ and RuO₂-based catalysts are prepared by forming a solid solution phase of these platinum group metal (PGM)-oxides with other transition metal oxides which have the following properties: i) irreducible by H₂ at operational temperatures of PEMFCs (~80 °C); and ii) stable in acidic media (pH ≈ 0-1) at the operational potentials of PEMFC anode, either during normal operating conditions, where the anode potential is at ~ 0 V_{RHE}, or at the high anode potentials (≥ 1 V_{RHE}) that occur during cell reversal and SUSD transients. TiO₂ and Nb₂O₅ are two suitable candidates for this application owing to their high thermodynamic stability at a wide potential range in acidic media^{19, 20} and their high reduction resistance in H₂-containing atmospheres at T < 800 °C.²¹⁻²³ The solid solution phases of IrO₂ or RuO₂ with Nb₂O₅ or TiO₂ are formed at high temperatures, then a ball-milling and a post annealing steps are followed to prepare solid solution catalysts with specific surface area of > 25 m² g⁻¹. The high reduction resistance of the solid solution catalysts is attributed to the stabilization effect of TiO₂ and Nb₂O₅ in the solid solution phases and a different

reduction reaction mechanism of these catalysts compared to the pure RuO_2 and IrO_2 catalysts. Due to the low thermodynamic stability of ruthenium at high potentials during OER, the rate of its dissolution and corrosion is unacceptably high and Ru or RuO_2 is typically not considered as a stable OER catalyst.^{24, 25} In order to further investigate whether the RuO_2 -based solid solution catalysts prepared in this study have higher stability than RuO_2 at high potentials during OER, electrochemical stability measurements are performed using MEAs in a PEM water electrolyzer (PEMWE).

Experimental

Stabilization procedure of RuO_2 and IrO_2 by solid solution approach.— Figure 1 shows the thermodynamic phase diagrams of TiO_2 - RuO_2 and TiO_2 - IrO_2 systems in air, reprinted with modification from K.T. Jacob et al.²⁶ and from C.L. McDaniel et al.²⁷, respectively. There are solid solution phases at each end of the phase diagrams and the solubility of the metal oxides increases by increasing the temperature, until the thermal decomposition of RuO_2 and IrO_2 to metallic Ru and Ir take place in the solid solutions at 1425 °C and 1040 °C, respectively. The RuO_2 -rich and TiO_2 -rich solid solution phases are denoted as ssTi-RuO_x and ssRu-TiO_x , respectively in Figure 1a. By the same denomination style, the IrO_2 -rich and TiO_2 -rich solid solution phases are denoted as ssTi-IrO_x and ssIr-TiO_x , respectively in Figure 1b. Since the aim of this study is producing solid solution catalysts with high OER activity, the RuO_2 - and IrO_2 -rich solid solution phases (i.e., ssTi-RuO_x and ssTi-IrO_x) are of the special interest in this study and the prepared samples are mainly composed of these phases. It should be noted that the solid solution phases prepared at high temperatures are not equilibrium phases at room temperature, as the metal oxides solubility decreases by decreasing the temperature based on the phase diagrams in Figure 1. As will be shown in the following, the samples are cooled down quickly in air (so-called air quench) after solid solution formation at the high temperatures in order to prevent

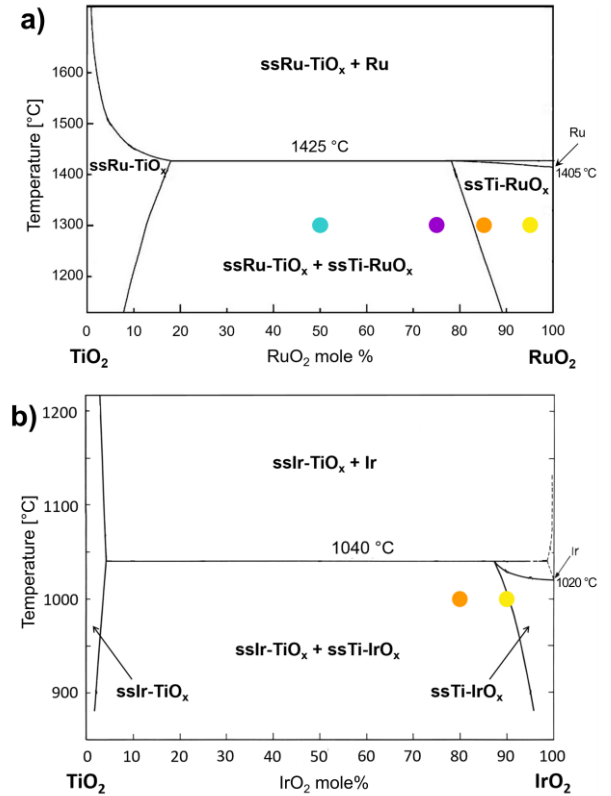


Figure 1. Thermodynamic equilibrium phase diagrams of a) TiO_2 - RuO_2 and b) TiO_2 - IrO_2 systems in air. The TiO_2 -rich and RuO_2 -rich solid solution phases are denoted as ssRu-TiO_x and ssTi-RuO_x , respectively in a) and the TiO_2 -rich and IrO_2 -rich solid solution phases are denoted as ssIr-TiO_x and ssTi-IrO_x , respectively in b). The dots mark the composition and the heat treatment temperature selected for the samples in this study. Reprinted with modification from K.T. Jacob et al.²⁶ with permission from Springer Nature and from C.L. McDaniel et al.²⁷ with permission from Journal of Research of NIST.

phase segregation upon cooling. We are not aware of any reported phase diagram for RuO_2 - Nb_2O_5 system and the sample compositions in this system are designed to target a possible RuO_2 -rich solid solution phase (ssNb-RuO_x) and the heat treatment for these samples are performed at the same temperature as the TiO_2 - RuO_2 samples (see below).

Table 1 summarizes the composition of the samples prepared in this study. Following the wt.% of the metal oxides of the samples in Table 1, a desired amount of TiO_2 (titanium(IV) oxide, rutile, 99.9 %; Alfa Aesar) or Nb_2O_5 (niobium(V) oxide, 99.95 %; Alfa Aesar) was weighted and added to the already weighted RuO_2

(ruthenium(IV) oxide, anhydrous, 99.9 %; Alfa Aesar) or IrO₂ in a mortar. Then, the resulting powder was hand mixed with a disposable plastic spatula and was added to a 500 ml round bottom flask containing 200 ml DI water (15MΩcm, E-POD, Merck Millipore KGaA) and was dispersed by ultrasonication for 30 min. The resulting dispersion was stirred overnight at room temperature and then centrifuged and dried at 70 °C. After the initial mixing of the pristine metal oxide powders as described above, the preparation of the solid solution catalysts is comprised of three steps as schematically shown in Figure 2: i) a high temperature heat treatment for the formation of solid solutions; ii) ball milling; and iii) a low temperature heat treatment to recover the reduction stability of the samples. In step i), the formation of RuO₂-TiO₂ and IrO₂-TiO₂ solid solutions were carried out at 1300 °C and 1000 °C, respectively (see the dots in the phase diagrams in Figure 1 marking the samples composition and heat treatment temperature). The formation of RuO₂-Nb₂O₅ solid solutions was also carried out at 1300 °C, similar to RuO₂-TiO₂ solid solutions. The heat treatments were performed in synthetic air atmosphere (0.5-1 L min⁻¹) in a tube furnace, where a quartz glass tube and an alumina tube were used for the heat treatment

at 1000 °C and 1300 °C, respectively. It is reported in the literature that volatile RuO₃ and RuO₄ or IrO₃ begin to form when RuO₂ or IrO₂ is heated in air at temperatures > 800 °C.²⁸⁻³⁰ The evaporation and loss of RuO₂ and IrO₂ in the samples upon extended heating at high temperatures would eventually result in the change of samples composition. To suppress evaporation of RuO₂ in RuO₂-TiO₂ mixtures at high temperatures, it is proposed in the literature to form a gas buffer zone around the samples during heat treatment. Such gas buffer zone is created by burying RuO₂-TiO₂ mixtures in sacrificial RuO₂ powder, where most of the volatilization during heat treatment occurs from the sacrificial powder with no significant RuO₂ loss from the sample.^{31, 32} In this case, the samples are compressed into pellets for better handling and easier separation of the samples from the sacrificial powder at the end of the experiments. Following these recommendations, a sacrificial RuO₂ or IrO₂ powder was used during the high temperature heat treatment of the samples in this study. A certain amount of the already mixed oxides powder (mixing based on ultrasonication and stirring in water as described above) were pressed into pellets and buried in the

Table 1. Composition of the samples prepared in this study and the as-received commercial benchmark IrO₂/TiO₂ (Umicore) catalyst. O_{RuO2} or O_{IrO2} wt.% is derived from the RuO₂ or IrO₂ content of each sample and it corresponds to the theoretical mass loss of the samples after the complete reduction of their RuO₂ or IrO₂ content to metallic Ru or Ir by H₂ (see Eq. 2-6) during the TGA experiments.

Sample	TiO ₂ or Nb ₂ O ₅ mole%	RuO ₂ or IrO ₂ mole%	TiO ₂ or Nb ₂ O ₅ wt.%	RuO ₂ or IrO ₂ wt.%	O _{RuO2} or O _{IrO2} wt.% (mass loss in TGA)
RuO ₂	0	100	0	100	24.1
Ti _{0.05} Ru _{0.95} O _x	5	95	3.1	96.9	23.4
Ti _{0.15} Ru _{0.85} O _x	15	85	9.6	90.4	21.8
Ti _{0.25} Ru _{0.75} O _x	25	75	16.7	83.3	20.1
Ti _{0.5} Ru _{0.5} O _x	50	50	37.5	62.5	15.1
Nb _{0.05} Ru _{0.95} O _x	2.6	97.4	5	95	22.9
Nb _{0.2} Ru _{0.8} O _x	11.1	88.9	20	80	19.3
Nb _{0.35} Ru _{0.65} O _x	21.2	78.8	35	65	15.7
Nb _{0.5} Ru _{0.5} O _x	33.3	66.7	50	50	12.1
IrO ₂	0	100	0	100	14.3
Ti _{0.1} Ir _{0.9} O _x	10	90	3.8	96.2	13.8
Ti _{0.2} Ir _{0.8} O _x	20	80	8.2	91.8	13.1
IrO ₂ /TiO ₂ (Umicore)	28.6	71.4	12.5	87.5	12.5

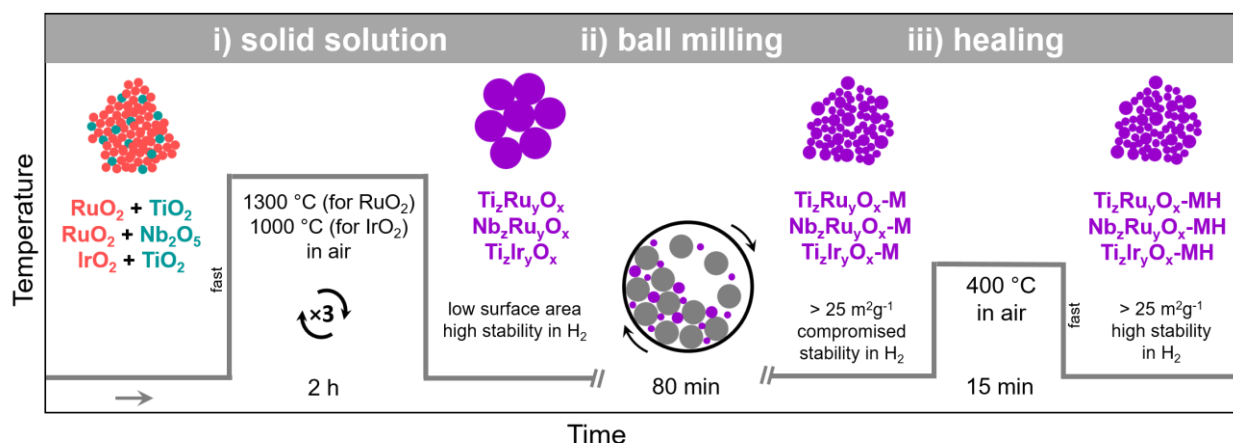


Figure 2. Scheme of the stabilization procedure of RuO_2 and IrO_2 by a solid solution approach. After mixing the pristine RuO_2 or IrO_2 with TiO_2 or Nb_2O_5 by ultrasonication and stirring in water (see text), the procedure comprises of three steps: *i) solid solution formation*: a heat treatment in air atmosphere (using gas buffer zone, see text) at a temperature of 1300 or 1000 °C for RuO_2 - or IrO_2 -based samples, respectively, to obtain the solid solution samples denoted as $\text{Ti}_z\text{Ru}_y\text{O}_x$, $\text{Nb}_z\text{Ru}_y\text{O}_x$, and $\text{Ti}_z\text{Ir}_y\text{O}_x$, where $z + y = 1$ (see Table 1). The heat treatment was performed by pushing a sample-containing crucible into a furnace which was pre-heated at the desired temperature, waiting for 2 h, and then pulling the sample-containing crucible out of the furnace to cool down to room temperature in the ambient environment. This process was repeated three times (with intermediate mixing for homogenization) to result in an overall heat treatment duration of 6 h; *ii) ball milling*: ball milling of the $\text{Ti}_z\text{Ru}_y\text{O}_x$, $\text{Nb}_z\text{Ru}_y\text{O}_x$, and $\text{Ti}_z\text{Ir}_y\text{O}_x$ samples in order to increase their specific surface area. After ball milling the samples for 80 min at 1000 RPM (see text for further details) to achieve specific surface areas of $> 25 \text{ m}^2 \text{ g}^{-1}$, the samples are denoted as $\text{Ti}_z\text{Ru}_y\text{O}_x\text{-M}$, $\text{Nb}_z\text{Ru}_y\text{O}_x\text{-M}$, and $\text{Ti}_z\text{Ir}_y\text{O}_x\text{-M}$, where M stands for the ball milling process; *iii) healing*: a post annealing step of the ball-milled samples in air atmosphere to partially recover their compromised reduction resistance, caused by the ball milling step. The healing was performed by pushing a sample-containing crucible into a furnace which was pre-heated at 400 °C, waiting for 15 min, and then pulling the sample-containing crucible out of the furnace to cool down to room temperature in the ambient environment. The ball-milled samples after the healing step are denoted as $\text{Ti}_z\text{Ru}_y\text{O}_x\text{-MH}$, $\text{Nb}_z\text{Ru}_y\text{O}_x\text{-MH}$, and $\text{Ti}_z\text{Ir}_y\text{O}_x\text{-MH}$, where H stands for healing.

corresponding sacrificial PGM-oxide powder in an alumina crucible. Then, the sample-containing crucible was pushed into the hot zone (1300 or 1000 °C for RuO_2 or IrO_2 -based samples, respectively) of the already heated tube furnace and heat treated for 2 h in synthetic air atmosphere. Then, the crucible was pulled out of the hot zone of the tube furnace to cool down to room temperature in the ambient environment. After cooling, the pellets were separated from the sacrificial powder, and they were crushed and ground using a mortar and a pestle, and then they were thoroughly hand-mixed using a disposable plastic spatula. The process of making pellets, heat treatment and grinding/hand mixing was repeated three times, resulting in an overall heat treatment duration of 6 h to obtain the solid solution samples denoted as $\text{Ti}_z\text{Ru}_y\text{O}_x$, $\text{Nb}_z\text{Ru}_y\text{O}_x$, and $\text{Ti}_z\text{Ir}_y\text{O}_x$, where $z + y = 1$, as shown in Table 1. After the heat

treatment at such high temperatures for extended time in step i), a ball milling process is required to increase the specific surface area of the samples, which is performed in step ii). The ball milling process is described in detail in our previous study,¹⁷ but in short, $\sim 30 \text{ g}$ ZrO_2 beads (1 mm diameter, FRITSCH GmbH, Germany) were placed in a grinding bowl (20 ml volume capacity, ZrO_2 sample container cased in stainless steel, FRITSCH GmbH, Germany), and $\sim 10 \text{ g}$ $\text{Ti}_z\text{Ru}_y\text{O}_x$, $\text{Nb}_z\text{Ru}_y\text{O}_x$, or $\text{Ti}_z\text{Ir}_y\text{O}_x$ were added on top of the beads in the grinding bowl. After adding $\sim 2.5 \text{ mL}$ DI water to the mixture in order to perform a wet ball milling, the grinding bowl was sealed with a cap and was placed in a planetary milling machine (Planetary Micro Mill PULVERISETTE 7 premium line, FRITSCH GmbH, Germany) to apply 80 cycles of ball milling. Each ball milling cycle was comprised of 1 minute of milling at 1000 rounds per minute (RPM)

and 4 minutes of pause (0 RPM) to prevent the grinding bowl heat-up. The active milling time after 80 ball milling cycles was 80 minutes. After ball milling, the sample was separated from the beads by washing it through a sieve by DI water. Then, the resulting solution was centrifuged at 10000 RPM (5810 R, Eppendorf) to separate the sample from water, and the resulting paste was dried in an oven at 70 °C for 12 h in air atmosphere. After drying, the samples were ground by a mortar and a pestle and stored in glass vials and denoted as $\text{Ti}_2\text{Ru}_y\text{O}_x\text{-M}$, $\text{Nb}_2\text{Ru}_y\text{O}_x\text{-M}$, and $\text{Ti}_2\text{Ir}_y\text{O}_x\text{-M}$, where M stands for 80 minutes of active ball milling process in step ii). As was shown in our previous study,¹⁷ the ball milling process partially compromises the reduction resistance of the heat-treated samples, therefore, a post annealing is performed on the ball-milled samples in step iii) in order to recover their reduction resistance. To do this, a certain amount of the ball-milled sample is placed in an alumina crucible and pushed into the hot zone of a pre-heated furnace at 400 °C in an air atmosphere. After 15 minutes, the sample is pulled out of the furnace to cool down to room temperature in the ambient environment. Since the stability of the samples is partially recovered after this post annealing step, it is referred to as the healing step throughout this study and the ball-milled samples after the healing step are denoted as $\text{Ti}_2\text{Ru}_y\text{O}_x\text{-MH}$, $\text{Nb}_2\text{Ru}_y\text{O}_x\text{-MH}$, and $\text{Ti}_2\text{Ir}_y\text{O}_x\text{-MH}$ as shown in Figure 2.

For comparison, pure RuO_2 and IrO_2 were also treated through the same thermal/mechanical treatment process as their solid solution counterparts. After an overall 6 h heat treatment at high temperature in step i), these samples are simply referred to as RuO_2 and IrO_2 throughout this study, and after the ball milling and healing in steps ii) and iii), they are referred to as $\text{RuO}_2\text{-MH}$ and $\text{IrO}_2\text{-MH}$, respectively. A commercial benchmark IrO_2 supported on TiO_2 OER catalyst ($\text{IrO}_2/\text{TiO}_2$ with 75 wt.% iridium, Elyst Ir75 0480 from Umicore, Germany) is used as a benchmark reference to compare the OER activity as well as the reduction resistance of the prepared catalysts in this study. According to the patent, the IrO_2 deposited onto the TiO_2 nano-particles is heat treated at $T \approx 400$ °C in an

air atmosphere.³³ This catalyst is referred to as $\text{IrO}_2/\text{TiO}_2$ (Umicore) throughout this study and it is used without any further modification/treatment.

Rotating disk electrode (RDE) measurements.—

Electrochemical measurements were carried out in a three-electrode cell using a static H_2 reference electrode (RE) consisted of a Pt wire sealed into one end of a glass tube which was drawn to a capillary and filled with electrolyte and a bubble of evolved H_2 (all voltages of RDE experiments throughout this work are quoted vs. the potential of this reversible hydrogen electrode (V_{RHE})), a high surface area Au wire as a counter electrode (CE), and a 5 mm diameter polycrystalline Au disk working electrode (WE) assembled in an interchangeable rotating ring-disk electrode (RRDE) shaft made of polyether ketone (Pine Research Instrumentation, USA). The reference electrode potential was calibrated in a H_2 saturated electrolyte prior to each experiment using the Pt ring of the RRDE. A 0.05 M H_2SO_4 aqueous solution was used as electrolyte, which was prepared by mixing high purity H_2SO_4 (Ultrapur, 96%, Merck Millipore KGaA, Germany) and ultra-pure water (18.2 M Ω cm at 20 °C, Merck Millipore KGaA, Germany). High purity Ar, H_2 , and O_2 (6.0-grade, Westfalen AG) were used to purge the electrolyte.

Before each measurement, the Au working electrode disk was removed from the RRDE shaft and was polished with 0.3 μm alumina polishing suspension (Buhler AG) and then sonicated in ultra-pure water for several times. The catalyst ink suspension was prepared using the catalyst powders, a pH = 3 solution of the high purity H_2SO_4 in ultra-pure water, and a Nafion® ionomer solution (5 wt.% ionomer in mixture of lower aliphatic alcohols and water, Sigma Aldrich). The ink composition was adjusted to achieve 0.98 mg $_{\text{Ru/Ir}}$ mL $^{-1}_{\text{ink}}$ and 2 wt.% ionomer content in the final dried coating consisting of catalyst and ionomer. The suspension was sonicated for 30 min in a sonication bath (Elmasonic S 30 H, Elma Schmidbauer GmbH) in order to achieve a homogenous ink. The temperature of the bath was maintained below 35 °C in order to prevent solvent evaporation. Finally, 20 μL of the prepared ink was

drop-casted on the polished and cleaned Au working electrode, resulting in a catalyst loading of $0.1 \text{ mg}_{\text{Ru/Ir}} \text{ cm}^{-2}_{\text{disk}}$.

All the RDE measurements (using the RRDE assembly) were performed using an Autolab potentiostat (PGSTAT302N, Metrohm AG) and a rotator (Pine Research Instrumentation). The electrode rotation rate was fixed at 2500 RPM and the electrolyte temperature was maintained at room temperature during the electrochemical measurements. Freshly coated working electrodes were dipped in Ar-saturated electrolyte and the uncompensated solution resistance between the reference and the working electrodes was determined by electrochemical impedance spectroscopy (EIS) from 100 kHz to 100 Hz frequency range at open circuit voltage (OCV). Then, cyclic voltammetry (CV) was performed between 0.05-1.35 V_{RHE} with 100 mV s^{-1} scan rate for 10 cycles, in order to record the characteristic voltammetry behavior of the catalyst powders in this potential range as well as to make sure of the physical stability of the coatings on Au working electrode disk during the experiments. After that, the electrolyte was fully saturated with O_2 and an OER polarization curve was recorded by collecting a CV between 1.3-1.6 V_{RHE} with 20 mV s^{-1} scan rate where only the very first positive-going scan is used for evaluations.

Membrane electrode assembly (MEA) preparation and cell assembly.— 5 cm^2 MEAs for PEM water electrolyzer (PEMWE) measurements were prepared by the decal transfer method. The electrodes for the hydrogen evolution reaction (HER) on the cathode were prepared from platinum supported on Vulcan XC72 carbon with a metal loading of 45.8 wt.% (TEC10V50E, from Tanaka, Japan). For the OER on the anode, $\text{IrO}_2/\text{TiO}_2$ (Umicore), $\text{Ti}_{0.15}\text{Ru}_{0.85}\text{O}_x\text{-MH}$, or $\text{RuO}_2\text{-MH}$ were used. The inks were prepared from catalyst powder, 2-propanol (purity $\geq 99.9\%$, from Sigma Aldrich), and Nafion[®] ionomer solution (1100 EW, 20 wt.% ionomer; D2021 from IonPower, USA). 5 mm ZrO_2 grinding beads were added and the ink was mixed for at least 18 h on a roller mill. The ink was coated onto a $50 \mu\text{m}$ thick PTFE foil (from

Angst+Pfister, Germany) using a Mayer-rod coating machine. After drying, electrodes with an active area of 5 cm^2 were punched from the coatings and hot-pressed onto a Nafion[™] 212 membrane ($50 \mu\text{m}$, from Quintech, Germany) for 3 min at 155°C at a pressure of 2.5 MPa. For the cathodes, the platinum loading was $0.39 \pm 0.01 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}_{\text{MEA}}$ and the ionomer:carbon ratio was adjusted to 0.6. The iridium loading for the $\text{IrO}_2/\text{TiO}_2$ (Umicore) anode was $1.54 \text{ mg}_{\text{Ir}} \text{ cm}^{-2}_{\text{MEA}}$ with an ionomer content of 12 wt.% relative to the total weight of the dried electrode. The ruthenium loadings for the $\text{Ti}_{0.15}\text{Ru}_{0.85}\text{O}_x\text{-MH}$ and $\text{RuO}_2\text{-MH}$ anodes were 1.54 and $1.35 \text{ mg}_{\text{Ru}} \text{ cm}^{-2}_{\text{MEA}}$, respectively, with an ionomer content of 13.8 wt.% relative to the total weight of both dried electrodes. Sintered titanium (from Mott Corporation, USA) with a porosity of $\sim 50\%$ as well as a carbon fiber paper (TGP-H-120 without MPL, 5 wt% PTFE; from Toray, Japan) were used as porous transport layers (PTLs) at the anode and at the cathode, respectively. The cell was sealed with virgin PTFE gaskets with an appropriate thickness to achieve $\sim 25\%$ compression of the carbon PTL (assuming the titanium PTL to be incompressible; for further details see Ref.³⁴).

Electrochemical measurements of the MEAs.— An automated test station from Greenlight Innovation, equipped with a potentiostat and booster (Reference 3000 and 30 A booster, Gamry), was used for electrochemical characterization of the MEAs. During all the experiments, the cell temperature was fixed to 80°C and deionized (DI) water was pre-heated to 80°C and fed to anode of the electrolysis cell at a rate of 5 ml min^{-1} .

After a warm-up step under N_2 atmosphere, CVs of the anode electrode were recorded at the beginning of life (BOL), using a scan rate of 100 mV s^{-1} in a potential range of 0.05-1.35 V at ambient pressure. The anode working electrode was flushed with H_2O at a flow rate of 5 ml min^{-1} , while the cathode counter electrode was purged with dry H_2 at 50 ml min^{-1} . After recording the BOL CVs, a galvanostatic polarization curve was recorded in a current range of 0.01 to $2 \text{ A cm}^{-2}_{\text{MEA}}$. At each current, the cell voltage was averaged over 10 s after 5 min equilibration time.

Galvanostatic AC impedance measurements between 100 kHz – 1 Hz were carried out after each polarization step. The amplitude of the current perturbation was chosen for each step to obtain a sufficient signal to noise ratio, while keeping the perturbation small enough to ensure a linear system response. The high-frequency resistance (HFR) was obtained from the high-frequency intercept of the Nyquist plot with the real axis. The product gas at the anode outlet was diluted with nitrogen (100 nccm) to prevent the formation of an explosive gas mixture, which can be produced by the permeation of H₂ through the membrane into the anode compartment. After recording the polarization curve, an electrochemical stability measurement was performed at a constant current of 1 A cm⁻²_{MEA} either for 50 h or until the cell voltage reached an upper cut-off value of 2.1 V. After the stability measurement, CVs were recorded at the end of test (EOT) under the same conditions as the CVs at the BOT.

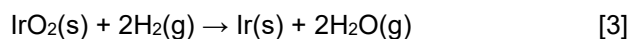
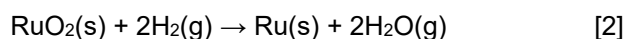
Thermogravimetric analysis (TGA).—

Thermogravimetric analysis (TGA) of the powder samples was performed by a Mettler Toledo TGA/DSC 1 instrument. ~ 3 mg of powder were weighed into a sapphire crucible (volume 70 µL) closed with a perforated sapphire lid and directly inserted into the TGA furnace. All the gases used in TGA experiments were 5.0-grade and supplied by Westfalen AG. Ar (20 mL min⁻¹) was used as the cell carrier gas in addition to the reactive gases during all TGA experiment steps. TGA experiments to investigate the reduction resistance of the catalysts in a H₂-containing atmosphere were composed of two main steps: i) an initial in-situ drying/cleaning step in oxidative atmosphere (mass profiles of this step are not shown in the figures); and ii) a subsequent metal oxide reduction step in reductive atmosphere.

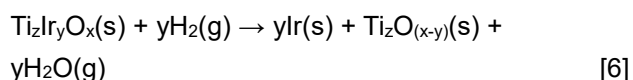
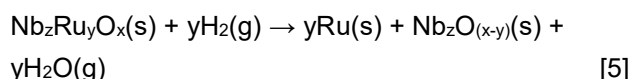
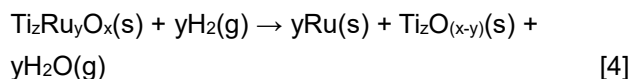
The in-situ drying/cleaning was performed at 200 °C for 10 min in an oxygen-containing atmosphere. Further details regarding this step can be found in our previous study.¹⁶ After the initial drying/cleaning step, the metal oxide reduction step was carried out in two different modes: i) a temperature ramp mode and ii) an isothermal mode. During the temperature ramp

experiment, the temperature was ramped from 25 to 500 °C (for IrO₂-based samples) or to 800 °C (for RuO₂-based samples) with a heating rate of 5 K min⁻¹ while supplying 5 vol.% H₂/Ar (40 mL min⁻¹). The isothermal reduction experiment was carried out by heating the TGA furnace from 25 °C to 80 °C with a heating rate of 5 K min⁻¹ in Ar (100 mL min⁻¹), followed by switching the gas supply from Ar to 5 vol.% H₂/Ar (40 mL min⁻¹) and keeping the furnace at 80 °C for 12 h. It should be noted that during all the metal oxide reduction steps in TGA experiments, the effective H₂ concentration was 3.3 vol.% H₂/Ar, since in addition to the 40 mL min⁻¹ 5 vol.% H₂/Ar an extra 20 mL min⁻¹ flow of Ar as cell carrier gas was supplied.

During the TGA experiments under the diluted H₂ atmosphere, RuO₂ and IrO₂ can be reduced according to the following reactions:



Stoichiometric RuO₂ (ruthenium(IV) oxide) and IrO₂ (iridium(IV) oxide) consist of 24 wt.% O and 14.3 wt.% O, respectively. Hence, the total mass loss of a RuO₂ or IrO₂ catalyst upon the complete reduction to the respective metals would be accompanied by the total loss of O, which would amount to a mass loss of the RuO₂ and IrO₂ catalysts of 24 wt.% and 14.3 wt.%, respectively. Assuming that TiO₂ and Nb₂O₅ components of the here prepared samples are not reduced by H₂ at the analyzed temperature range (25–800 °C),^{21–23} the observed mass loss of the solid solutions during the TGA experiments is attributed to the reduction of RuO₂ or IrO₂ and loss of O_{RuO2} or O_{IrO2} of these samples according to Eq. 2 and 3. Therefore, a generalized reduction reaction of the here prepared samples during the TGA experiments can be written as following:



Assuming that RuO₂ and IrO₂ consist of 24 wt.% O_{RuO2} and 14.3 wt.% O_{IrO2}, respectively (as explained

above), the amount of O_{RuO_2} and O_{IrO_2} of the here prepared samples can be estimated from their RuO_2 and IrO_2 content as shown in Table 1. These values will be used to mark the theoretical mass loss of the samples upon the full reduction of their RuO_2 and IrO_2 content during the later shown TGA data.

X-ray powder diffraction (XPD) measurements.—

X-ray powder diffraction (XPD) was performed using a Stadi P instrument (Stoe & Cie GmbH, Germany) with $Cu-K_{\alpha 1}$ radiation ($\lambda = 1.54059 \text{ \AA}$, 50 kV, 30 mA, Ge(111) monochromatized) and a Mythen 1 K position-sensitive detector (Dectris Ltd., Switzerland) in transmission mode. ~ 5 mg of each powder sample was smoothly spread onto a scotch tape and placed in the center of the sample holder hole. The XPD patterns were recorded in the 2θ range of $20-90^\circ$ with one data point every $0.015^\circ/2\theta$ and a total measurement time of 2 h for each diffractogram. The XPD data were analyzed with the software package Topas.

The whole diffractograms were refined in the $P42/mnm$ and $P2/m$ space groups according to the Le Bail method. For the fit of the background, a Chebyshev polynomial with 8 parameters was used. The zero error, axial divergence and the instrumental contribution to the peak broadening were determined using a Si standard material and only included into the refinement after reaching a stable refinement result. The instrumental peak broadening was described using the Thompson-Cox-Hastings pseudo-Voigt function (TCHZ) and kept constant during the refinement. Any additional isotropic peak broadening from the sample was included using a Double-Voigt approach (LVol-FWHM). We are mainly interested in the RuO_2 -rich (ssTi- RuO_x and ssNb- RuO_x) and IrO_2 -rich (ssTi- IrO_x) solid solution phases with $P42/mnm$ space group, and the refined lattice parameters of these phases are used to monitor the solubility of the metal oxides. The theoretical lattice parameters of the tetragonal $P42/mnm$ symmetry of RuO_2 ($a = b = 4.543 \text{ \AA}$, $c = 3.14 \text{ \AA}$, $c/a = 0.6912$),³⁵ IrO_2 ($a = b = 4.545 \text{ \AA}$, $c = 3.19 \text{ \AA}$, $c/a = 0.7019$),³⁶ and TiO_2 ($a = b = 4.58 \text{ \AA}$, $c = 2.95 \text{ \AA}$, $c/a = 0.6441$)³⁷ are used to draw the Vegard's line to compare the refinement

results of the solid solutions. The TiO_2 -rich and Nb_2O_5 -rich side phases with $P42/mnm$ and $P2/m$ space groups, respectively, are not of special interest in this study due to their expected low OER activity.

N_2 -physisorption measurements.— Specific surface area of the samples was measured by N_2 physisorption at 77 K using an Autosorb iQ gas sorption analyzer (Quantachrome Instruments, USA). All samples were evacuated at 120°C for 12 h prior to the experiments. Adsorption isotherms were measured with 11 data points in the relative pressure range of $0.05 \leq p/p_0 \leq 0.30$, where p represents the gas pressure and p_0 the saturation pressure of N_2 . The specific surface area was calculated according to the Brunauer-Emmet-Teller (BET) theory, whereby the ideal linear range is selected by the Micropore BET Assistant of the ASiQwin software (typically 7 out of the 11 points).

Results and discussion

The preparation of solid solution catalysts has been the subject of several studies in the literature. High surface area RuO_2 - TiO_2 , RuO_2 - Nb_2O_5 , and IrO_2 - TiO_2 mixtures are typically prepared by a solvothermal/thermal treatment at temperatures $< 500^\circ\text{C}$,³⁸⁻⁴³ where tuned catalytic or structural properties of RuO_2 and IrO_2 in these mixtures is occasionally attributed to the formation of a solid solution of these PGM-oxides with the other transition metal oxide in the mixture.^{38, 39, 43} At least based on the thermodynamic equilibrium phase diagrams of RuO_2 - TiO_2 and IrO_2 - TiO_2 systems shown in Figure 1, a considerable solubility of the crystalline rutile phases of these oxides is achieved at relatively high temperatures, namely at $> 1200^\circ\text{C}$ for RuO_2 - TiO_2 (also see Ref.³²) and at $> 900^\circ\text{C}$ for IrO_2 - TiO_2 . The tuned structural properties of RuO_2 and IrO_2 in “low temperature solid solutions” reported in the literature could be due to the presence of particle-support interactions, such as the epitaxial particle growth during the co-precipitation synthesis.^{42, 44} This hypothesis should be quite reasonable in view of the fact that for the finely mixed metal oxides with small particle size, a high interface contact between the

PGM-oxide and the transition metal oxide is expected, and therefore the structure of the PGM-oxide might be affected by the transition metal oxide at/near the interface region. On the other hand, if a “real solid solution” is prepared at high temperatures based on the equilibrium phase diagrams in Figure 1, a severe particle agglomeration and growth is expected to occur during its preparation process and the resulting solid solution might not be a desirable material for catalysis applications. Here, we attempt to prepare “real solid solutions” with high specific surface area and investigate their properties for application as OER co-catalysts in PEMFC anode.

Preparation of the solid solution catalysts.— The structural transformation upon the formation of solid solutions is investigated using XPD. Figure 3 shows the XPD patterns of $\text{Ti}_2\text{Ru}_y\text{O}_x$, $\text{Nb}_2\text{Ru}_y\text{O}_x$, and $\text{Ti}_2\text{Ir}_y\text{O}_x$ powders, together with the RuO_2 and IrO_2 powders heat treated at the same conditions (see experimental section). It should be noted that the diffractograms were measured at $2\theta = 20\text{--}90^\circ$ and then the whole

diffractograms were refined with the Le Bail method, but Figure 3 only shows the strongest crystalline reflections of the samples occurring at low 2θ region for a better representation of crystalline phase differences between the samples. Based on Figure 3, the powders exhibit a well-defined crystalline structure which can mainly be indexed according to the tetragonal RuO_2 or IrO_2 rutile structure with the $P42/mnm$ symmetry, as marked with the HKL ticks. It can be seen that by increasing TiO_2 content above 15% in $\text{Ti}_2\text{Ru}_y\text{O}_x$ samples and above 10% in $\text{Ti}_2\text{Ir}_y\text{O}_x$ samples in Figure 3a and c, respectively, side crystalline phases start to form as indicated by arrows in these figures. The formation of side crystalline phases by increasing TiO_2 content can be predicted based on the position of $\text{Ti}_2\text{Ru}_y\text{O}_x$ and $\text{Ti}_2\text{Ir}_y\text{O}_x$ samples in the phase diagrams in Figure 1. Based on Figure 1a, $\text{Ti}_{0.05}\text{Ru}_{0.95}\text{O}_x$ and $\text{Ti}_{0.15}\text{Ru}_{0.85}\text{O}_x$ should only be composed of ssTi-RuO_x phase, while $\text{Ti}_{0.25}\text{Ru}_{0.75}\text{O}_x$ and $\text{Ti}_{0.5}\text{Ru}_{0.5}\text{O}_x$ samples should be composed of ssRu-TiO_x and ssTi-RuO_x phases. Similarly in

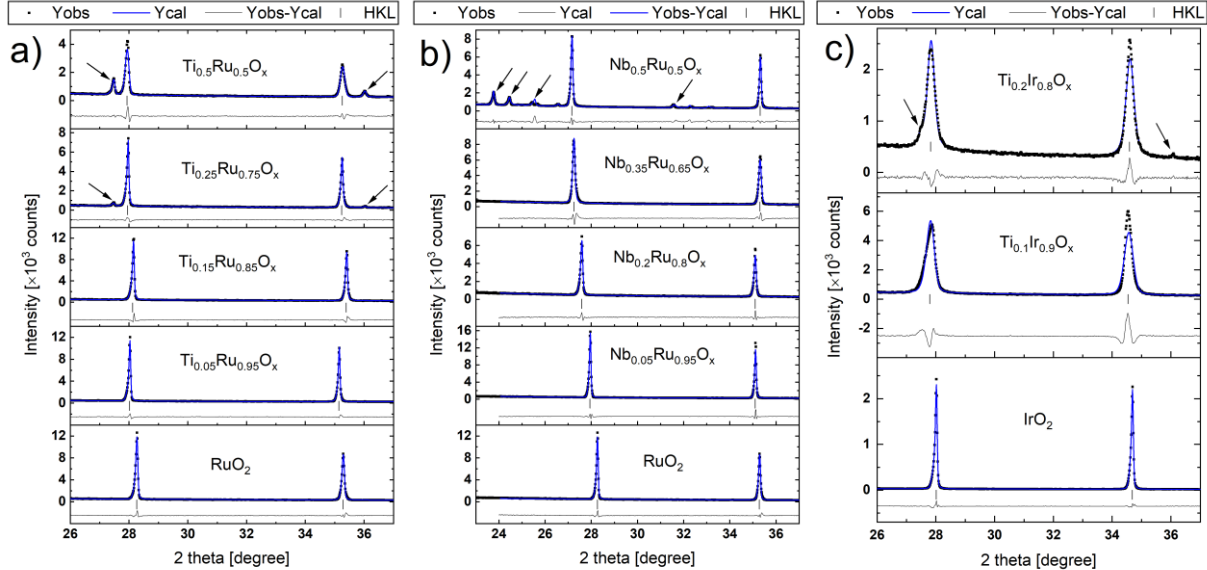


Figure 3. X-ray powder diffraction results of the a) $\text{Ti}_2\text{Ru}_y\text{O}_x$, b) $\text{Nb}_2\text{Ru}_y\text{O}_x$, and c) $\text{Ti}_2\text{Ir}_y\text{O}_x$ powders. The data were collected at our in-house Cu-diffractometer ($\lambda = 1.54059 \text{ \AA}$) at $2\theta = 20\text{--}90^\circ$ and then the whole diffractograms were refined in the $P42/mnm$ and $P2/m$ space groups according to the Le Bail method. However, the plots only show the strongest crystalline reflections at low 2θ region for a better representation. The observed (black points), calculated (blue lines), and difference diffraction profiles (black lines) are shown. Here, we put a special emphasis on the RuO_2 - and IrO_2 -rich phases with $P42/mnm$ space group, and the position of the Bragg peaks of these phases are marked with the black ticks, and the detailed fitting parameters of these phases can be found in Table 2. The arrows mark the reflection peaks of the TiO_2 - and Nb_2O_5 -rich side phases with $P42/mnm$ and $P2/m$ space groups, respectively.

Figure 1b, $\text{Ti}_{0.1}\text{Ir}_{0.9}\text{O}_x$ sample should mainly be composed of ssTi-IrO_x phase, while $\text{Ti}_{0.2}\text{Ir}_{0.8}\text{O}_x$ sample should be composed of ssIr-TiO_x and ssTi-IrO_x phases. Therefore, the crystalline reflections marked with the HKL ticks in Figure 3a and c would belong to ssTi-RuO_x and ssTi-IrO_x phases, respectively, while the arrows most likely mark the crystalline reflections of ssRu-TiO_x and ssIr-TiO_x phases in Figure 3a and c, respectively. In fact, the crystalline reflections of the side phases marked with the arrows in Figure 3a and c match with the crystalline reflections of a rutile TiO₂ phase with the $P42/mnm$ symmetry reported in the literature,⁴⁵ further indicating TiO₂-rich nature of these phases. As mentioned in the experimental section, we are not aware of any reported thermodynamic phase diagram for RuO₂-Nb₂O₅ system in the literature. However, the XPD patterns of the here prepared Nb₂Ru_yO_x samples shown in Figure 3b did not show any side crystalline phases when increasing the NbO_{2.5} content to 35%, and side crystalline phases (indicated by arrows) only start to form when NbO_{2.5} content is further increased to 50%. This would mean that the crystalline reflections marked with the HKL ticks in Figure 3b could belong to a possible ssNb-RuO_x phase and the arrows most likely mark the crystalline reflections of a Nb₂O₅-rich phase. In fact, the crystalline reflections of the side phase marked with the arrows in Figure 3b match with the crystalline reflections of an H-Nb₂O₅ phase with the $P2/m$ symmetry reported in the literature.⁴⁶

For further evaluation of the XPD data, the diffractograms were refined with the Le Bail method. Since we are mainly interested in the ssTi-RuO_x, ssNb-RuO_x, and ssTi-IrO_x phases for OER catalysis application, with put a special emphasis on these RuO₂- and IrO₂-rich phases with the tetragonal rutile $P42/mnm$ space group marked with the HKL ticks in Figure 3, and Table 2 summarizes the refinement results of these phases together with the pure RuO₂ and IrO₂ samples. In order to track the structural changes upon the formation of solid solutions, the lattice constant (*c/a*) values of the samples is compared. Taking the ratio of the two lattice parameters (*c/a*) is more reliable than taking the

individual lattice parameters (*c* or *a*) for investigating the structural changes, since any instrumental shift or fitting error can be cancelled or minimized by dividing the lattice parameters. For a better representation of the changes in *c/a* values upon the formation of solid solutions, Figure 4 shows the changes in *c/a* values vs the molar fractions of TiO₂ and NbO_{2.5} in the samples. Note that the data at 0 molar% TiO₂ and at 0 molar% NbO_{2.5}, respectively in Figures 4a and b, mark the *c/a* values of pure RuO₂ samples and the data at 0 molar% TiO₂ in Figure 4c mark the *c/a* value of pure IrO₂ samples. To compare the experimental results with the behavior in an ideal solid solution, a Vegard derived linear interpolation between the theoretical *c/a* values of a rutile RuO₂ (0.6912, at 0 molar% TiO₂)³⁵ and a rutile TiO₂ (0.6441, at 100 molar% TiO₂)³⁷ in Figure 4a, and a rutile IrO₂ (0.7019, at 0 molar% TiO₂)³⁶ and a rutile TiO₂ (0.6441, at 100 molar% TiO₂) in Figure 4c are shown as well. It was not possible to draw a theoretical Vegard's line for RuO₂-Nb₂O₅ system due to the different crystal structures of RuO₂ ($P42/mnm$) and Nb₂O₅ ($P2/m$), and instead a linear fit of the experimental *c/a* values of Nb₂Ru_yO_x samples in the range of 0% ≤ NbO_{2.5} ≤ 35% is used for evaluations in Figure 4b.

Based on Figure 4a, the *c/a* values of the pure RuO₂ (0 molar% TiO₂) and the ssTi-RuO_x phase of Ti_zRu_yO_x samples follow the Vegard's line up to 15% TiO₂, and then they deviate from the Vegard's line by further increasing TiO₂ content to 25% and 50%, where a relatively constant *c/a* value of ~0.683 is reached. Such deviation of *c/a* values from Vegard's line would mean that there is a miscibility gap in the solid solution system,⁴⁷ and a second phase would start to form by further increasing TiO₂ content to 25% and 50%. This agrees well with the observation of a TiO₂-rich phase marked by the arrows in the XPD patterns of Ti_{0.25}Ru_{0.75}O_x and Ti_{0.5}Ru_{0.5}O_x samples in Figure 3a and with the positions of these samples in the thermodynamic phase diagram in Figure 1a, where two separate phases are expected to form. The maximum solubility of TiO₂ in ssTi-RuO_x phase of the Ti_zRu_yO_x samples could be estimated if the *c/a* value of Ti_{0.25}Ru_{0.75}O_x or Ti_{0.5}Ru_{0.5}O_x samples (~0.683) is

Table 2. Refinement results of the RuO₂- and IrO₂-rich phases of the samples with *P42/mnm* space group marked with the HKL ticks in diffractograms in Figures 3 and A-1. The table summarizes the quality factors (R-values and χ^2), lattice parameters (a and c) and lattice constant (c/a) values of these phases. Errors are given in parenthesis.

Sample	R _{wp} [%]	R _{bragg} [%]	χ^2	a [Å]	c [Å]	c/a
RuO ₂	9.96	3.69	1.66	4.49620(6)	3.10839(5)	0.6913
Ti _{0.05} Ru _{0.95} O _x	7.58	1.01	1.20	4.50037(3)	3.09797(2)	0.6884
Ti _{0.15} Ru _{0.85} O _x	9.30	0.99	1.52	4.51331(3)	3.08740(3)	0.6841
Ti _{0.25} Ru _{0.75} O _x	6.26	0.65	0.96	4.51017(5)	3.08240(3)	0.6834
Ti _{0.5} Ru _{0.5} O _x	6.92	1.16	1.05	4.5138(1)	3.07858(9)	0.6820
RuO ₂ -MH	3.98	3.69	2.88	4.49620(6)	3.10839(5)	0.6913
Ti _{0.05} Ru _{0.95} O _x -MH	5.23	0.48	0.82	4.513(1)	3.1019(7)	0.6873
Ti _{0.15} Ru _{0.85} O _x -MH	3.84	0.33	1.10	4.5137(1)	3.0852(2)	0.6835
Nb _{0.05} Ru _{0.95} O _x	9.41	1.41	1.55	4.51208(4)	3.09915(3)	0.6869
Nb _{0.2} Ru _{0.8} O _x	6.44	1.04	1.03	4.56941(3)	3.08167(3)	0.6744
Nb _{0.35} Ru _{0.65} O _x	10.43	1.94	1.70	4.6248(1)	3.03971(7)	0.6573
Nb _{0.5} Ru _{0.5} O _x	7.65	0.27	1.63	4.6395(3)	3.03454(7)	0.6541
Nb _{0.2} Ru _{0.8} O _x -MH	3.21	0.18	0.96	4.5623(3)	3.0774(2)	0.6745
Nb _{0.35} Ru _{0.65} O _x -MH	2.90	0.09	0.86	4.6152(2)	3.0418(2)	0.6591
IrO ₂	8.78	0.69	1.48	4.50134(2)	3.15623(2)	0.7012
Ti _{0.1} Ir _{0.9} O _x	13.81	2.62	2.42	4.5357(4)	3.1640(2)	0.6976
Ti _{0.2} Ir _{0.8} O _x	6.06	0.49	0.97	4.5309(3)	3.1585(2)	0.6971
IrO ₂ -MH	5.06	0.47	1.74	4.5175(3)	3.1647(2)	0.7005
Ti _{0.1} Ir _{0.9} O _x -MH	4.78	0.36	1.57	4.5348(1)	3.1674(2)	0.6985

intercepted with Vegard's line in Figure 4a. By doing so, a maximum TiO₂ solubility of ~18 molar% in ssTi-RuO_x phase is estimated for the Ti_zRu_yO_x samples prepared in this study, which agrees well with the solubility limit of TiO₂ of ~16 molar% in ssTi-RuO_x phase at 1300 °C in the phase diagram in Figure 1a. This means that Ti_{0.05}Ru_{0.95}O_x and Ti_{0.15}Ru_{0.85}O_x samples are only composed of ssTi-RuO_x phase. The c/a values of the ssTi-IrO_x phase of Ti_zIr_yO_x samples in Figure 4c deviate from the Vegard's line already at 10% TiO₂, and a relatively constant c/a value of ~0.6974 is reached by further increasing TiO₂ content to 20%. This agrees well with the observation of a TiO₂-rich phase marked by the arrows in the XPD pattern of Ti_{0.2}Ir_{0.8}O_x sample in Figure 3c and with the position of this sample in the thermodynamic phase diagram in Figure 1b, where two separate phases are expected to form. If the c/a value of Ti_{0.1}Ir_{0.9}O_x or Ti_{0.2}Ir_{0.8}O_x samples (~0.6974) is intercepted with the

Vegard's line in Figure 4b, a maximum TiO₂ solubility of ~6 molar% in ssTi-IrO_x phase is estimated for the Ti_zIr_yO_x samples prepared in this study, which is in close agreement with the solubility limit of TiO₂ of ~9 molar% in ssTi-IrO_x phase at 1000 °C in the phase diagram in Figure 1b. The same approach can be taken for the interpretation of Figure 4b, where the c/a value of the RuO₂-rich phase (possibly ssNb-RuO_x) of Nb_{0.5}Ru_{0.5}O_x sample deviates from the linear trend of c/a vs NbO_{2.5} content of Nb_zRu_yO_x samples observed at 0% ≤ NbO_{2.5} ≤ 35%. This behavior agrees well with the observation of a Nb₂O₅-rich phase marked by the arrows in the XPD pattern of Nb_{0.5}Ru_{0.5}O_x sample in Figure 3b. If the c/a value of Nb_{0.5}Ru_{0.5}O_x sample (~0.654) is intercepted with the linear fit of the data at 0% ≤ NbO_{2.5} ≤ 35% in Figure 4b, a maximum NbO_{2.5} solubility of ~39 molar% in ssNb-RuO_x phase is estimated for the Nb_zRu_yO_x samples prepared at 1300 °C in this study. This means that Nb_{0.05}Ru_{0.95}O_x,

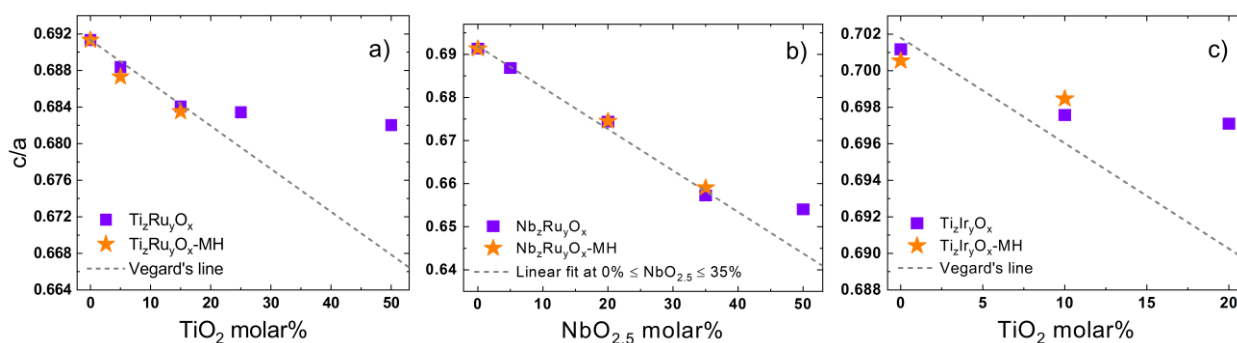


Figure 4. Experimental c/a values of a) $\text{Ti}_2\text{Ru}_y\text{O}_x$ and $\text{Ti}_2\text{Ru}_y\text{O}_x\text{-MH}$, b) $\text{Nb}_2\text{Ru}_y\text{O}_x$ and $\text{Nb}_2\text{Ru}_y\text{O}_x\text{-MH}$, and c) $\text{Ti}_2\text{Ir}_y\text{O}_x$ and $\text{Ti}_2\text{Ir}_y\text{O}_x\text{-MH}$ samples obtained from the refinement of RuO_2 - and IrO_2 -rich phases with the $P42/mnm$ space group in the diffractograms of these samples (see Figure 3) as summarized in Table 2. Vegard's lines are derived from a linear interpolation between the theoretical c/a values of a rutile RuO_2 (0.6913) and a rutile TiO_2 (0.6444) in a), and a rutile IrO_2 (0.7005) and a rutile TiO_2 (0.6444) in c). Due to the different crystal structures of RuO_2 ($P42/mnm$) and Nb_2O_5 ($P2/m$), a linear fit of the experimental c/a values of $\text{Nb}_2\text{Ru}_y\text{O}_x$ samples in the range of $0\% \leq \text{NbO}_{2.5} \leq 35\%$ is used for evaluations in b).

$\text{Nb}_{0.2}\text{Ru}_{0.8}\text{O}_x$, and $\text{Nb}_{0.35}\text{Ru}_{0.65}\text{O}_x$ samples are only composed of ssNb-RuO_x phase. Heat treatment at high temperature for the formation of solid solutions (see experimental section and Figure 2) would lead to the particle agglomeration and growth and loss of specific surface area of the samples, therefore, a ball milling and a healing step are performed on some selected samples to increase their specific surface area for OER catalysis. The desired solid solution phases for OER catalysis are ssTi-RuO_x , ssNb-RuO_x , and ssTi-IrO_x due to the high amount of RuO_2 or IrO_2 dissolved in their structure. Therefore, some samples that mostly consist of these phases ($\text{Ti}_{0.05}\text{Ru}_{0.95}\text{O}_x$, $\text{Ti}_{0.15}\text{Ru}_{0.85}\text{O}_x$, $\text{Nb}_{0.2}\text{Ru}_{0.8}\text{O}_x$, $\text{Nb}_{0.35}\text{Ru}_{0.65}\text{O}_x$, and $\text{Ti}_{0.1}\text{Ir}_{0.9}\text{O}_x$ samples) together with the pure RuO_2 and IrO_2 samples are selected for the ball milling and healing processes. The significance of the healing step is described in detail in our previous study.¹⁷ In short, a compromised reduction resistance of an IrO_2 sample measured by TGA in 3.3 vol.% H_2/Ar was observed after the ball milling step, which was attributed to the formation of lattice crystal defects in a few atomic monolayers (ML) on catalyst surface due to the high impact of beads during ball milling process. The compromised reduction resistance of the ball-milled sample was recovered after a short heat treatment at 400 °C, which was attributed to the

annihilation of the defects during this healing step.

Figure A-1 shows the XPD patterns of the ball-milled and healed samples, where the diffractograms can only be indexed according to the tetragonal rutile structure of the RuO_2 - or IrO_2 -rich phases with the $P42/mnm$ symmetry, as marked with the HKL ticks. The refinement results of these diffractograms can also be found in Table 2. The c/a values of the ball-milled and healed samples plotted in Figure 4 have a close agreement with the c/a values of the samples before ball milling and healing steps, which indicates that the ball milling and healing steps did not have a significant structural effect at least on the bulk crystalline phases of the samples. However, the effect of ball milling and healing on the reduction resistance of the solid solutions will be further investigated in the next sections. The specific surface area (A_{BET}) of some of the ball-milled and healed samples is measured by N_2 -physisorption as shown in Table 3. It can be seen that all the samples have $A_{\text{BET}} > 20 \text{ m}^2 \text{ g}^{-1}$, with A_{BET} of $\sim 40\text{-}50 \text{ m}^2 \text{ g}^{-1}$ of the RuO_2 -based samples and A_{BET} of $\sim 25\text{-}30 \text{ m}^2 \text{ g}^{-1}$ of the IrO_2 -based samples, which are comparable to the A_{BET} value of $27.2 \text{ m}^2 \text{ g}^{-1}$ of the commercial benchmark $\text{IrO}_2/\text{TiO}_2$ (Umicore) catalyst. In the next section, the stability of solid solutions in a H_2 -containing atmosphere will be investigated using TGA.

Table 3. Comparison of the specific surface area of the samples measured by the BET method (A_{BET}).

Sample	$\text{RuO}_2\text{-MH}$	$\text{Ti}_{0.05}\text{Ru}_{0.95}\text{O}_x\text{-MH}$	$\text{Ti}_{0.15}\text{Ru}_{0.85}\text{O}_x\text{-MH}$	$\text{Nb}_{0.35}\text{Ru}_{0.65}\text{O}_x\text{-MH}$	$\text{IrO}_2\text{-MH}$	$\text{Ti}_{0.1}\text{Ir}_{0.9}\text{O}_x\text{-MH}$	$\text{IrO}_2/\text{TiO}_2$ (Umicore)
A_{BET} [$\text{m}^2 \text{g}^{-1}$]	42.6	44.7	50.5	44.4	24.8	30.1	27.2

Fundamental aspects of the stability of the solid solutions in H_2 -containing atmospheres.—

Figure 5 shows the TGA temperature ramp experiments of $\text{Ti}_2\text{Ru}_y\text{O}_x$ and $\text{Nb}_2\text{Ru}_y\text{O}_x$ powders and Figure 6 shows the TGA temperature ramp experiments of $\text{Ti}_2\text{Ir}_y\text{O}_x$ powders in 3.3 vol.% H_2/Ar at a heating rate of 5 K min^{-1} . TGA curves of RuO_2 and IrO_2 powders heat treated at the same conditions as the samples shown in Figures 5 and 6 are also plotted for comparison. It can be seen in Figures 5 and 6 that all the TGA curves reach the theoretical mass loss that would be expected for the full reduction of RuO_2 or IrO_2 content of the samples by H_2 to metallic Ru or Ir (see Table 1 and Eq. 2-6) by the end of the experiments. Since TiO_2 and Nb_2O_5 are not reducible by H_2 at the temperature range of the TGA experiment (up to 800°C),²¹⁻²³ the TGA curves imply that the entire mass loss during the experiments correspond to the reduction of RuO_2 and IrO_2 content of the samples through Eq. 2-6. The reduction of pure RuO_2 and IrO_2 samples already starts to take place at $\sim 130^\circ\text{C}$ and $\sim 210^\circ\text{C}$ in Figures 5 and 6, respectively. However, the reduction of RuO_2 in $\text{Ti}_2\text{Ru}_y\text{O}_x$ and $\text{Nb}_2\text{Ru}_y\text{O}_x$ samples and the reduction of IrO_2 in $\text{Ti}_2\text{Ir}_y\text{O}_x$ samples take place at higher temperatures than the pure RuO_2 and pure IrO_2 powders, respectively in Figures 5 and 6. Interestingly, Figure 5 shows that the reduction resistance of RuO_2 in $\text{Ti}_2\text{Ru}_y\text{O}_x$ and $\text{Nb}_2\text{Ru}_y\text{O}_x$ samples increases by increasing TiO_2 or $\text{Nb}_2\text{O}_{2.5}$ content of these samples. In case of $\text{Ti}_2\text{Ru}_y\text{O}_x$ samples in Figure 5a, the onset of RuO_2 reduction increases to $\sim 200^\circ\text{C}$ by increasing TiO_2 content to 15%, and further increasing TiO_2 content to 25% and 50% does not further increase the onset of RuO_2 reduction in these samples. It was shown in Figures 3a and 4a that RuO_2 in $\text{Ti}_2\text{Ru}_y\text{O}_x$ samples only exists in a dissolved form in ssRu-TiO_x and ssTi-RuO_x phases (no pure RuO_2 phase was detected), where it was shown that $\text{Ti}_{0.05}\text{Ru}_{0.95}\text{O}_x$ and

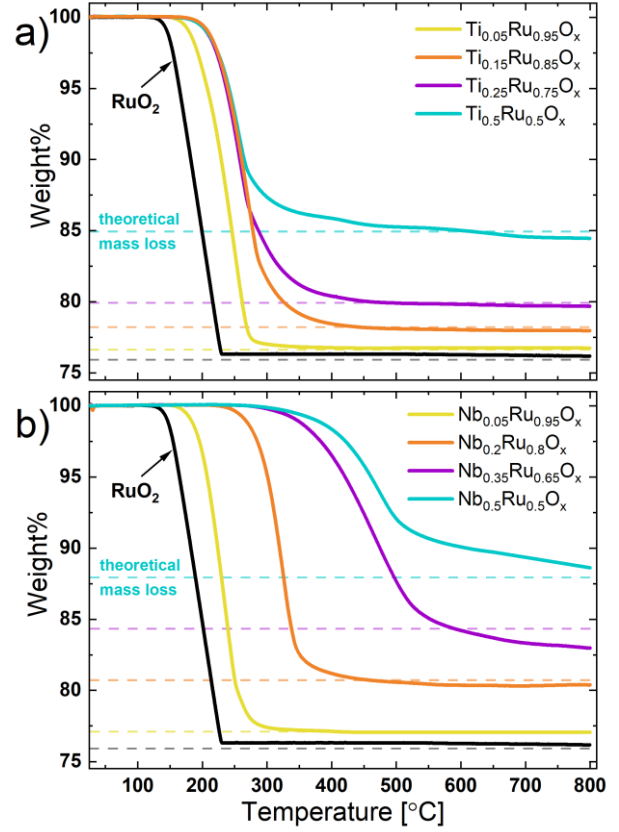


Figure 5. TGA temperature ramp experiments with the a) $\text{Ti}_2\text{Ru}_y\text{O}_x$ and b) $\text{Nb}_2\text{Ru}_y\text{O}_x$ powders under 3.3 vol.% H_2/Ar at a heating rate of 5 K min^{-1} (following the drying/cleaning step; see experimental section). TGA plot of the RuO_2 powder heat treated at the same conditions as the $\text{Ti}_2\text{Ru}_y\text{O}_x$ and $\text{Nb}_2\text{Ru}_y\text{O}_x$ samples is also shown for comparison. The horizontal dashed lines mark the theoretical mass loss of each sample upon the complete reduction of their RuO_2 content by H_2 to metallic Ru (see Table 1).

$\text{Ti}_{0.15}\text{Ru}_{0.85}\text{O}_x$ samples are only composed of ssTi-RuO_x phase, while $\text{Ti}_{0.25}\text{Ru}_{0.75}\text{O}_x$ and $\text{Ti}_{0.5}\text{Ru}_{0.5}\text{O}_x$ samples are composed of ssRu-TiO_x and ssTi-RuO_x phases. The maximum solubility of TiO_2 in ssTi-RuO_x phase in here prepared samples was estimated $\sim 16\text{-}18$ molar% based on the thermodynamic phase diagram in Figure 1a and the structural analysis in Figures 3a and 4a. If the conclusions drawn from Figures 3a and 4a were to be used to interpret the

observed TGA mass loss curves for RuO_2 reduction in $\text{Ti}_2\text{Ru}_y\text{O}_x$ samples in Figure 5a, one could conclude the following: i) the RuO_2 that only exists in a dissolved form in the ssTi-RuO_x phase in $\text{Ti}_{0.05}\text{Ru}_{0.95}\text{O}_x$ and $\text{Ti}_{0.15}\text{Ru}_{0.85}\text{O}_x$ samples is harder to reduce (requires higher temperature) than the pure RuO_2 sample; ii) by increasing the TiO_2 amount dissolved in ssTi-RuO_x phase, it becomes harder to reduce the RuO_2 that is dissolved in this phase (compare the mass loss curves of $\text{Ti}_{0.05}\text{Ru}_{0.95}\text{O}_x$ and $\text{Ti}_{0.15}\text{Ru}_{0.85}\text{O}_x$ samples in Figure 5a); and iii) increasing TiO_2 content of $\text{Ti}_2\text{Ru}_y\text{O}_x$ samples beyond the solubility limit of TiO_2 in ssTi-RuO_x phase (~16-18 molar% TiO_2) does not further increase the reduction resistance of the RuO_2 that is dissolved in ssTi-RuO_x phase; the onset temperatures of the reduction of RuO_2 dissolved in ssTi-RuO_x phase in $\text{Ti}_{0.15}\text{Ru}_{0.85}\text{O}_x$, $\text{Ti}_{0.25}\text{Ru}_{0.75}\text{O}_x$, and $\text{Ti}_{0.5}\text{Ru}_{0.5}\text{O}_x$ samples overlap at ~200 °C in Figure 5a. The increased reduction resistance of RuO_2 in $\text{Nb}_2\text{Ru}_y\text{O}_x$ samples compared to the pure RuO_2 in Figure 5b can also be explained by the conclusions drawn from the structural analysis of these samples in Figures 3b and 4b. It was shown in Figures 3b and 4b that RuO_2 only exists in a dissolved form in ssNb-RuO_x phase in

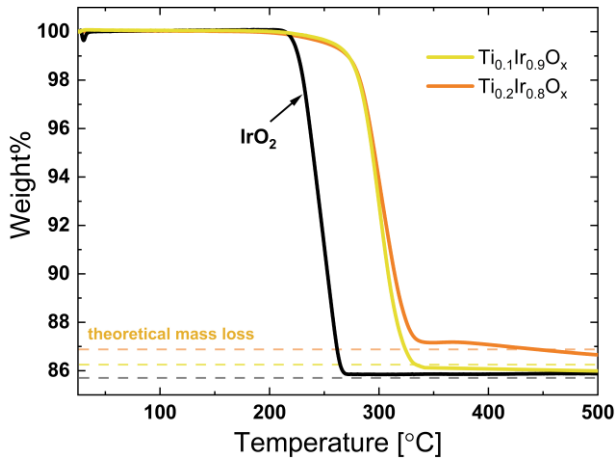


Figure 6. TGA temperature ramp experiments with the $\text{Ti}_2\text{Ir}_y\text{O}_x$ powders under 3.3 vol.% H_2/Ar at a heating rate of 5 K min⁻¹ (following the drying/cleaning step; see experimental section). TGA plot of the IrO_2 powder heat treated at the same conditions as the $\text{Ti}_2\text{Ir}_y\text{O}_x$ samples is also shown for comparison. The horizontal dashed lines mark the theoretical mass loss of each sample upon the complete reduction of their IrO_2 content by H_2 to metallic Ir (see Table 1).

$\text{Nb}_{0.05}\text{Ru}_{0.95}\text{O}_x$, $\text{Nb}_{0.2}\text{Ru}_{0.8}\text{O}_x$, and $\text{Nb}_{0.35}\text{Ru}_{0.65}\text{O}_x$ samples, and the maximum solubility of $\text{NbO}_{2.5}$ in ssNb-RuO_x phase in here prepared samples was estimated ~39 molar%. Interestingly, Figure 5b shows that by increasing $\text{NbO}_{2.5}$ content of the $\text{Nb}_2\text{Ru}_y\text{O}_x$ samples up to 35%, the onset temperature for the reduction of RuO_2 (that only exists as the ssNb-RuO_x phase in these samples) increases significantly, where an onset temperature of ~310 °C is achieved for the reduction of RuO_2 in ssNb-RuO_x phase in $\text{Nb}_{0.35}\text{Ru}_{0.65}\text{O}_x$ sample. Therefore, the RuO_2 dissolved in ssNb-RuO_x phase is harder to reduce than the pure RuO_2 , and by increasing the $\text{NbO}_{2.5}$ amount dissolved in ssNb-RuO_x phase, it becomes harder to reduce the RuO_2 that is dissolved in this phase. It can also be seen in Figure 5b that the onset temperature for the reduction of RuO_2 dissolved in ssNb-RuO_x phase in $\text{Nb}_{0.5}\text{Ru}_{0.5}\text{O}_x$ sample is not significantly higher than that of the $\text{Nb}_{0.35}\text{Ru}_{0.65}\text{O}_x$ sample. This is due to the fact that the maximum solubility of $\text{NbO}_{2.5}$ in ssNb-RuO_x phase is ~39 molar% for the here prepared samples, and further increasing $\text{NbO}_{2.5}$ content of the sample to 50% only results in the formation of a second phase as was shown in Figure 4b.

Similarly, the higher reduction resistance of IrO_2 in $\text{Ti}_2\text{Ir}_y\text{O}_x$ samples compared to the pure IrO_2 in Figure 6 can be explained by the conclusions drawn from the structural analysis of these samples in Figures 3c and 4c. It was shown in Figures 3c and 4c that IrO_2 in $\text{Ti}_{0.1}\text{Ir}_{0.9}\text{O}_x$ sample mainly exists in a dissolved form in ssTi-IrO_x phase, and the maximum solubility of TiO_2 in ssTi-IrO_x phase in the here prepared samples was estimated ~6-9 molar% based on the thermodynamic phase diagram in Figure 1b and the structural analysis in Figures 3c and 4c. Figure 6 shows that the IrO_2 that mainly exists in a dissolved form in the ssTi-IrO_x phase in $\text{Ti}_{0.1}\text{Ir}_{0.9}\text{O}_x$ sample is harder to reduce than the pure IrO_2 sample. However, further increasing TiO_2 content of the samples to 20% does not result in increasing the reduction resistance of the IrO_2 that is dissolved in ssTi-IrO_x phase, as the onset temperatures of the reduction of IrO_2 dissolved in ssTi-IrO_x phase in $\text{Ti}_{0.1}\text{Ir}_{0.9}\text{O}_x$ and $\text{Ti}_{0.2}\text{Ir}_{0.8}\text{O}_x$ samples overlap in Figure 6. This is due to the fact that the maximum solubility of

TiO₂ in ssTi-IrO_x phase is ~6-9 molar% for the here prepared samples, and further increasing TiO₂ content to 20% only results in the formation of a second phase as was shown in Figure 4c.

Based on the here shown TGA data it is clear that the reduction resistance of RuO₂ and IrO₂ can be increased by making a solid solution of these oxides with TiO₂ or Nb₂O₅ in form of ssTi-RuO_x, ssNb-RuO_x, and ssTi-IrO_x phases. The increased reduction resistance of RuO₂ and IrO₂ in the solid solution phases can be attributed to the stabilization effect of TiO₂ and Nb₂O₅, as these oxides are not easily reduced by H₂ at low temperatures.²¹⁻²³ This might mean that the reduction of pure RuO₂ and IrO₂ fundamentally occurs through different mechanisms compared to the reduction of these oxides in the solid solution phases. The reduction of pure RuO₂ and IrO₂ through Eq. 2 and 3 would follow the general steps of the reduction reaction mechanism of metal oxides described in the literature:^{48, 49} i) dissociation of the physisorbed hydrogen molecule on the particle surface; ii) diffusion of the chemisorbed hydrogen through the solid product layer (metallic Ru or Ir) to the reaction interface between the metal oxide and the product metal; iii) chemical reaction of hydrogen with oxygen from the metal oxide at metal oxide/metal interface; iv) formation of O²⁻ vacancies in the metal oxide lattice at the reaction interface and removal of product H₂O upon diffusion through the product metal layer; v) annihilation of O²⁻ vacancies by the rearrangement of lattice with the eventual formation of metal product; and vi) further movement of the reaction interface to sub-surface oxide layers. A general schematic representation of this process is shown for pure RuO₂ or IrO₂ in the upper diagram in Figure 7.

It is speculated that the reduction of RuO₂ and IrO₂ dissolved in the solid solution phases through Eq. 4-6 would follow the six general steps described above, but with differences in steps iv) and v). Assuming that RuO₂ or IrO₂ dissolved in the solid solution phases are the only reducible components of these phases, the O²⁻ vacancies formed in the solid solution lattice in step iv) are due to the removal of O_{RuO2} or O_{IrO2} and

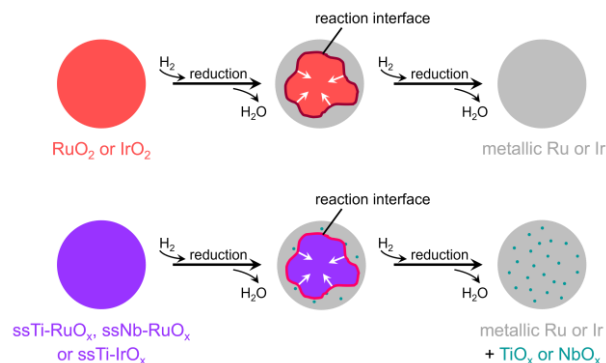


Figure 7. Schematic representation of the reduction of the pure RuO₂ or IrO₂ (upper diagram) and the solid solution phases prepared in this study (lower diagram). The reduction reaction mechanism of the solid solutions in the lower diagram is suggested based on the assumption that RuO₂ or IrO₂ dissolved in the solid solution phases is the only reducible component of these phases and TiO_x or NbO_x domains would form at the end of the reaction due to their negligible solubility in metallic Ru or Ir.

the formation of O²⁻_{RuO2} or O²⁻_{IrO2} vacancies in the solid solution lattice. Since O_{TiO2} or O_{NbO2.5} are not removed from the solid solution lattice, they would remain in form of [Ti-O] or [Nb-O] units at the reaction interface at the end of step iv). In step v), rearrangement of the solid solution lattice to form metallic Ru or Ir would be accompanied with the annihilation of O²⁻_{RuO2/IrO2} vacancies. In this case, the remaining [Ti-O] or [Nb-O] units at the reaction interface would have to diffuse and combine to form TiO_x or NbO_x domains next to the metallic Ru or Ir product. Note that this hypothesis is based on the assumption that TiO_x and NbO_x have negligible solubilities in metallic Ru or Ir and they would have to precipitate as separate domains after the reduction of RuO₂ or IrO₂ in the solid solution phases. This assumption should be quite reasonable at least in case of TiO_x solubility in metallic Ru and Ir based on the thermodynamic phase diagrams in Figure 1, where it can be seen that after the thermal decomposition of RuO₂ and IrO₂ to metallic Ru and Ir at T > 1425 °C and T > 1040 °C in Figure 1a and b, respectively, no significant TiO₂ solubility in the metallic Ru or Ir would be expected. The precipitation of TiO_x or NbO_x domains during the reduction reaction would add an additional energy barrier for the reduction of RuO₂ and IrO₂ dissolved in the solid solution phases and that might explain their increased

reduction resistance compared to the pure RuO_2 and IrO_2 . A general schematic representation of the reduction of RuO_2 and IrO_2 dissolved in the solid solution phases is suggested in the lower diagram in Figure 7. Next, we will investigate the effect of ball milling process on the reduction resistance of the solid solution catalysts.

Effect of ball milling on the reduction resistance of the solid solution catalysts.—

As discussed in the previous sections, the high temperature heat treatment for the formation of solid solutions (see experimental section and Figure 2) would lead to a loss of specific surface area of the samples, and therefore, a ball milling step is required. A healing step is also required for the partial recovery of the reduction resistance of the samples after the ball milling step, as was shown in our previous study.¹⁷ Since ssTi-RuO₂, ssNb-RuO₂, and ssTi-IrO₂ phases are mainly composed of RuO_2 or IrO_2 , they are the desired solid solution phases for OER catalysis, and the samples selected for ball milling and healing are mainly composed of these phases. That being said, $\text{Ti}_{0.05}\text{Ru}_{0.95}\text{O}_x$, $\text{Ti}_{0.15}\text{Ru}_{0.85}\text{O}_x$, $\text{Nb}_{0.2}\text{Ru}_{0.8}\text{O}_x$, $\text{Nb}_{0.35}\text{Ru}_{0.65}\text{O}_x$, and $\text{Ti}_{0.1}\text{Ir}_{0.9}\text{O}_x$ samples were selected for the ball milling and healing steps together with the pure RuO_2 and IrO_2 samples. TGA temperature ramp experiments of these samples in 3.3 vol.% H_2/Ar at a heating rate of 5 K min⁻¹ before and after ball milling and healing steps are shown in Figures 8 and 9. TGA plots of RuO_2 -MH and IrO_2 -MH vs RuO_2 and IrO_2 in Figures 8 and 9, respectively, show a lower reduction resistance for the ball milled and healed samples in form of an even shift of the entire mass loss curves to lower temperatures. In our previous study, we showed that the decrease of reduction resistance of this IrO_2 sample after ball milling and healing steps is mainly due to a ~28 times decrease of its average particle size,¹⁷ as smaller particles are expected to be reduced easier.⁴⁸ Similarly, the lower reduction resistance of RuO_2 -MH compared to RuO_2 in Figure 8 is also expected to be due to a smaller particle size of RuO_2 -MH compared to RuO_2 .

Interestingly, the decrease of reduction resistance of $\text{Ti}_2\text{Ru}_y\text{O}_x$, $\text{Nb}_2\text{Ru}_y\text{O}_x$, and $\text{Ti}_2\text{Ir}_y\text{O}_x$ samples after ball

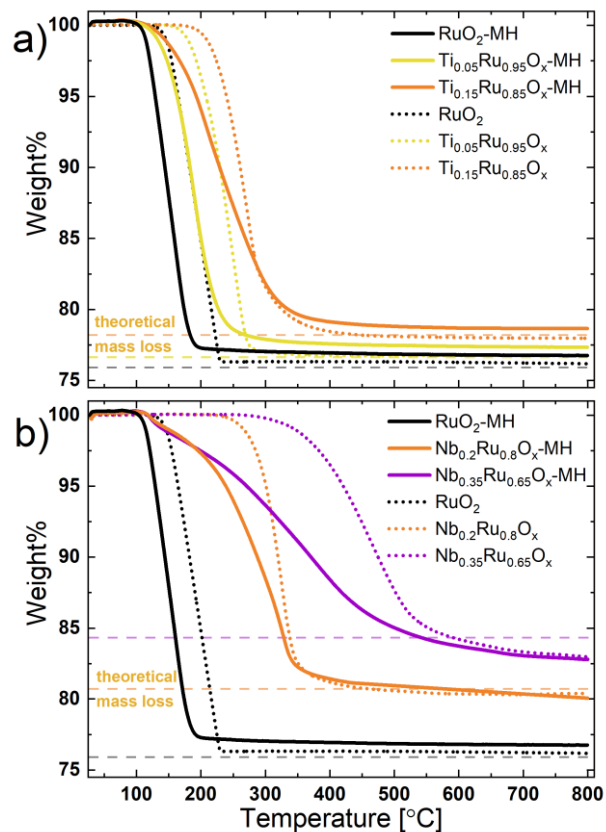


Figure 8. TGA temperature ramp experiments with the a) $\text{Ti}_2\text{Ru}_y\text{O}_x$ -MH and $\text{Ti}_2\text{Ru}_y\text{O}_x$ and b) $\text{Nb}_2\text{Ru}_y\text{O}_x$ -MH and $\text{Nb}_2\text{Ru}_y\text{O}_x$ powders under 3.3 vol.% H_2/Ar at a heating rate of 5 K min⁻¹ (following the drying/cleaning step; see experimental section). TGA plots of the RuO_2 and RuO_2 -MH powders are also shown for comparison. The horizontal dashed lines mark the theoretical mass loss of each sample upon the complete reduction of their RuO_2 content by H_2 to metallic Ru (see Table 1).

milling and healing is not in form of an even shift of the entire mass loss curves to lower temperatures in Figures 8 and 9. Instead, the TGA curves of $\text{Ti}_2\text{Ru}_y\text{O}_x$ -MH, $\text{Nb}_2\text{Ru}_y\text{O}_x$ -MH, and $\text{Ti}_2\text{Ir}_y\text{O}_x$ -MH samples show lower reduction resistance but an uneven mass loss behavior with increasing temperature compared to $\text{Ti}_2\text{Ru}_y\text{O}_x$, $\text{Nb}_2\text{Ru}_y\text{O}_x$, and $\text{Ti}_2\text{Ir}_y\text{O}_x$ samples. This behavior is more obvious in Figure 8b, where unlike the TGA curves of $\text{Nb}_2\text{Ru}_y\text{O}_x$ samples, the TGA curves of $\text{Nb}_2\text{Ru}_y\text{O}_x$ -MH samples overlap at the beginning of the reduction reaction at $T < 200$ °C, and then they start to deviate when the reduction reaction proceeds by increasing the temperature to > 200 °C. It was shown in Figures 5 and 6 that the temperature that is required for the reduction reaction of ssTi-RuO_x, ssNb-

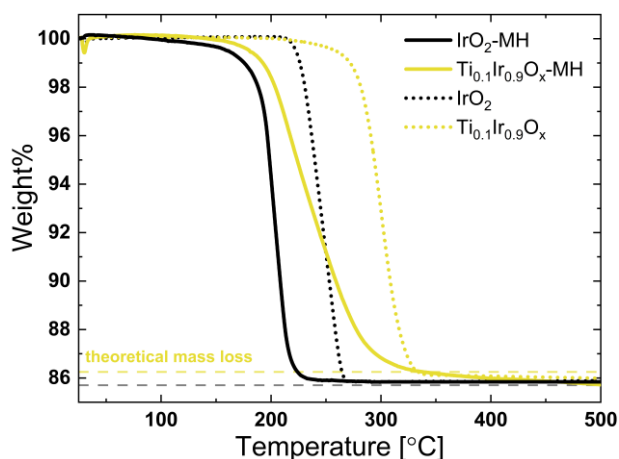


Figure 9. TGA temperature ramp experiments with the $\text{Ti}_{0.1}\text{Ir}_{0.9}\text{O}_x$ -MH and $\text{Ti}_{0.1}\text{Ir}_{0.9}\text{O}_x$ powders under 3.3 vol.% H_2/Ar at a heating rate of 5 K min^{-1} (following the drying/cleaning step; see experimental section). TGA plots of the IrO_2 -MH and IrO_2 powders are also shown for comparison. The horizontal dashed lines mark the theoretical mass loss of each sample upon the complete reduction of their IrO_2 content by H_2 to metallic Ir (see Table 1).

RuO_x , and ssTi-Ir O_x phases to take place can be directly correlated to the amount of TiO_2 or $\text{NbO}_{2.5}$ dissolved in these phases, and the higher the amount of dissolved TiO_2 or $\text{NbO}_{2.5}$ in these solid solution phases, the higher the temperature required for the reduction to take place. Considering that $\text{Nb}_{0.2}\text{Ru}_{0.8}\text{O}_x$ and $\text{Nb}_{0.35}\text{Ru}_{0.65}\text{O}_x$ samples are only composed of ssNb-Ru O_x phase but with different dissolved amounts of $\text{NbO}_{2.5}$ (see Figure 4b), the TGA curves of $\text{Nb}_{0.2}\text{Ru}_{0.8}\text{O}_x$ -MH and $\text{Nb}_{0.35}\text{Ru}_{0.65}\text{O}_x$ -MH samples in Figure 8b should not have overlapped at the beginning of the reduction reaction at $T < 200 \text{ }^\circ\text{C}$ unless a partial phase segregation had occurred. The same argument can be made for $\text{Ti}_2\text{Ru}_y\text{O}_x$ -MH samples in Figure 8a and for $\text{Ti}_{0.1}\text{Ir}_{0.9}\text{O}_x$ -MH vs IrO_2 -MH samples in Figure 9. Therefore, these observations suggest that the decrease of reduction resistance of $\text{Ti}_2\text{Ru}_y\text{O}_x$, $\text{Nb}_2\text{Ru}_y\text{O}_x$, and $\text{Ti}_2\text{Ir}_y\text{O}_x$ samples after ball milling and healing is not merely due to the decrease of their average particle size, but structural alteration of the samples might have also occurred, where the dissolved TiO_2 or $\text{NbO}_{2.5}$ in the solid solution phases might have partially segregated. It should be mentioned that the decrease in reduction resistance of the solid solution samples already occurred after the ball milling step, and the healing

step partially recovered the compromised reduction resistance of the samples caused by ball milling (data are not shown here), therefore, a possible segregation of TiO_2 and $\text{NbO}_{2.5}$ from the solid solution phases might have happened during the ball milling step. This means that the high impact of zirconia beads during the ball milling step can cause such phase segregation.

In fact, it is known in mechanochemistry that plastic deformations lead to the formation of thermodynamic equilibrium nanocrystalline phases via local atomic rearrangements.⁵⁰ Ball milling is one of the mechanochemical synthesis routes, where the high impact of the beads can provide the mechanical stress required for the formation of nanocrystalline materials.^{51, 52} However, it is also shown in the literature that the formation of nanocrystals upon ball milling is often accompanied by the formation of amorphous domains in the near surface region of the ball milled materials.⁵³⁻⁵⁵ Based on the phase diagrams in Figure 1, the ssTi-Ru O_x and ssTi-Ir O_x phases prepared in this study are not thermodynamic equilibrium phases at room temperature, as they are trapped in a highly supersaturated state upon fast cooling after the high temperature heat treatment during synthesis (see experimental section and Figure 2). Assuming that ssNb-Ru O_x is also a non-equilibrium phase at room temperature, and it is also trapped in a supersaturated state, one would expect that the solid solution phases prepared in this study would thermodynamically segregate to their corresponding metal oxide phases if enough kinetic energy were provided to these systems. As the ball milling process can provide the required mechanical energy for the solid-state reactions and the formation of equilibrium phases that are stable at low temperatures, it can also cause the partial segregation of TiO_2 or $\text{NbO}_{2.5}$ in the supersaturated and non-equilibrium solid solution phases prepared in this study, which would result in the partial loss of reduction resistance of these materials. However, ball milling induced structural changes in form of nanocrystalline segregations or near-surface amorphous domains were not detectable by XPD, as

the diffractograms of the ball milled and healed samples in Figure A-1 were only composed of the reflections of the highly crystalline bulk solid solution phases and their refinement results in Figure 4 shows that the bulk crystalline phases are not significantly affected by the ball milling process.

Overall, the TGA temperature ramp experiments showed that although the decrease in reduction resistance of the solid solutions after ball milling and healing is more severe than the pure RuO_2 or IrO_2 , the ball milled and healed solid solution catalysts still have higher reduction resistances than the respective $\text{RuO}_2\text{-MH}$ or $\text{IrO}_2\text{-MH}$ samples. Therefore, to show the significance of such improvement in reduction resistance of the solid solution catalysts, next section will demonstrate the stability of these materials at conditions that more closely reflect those in a real PEMFC anode.

Stability of the solid solution catalysts in a simulated PEMFC anode reductive environment.—

We have shown in our previous studies that the near-surface layer(s) of conventionally prepared IrO_2 anode co-catalysts can be completely reduced to metallic Ir upon exposure to H_2 under the normal operating conditions of a PEMFC anode.^{16, 17} Metallic Ir formed on the catalyst surface can dissolve during anode potential transients between $\sim 0 V_{\text{RHE}}$ and $\sim 1 V_{\text{RHE}}$ caused by the passage of $\text{H}_2/\text{air}_{\text{anode}}$ front during SUSD cycles,^{16, 17} as metallic Ir surfaces have significantly higher transient dissolution rate compared to the heat treated IrO_2 surfaces upon potential cycling at this potential window.⁵⁶ Similarly, metallic Ru surfaces are also reported to have significantly higher transient dissolution rate than the heat treated RuO_2 surfaces during potential transients between $\sim 0 V_{\text{RHE}}$ and $\sim 1 V_{\text{RHE}}$.¹⁸ Therefore, reduction resistance of RuO_2 or IrO_2 anode co-catalysts under the normal operation conditions of a PEMFC anode is a good measure to predict their transient dissolution stability during SUSD cycles. Long-term isothermal TGA experiments in 3.3 vol.% H_2/Ar at 80 °C can reliably estimate the reduction resistance of a catalyst under the simulated reductive environment of a PEMFC hydrogen anode.^{16, 17} This technique is

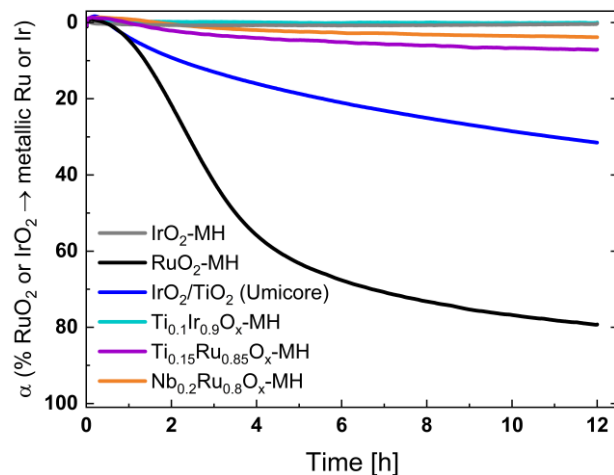


Figure 10. Long-term isothermal TGA experiments (following the drying/cleaning step; see experimental section) on the reduction of the catalysts prepared in this study and the $\text{IrO}_2/\text{TiO}_2$ (Umicore) catalyst in 3.3 vol.% H_2/Ar at 80 °C, aiming to simulate the PEMFC hydrogen anode reductive environment. Assuming that RuO_2 and IrO_2 are the only reducible components of the samples, the y-axis represents the fraction of RuO_2 or IrO_2 of the samples (see Table 1 for RuO_2 or IrO_2 content of the samples) that is reduced to metallic Ru or Ir (α).

utilized for screening of the stability of different catalysts in this study and the results are shown in Figure 10. Since RuO_2 and IrO_2 are the only reducible components of the samples based on Eq. 2-6, the mass losses during this experiment are converted to the fraction of RuO_2 or IrO_2 of the samples (see Table 1 for RuO_2 or IrO_2 content of the samples) reduced to metallic Ru or Ir (α), as shown at the y-axis in Figure 10. It should be noted that any mass loss observed during this isothermal TGA experiment would correspond to the reduction of RuO_2 or IrO_2 of the samples by H_2 through Eq. 2-6, and the desorption of adsorbed water or any other organic residues on the catalysts surface does not contribute to the observed mass loss due to the in situ drying/cleaning step prior to the TGA measurement under reducing atmosphere (see experimental section). It can be seen in Figure 10 that $\sim 30\%$ of IrO_2 phase of the commercial benchmark $\text{IrO}_2/\text{TiO}_2$ (Umicore) catalyst is reduced to metallic Ir after 12 h of the TGA experiment at 80 °C. It was shown in our previous study that this catalyst consists of $\sim 50/50$ mixture of crystalline IrO_2 (c- IrO_2) and amorphous IrO_2 (a- IrO_x), and the low

reduction resistance of this catalyst was attributed to the reduction of a-IrO_x species at low temperatures.¹⁶ However, no significant reduction is observed for IrO₂-MH sample in Figure 10. Such reduction stability was attributed to the dominance of c-IrO₂ species in this sample due to the heat treatment at 1000 °C in our previous study, as c-IrO₂ species were shown to have high reduction resistance.¹⁷ Based on the TGA temperature ramp experiments in Figure 9, Ti_{0.1}Ir_{0.9}O_x-MH sample has a slightly higher reduction resistance than IrO₂-MH sample. However, since IrO₂-MH sample is not reduced after 12 h at 80 °C in Figure 10, no significant reduction is neither observed for Ti_{0.1}Ir_{0.9}O_x-MH sample after 12 h of TGA experiment in Figure 10.

Interestingly, ~80% of RuO₂-MH sample is reduced to metallic Ru at the end of the TGA experiment in Figure 10. Considering that the temperature for the heat treatment of RuO₂-MH (1300 °C) is even higher than that of IrO₂-MH (1000 °C), the lower reduction resistance of RuO₂-MH compared to IrO₂-MH in Figure 10 indicates that unlike IrO₂, RuO₂ does not gain enough reduction resistance to be irreducible at 80 °C only by heat treatment in air at high temperatures. The lower reduction resistance of RuO₂-MH than IrO₂-MH is also reflected by the observation that the reduction of RuO₂-MH in TGA temperature ramp experiment in Figure 8 occurs at ~50-60 °C lower than that of IrO₂-MH in Figure 9. Therefore, the formation of RuO₂-based solid solutions significantly improves the reduction resistance of RuO₂ in Figure 10, where only ~4% and ~7% of RuO₂ respectively in Nb_{0.2}Ru_{0.8}O_x-MH and Ti_{0.15}Ru_{0.85}O_x-MH samples is reduced after 12 h of the TGA experiment at 80 °C. It should be noted that due to a possible anisotropy in the structure of Nb_{0.2}Ru_{0.8}O_x-MH and Ti_{0.15}Ru_{0.85}O_x-MH samples (as suggested in the previous section), their TGA temperature ramp experiments show an uneven mass loss behavior with increasing temperature in Figure 8, where RuO₂ reduction in these samples becomes more difficult (occurs at higher temperature) as the reduction reaction continues to take place. This means that unlike RuO₂-MH sample, the reduction

kinetics of RuO₂ in the solid solution samples at 80 °C will become much slower as the reduction reaction proceeds, i.e., the mass loss rates observed for these samples in Figure 10 will become much smaller upon extended time. Although the reduction of a few monolayers of oxide (ML_{oxide}) on a catalyst surface is sufficient to change its electrochemical properties (its OER activity and its stability during SUSD events),¹⁶ based on the data provided here, it will take much longer for the reduction of a few ML_{RuO₂} on the surface of solid solution catalysts compared to that of RuO₂-MH catalyst and compared to the reduction of a few ML_{IrO₂} on the surface of the commercial benchmark IrO₂/TiO₂ (Umicore) catalyst. However, additional stabilization strategies might be required to further increase the reduction resistance of RuO₂ and making it comparable to the reduction resistance of IrO₂-MH and Ti_{0.1}Ir_{0.9}O_x-MH catalysts. In the next section, the OER activity of the prepared catalysts will be investigated using the RDE technique.

OER activity of the solid solution catalysts measured by the RDE technique.

— In our previous study, we have shown that the OER activity of an IrO₂ catalyst measured by the RDE technique does not always reflect the activity of the same catalyst in the anode of an MEA during cell reversal tests in a PEMFC.¹⁶ This is due to the fact that when an IrO₂ catalyst is reducible in the PEMFC H₂ anode reductive environment, metallic Ir forms in the near-surface region of the catalyst and drastically increases the OER activity of the catalyst due to the higher intrinsic OER activity of metallic Ir surfaces compared to the heat-treated IrO₂ surfaces.¹⁶ Nevertheless, since the RDE technique is a quick and straightforward screening tool for the investigation of the OER activity of catalysts synthesized by different routes, it can still provide useful hints for comparing the OER activity of the as-synthesized catalysts in this study, as long as the data is being carefully interpreted by considering the reduction resistance of the catalysts in a PEMFC H₂ anode conditions.

The OER activity of the catalysts is measured by the RDE technique and the OER polarization curves are shown in Figure 11, whereby the potential that

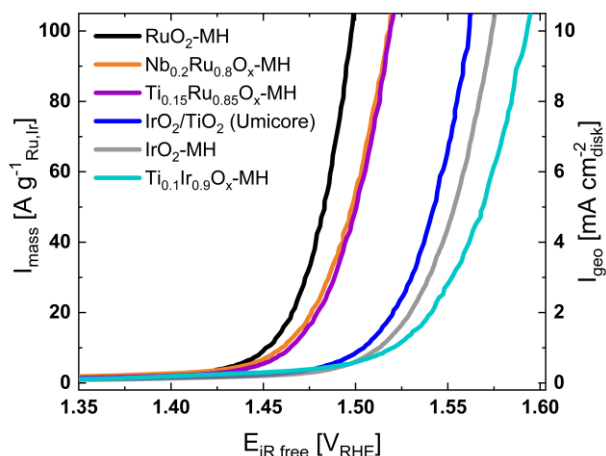


Figure 11. OER activity measurement of the catalysts using the RDE technique in a 0.05 M H₂SO₄ electrolyte at room temperature and a catalyst loading of 0.1 mg_{Ru/Ir} cm⁻²_{disk}. The polarization curves are recorded at 20 mV s⁻¹ and an electrode rotation rate of 2500 RPM in the O₂-saturated electrolyte. The left y-axis represents the current normalized to the ruthenium or iridium mass of the catalyst layers (I_{mass}), while the current normalized to the geometric area of the disk electrode (I_{geo}) is given on the right y-axis.

corresponds to the electrode current of 10 mA cm⁻²_{disk} is frequently taken as a measure of the OER activity.⁵⁷ The OER polarization curve of the IrO₂/TiO₂ (Umicore) catalyst is shown as a commercial benchmark reference to compare the activity of the catalysts prepared in this study. It can be clearly seen that all the RuO₂-based catalysts show higher OER activities than the IrO₂-based catalysts, with RuO₂-MH having a better OER activity by ~75 mV compared to IrO₂-MH at an electrode current of 10 mA cm⁻²_{disk}. Considering that the A_{BET} of RuO₂-MH catalyst (42.6 m² g⁻¹) is only by a factor of ~1.7 higher than that of IrO₂-MH catalyst (24.8 m² g⁻¹) as shown in Table 3, such higher OER mass activity of RuO₂-MH than IrO₂-MH is mainly attributed to the higher intrinsic OER activity of RuO₂ compared to IrO₂.^{58, 59} The IrO₂/TiO₂ (Umicore) catalyst shows a better OER activity by ~15 mV compared to IrO₂-MH at an electrode current of 10 mA cm⁻²_{disk}. Although both catalysts have comparable A_{BET} values (see Table 3), the difference in OER mass activities is due to the presence of more OER active a-IrO_x species in the benchmark catalyst consisting of a ~50/50 mixture of a-IrO_x/c-IrO₂ species compared to the dominating c-IrO₂ species with lower OER activity

in IrO₂-MH catalyst.¹⁷

The solid solution catalysts show lower OER activities by ~20 mV compared to their parent RuO₂-MH or IrO₂-MH catalysts in Figure 11. The A_{BET} measurements in Table 3 show similar or slightly higher A_{BET} values for the solid solution catalysts compared to the parent RuO₂-MH or IrO₂-MH catalysts, therefore, the observed lower OER activities of the solid solution catalysts than RuO₂-MH or IrO₂-MH catalysts in Figure 11 might be related to the effect of TiO₂ or NbO_{2.5} in the solid solution catalysts structure. The binding energy of OER intermediates on oxide surfaces is frequently taken as a descriptor for OER activity of oxide catalysts in the literature, where low OER activity is commonly predicted for oxide surfaces such as TiO₂ and NbO₂, which bind the oxygen from the OER intermediates too strongly or too weakly.⁶⁰⁻⁶² The incorporation of TiO₂ or NbO_{2.5} in the structure of the solid solution catalysts might as well affect the binding energy of the OER intermediates and the catalyst surface and therefore result in the lower OER activity of the solid solutions compared to RuO₂-MH and IrO₂-MH. Although Ti_{0.1}Ir_{0.9}O_x-MH catalyst has the lowest OER activity among the catalysts measured in Figure 11, Nb_{0.2}Ru_{0.8}O_x-MH and Ti_{0.15}Ru_{0.85}O_x-MH catalysts have ~55 mV better OER activity than the reduction-resistant IrO₂-MH catalyst. Such high OER activity of Nb_{0.2}Ru_{0.8}O_x-MH and Ti_{0.15}Ru_{0.85}O_x-MH catalysts and their better reduction resistance than the benchmark IrO₂/TiO₂ (Umicore) catalyst (see Figure 10) make these solid solution catalysts attractive anode co-catalyst candidates for PEMFC applications. Whether these RuO₂-based catalysts have sufficient stability at high OER potentials during cell reversal events (>> 1 V_{RHE}) will be investigated by MEA measurements in the next section.

Electrochemical stability of the RuO₂-based catalysts measured in an MEA.— During cell reversal events in a PEMFC, the anode potential rises to >> 1 V_{RHE}, where COR and OER take place. The low onset potential of the OER on anode co-catalysts prevents the anode potential from reaching high values during cell reversal, and thus significantly reduces the extent of the COR on the Pt/C anode

catalyst at the anode electrode. However, the anode OER co-catalyst should be stable at high potentials during OER in order to mitigate the damages caused by repetitive cell reversal events. Although RuO_2 has superior OER activity to IrO_2 and can significantly reduce the COR rate during cell reversals, due to the low thermodynamic stability of ruthenium at high potentials during OER, the rate of its dissolution and corrosion is unacceptably high and RuO_2 is typically not considered as a stable OER catalyst.^{24, 25} OER durability tests are performed here in order to get a better insight of the stability of RuO_2 -MH catalyst, and to investigate whether the RuO_2 -based solid solution catalysts have higher stability than RuO_2 -MH catalyst at high potentials during OER. Since OER durability tests using RDE technique are not reliable due to the artefact caused by the accumulation of O_2 bubbles within the catalyst layer,⁶³⁻⁶⁵ stability tests are performed using MEAs in a PEMWE as shown in Figure 12. The MEAs with 5 cm^2 active area are

composed of a Pt/C catalyst at the H_2 cathode electrode and the investigated OER catalysts at the O_2 anode electrode, namely RuO_2 -MH, $\text{Ti}_{0.15}\text{Ru}_{0.85}\text{O}_x$ -MH, and the benchmark $\text{IrO}_2/\text{TiO}_2$ (Umicore) catalyst. The benchmark $\text{IrO}_2/\text{TiO}_2$ (Umicore) catalyst was shown to be an active and stable OER catalyst for PEMWE applications in our previous studies,^{66, 67} and it is used as a reference to compare the stability of the here-investigated RuO_2 -based catalysts. After cell assembly and warm up, anode cyclic voltammograms (CVs) were recorded at the beginning of test (BoT) as shown in Figure 12a. The CVs are measured in order to obtain insights into the stability of the anode catalysts during OER stability tests, where Figure 12a shows comparable CV sizes of the catalysts at the BoT. It should be noted that electrochemical conditioning of MEAs at high cell voltages is typically performed prior to electrochemical investigations in our previous studies, where OER at the anode and HER at the cathode take place during the conditioning

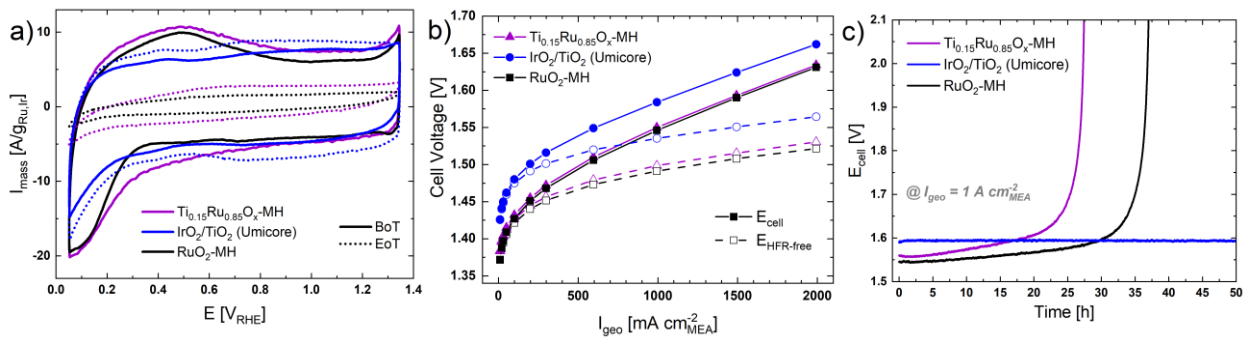


Figure 12. Stability investigation of the OER catalysts using 5 cm^2 MEAs in a single cell PEMWE setup. All the experiments were performed at ambient pressure and at 80 °C, while supplying DI water (5 ml min^{-1}) to the anode of the electrolysis cell. The prepared MEAs using a Nafion™ 212 membrane were composed of a Pt/C catalyst at the H_2 cathode electrode ($0.39 \pm 0.01 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}_{\text{MEA}}$) and the investigated OER catalysts at the O_2 anode electrode, namely $\text{Ti}_{0.15}\text{Ru}_{0.85}\text{O}_x$ -MH ($1.54 \text{ mg}_{\text{Ru}} \text{ cm}^{-2}_{\text{MEA}}$), $\text{IrO}_2/\text{TiO}_2$ (Umicore, $1.54 \text{ mg}_{\text{Ir}} \text{ cm}^{-2}_{\text{MEA}}$), and RuO_2 -MH ($1.35 \text{ mg}_{\text{Ru}} \text{ cm}^{-2}_{\text{MEA}}$). a) Anode CVs measured at the beginning of test (BoT, before ever conditioning the cells or performing any electrochemical measurement) and at the end of test (EoT, after measuring a polarization curve as shown in b) and performing a constant current stability test as shown in c)). The y-axis represents the current normalized to the ruthenium or iridium mass of the anode electrodes (i_{mass}). CVs were recorded at a scan rate of 100 mV s^{-1} while supplying dry H_2 to the cathode at 50 ml min^{-1} (the Ru/Ir-based anodes served as working electrodes, and the Pt-based cathodes as counter and reference electrode). b) Ambient pressure polarization curves of the MEAs measured directly after measuring the BoT CVs. The full lines and symbols represent the measured cell voltage, the dashed lines and empty symbols give the cell voltage corrected by HFR-values measured at each current density, with HFR-values ranging at $\sim 49\text{-}56 \text{ m}\Omega \text{ cm}^2_{\text{MEA}}$ (data not shown here). c) Constant current stability tests at $1 \text{ A cm}^{-2}_{\text{MEA}}$ measured directly after recording the polarization curves. The tests are performed either for 50 h or until the cell voltage reaches an upper cut-off voltage of 2.1 V.

step.^{34, 67} However, it was noticed during preliminary experiments in this study that the RuO₂-based catalysts already show a high degradation rate during such electrochemical conditioning steps at high anode potentials. Therefore, no electrochemical conditioning of the MEAs was performed in this study in order to prevent a premature degradation of the RuO₂-based catalysts before the actual electrochemical investigations. After recording the BoT anode CVs, polarization curves were recorded at 80 °C and ambient pressure (i.e., H₂ and O₂ partial pressures of ~53 kPa) as shown in Figure 12b. For the MEAs with the RuO₂-based catalysts, the HFR-free cell voltage is lower than for the MEA based on the benchmark IrO₂/TiO₂ (Umicore) catalyst by ~50 mV at 0.1 A cm⁻²_{MEA} and by ~35 mV at 2 A cm⁻²_{MEA}. Considering the relatively similar anode catalyst loadings (1.35-1.54 mg_{Ru/Ir} cm⁻²_{MEA}), this can be explained by a lower overpotential for the OER due to the much higher mass activities of the RuO₂-based catalysts than the benchmark catalyst (same was suggested by the RDE data shown in Figure 11).

After recording the polarization curves, constant current (1 A cm⁻²_{MEA}) stability test was performed at 80 °C and ambient pressure as shown in Figure 12c. At the beginning of the stability test (time = 0 h) in Figure 12c, the cell voltage for the MEAs with the RuO₂-based catalysts is ~40 mV lower than for the MEA based on the benchmark catalyst, which agrees relatively well with the data recorded at 1 A cm⁻²_{MEA} in the polarization curves in Figure 12b. The MEA based on the benchmark IrO₂/TiO₂ (Umicore) catalyst shows a stable cell voltage of ~1.590-1.595 V over the 50 h of the constant current stability test in Figure 12c. However, the cell voltages of the MEAs with the RuO₂-based catalysts show a gradual increase over time, followed by a sudden jump to the upper cut-off voltage of 2.1 V after ~27.5 h and ~37 h for the MEAs based on Ti_{0.15}Ru_{0.85}O_x-MH and RuO₂-MH, respectively.

In order to check if such MEA performance loss is associated with the loss of anode active materials, anode CVs were recorded at the end of test (EoT) right after the constant current stability tests, as shown in Figure 12a. Following the stable performance of the

MEA with the benchmark IrO₂/TiO₂ (Umicore) catalyst in Figure 12c, its CV at the EoT in Figure 12a does not significantly differ from the CV at the BoT. In fact, the slightly bigger CV at the EoT than the BoT for the IrO₂/TiO₂ (Umicore) catalyst might be due to the electrochemical conditioning of the MEA upon recording a polarization curve (Figure 12b) and the constant current stability test (Figure 12c), as no electrochemical conditioning of the MEAs was performed prior to recording the CVs at the BoT. However, the performance loss of the MEAs with the RuO₂-based catalysts during the stability test in Figure 12c is accompanied by > 80% reduction in the size of the CVs at the EoT compared to the BoT as shown in Figure 12a. This can be attributed to the thermodynamic instability of ruthenium and its dissolution at high anode potentials during OER stability test, which results in a significant loss of the anode active material.

Interestingly, the MEA with Ti_{0.15}Ru_{0.85}O_x-MH shows a faster performance degradation and failure than the MEA with RuO₂-MH in Figure 12c, indicating that the RuO₂-based solid solution catalyst is less stable than the pure RuO₂ during the OER stability test. Due to the lower mass activity and higher OER overpotential of Ti_{0.15}Ru_{0.85}O_x-MH than RuO₂-MH (as suggested by the RDE data in Figure 11), the MEA with Ti_{0.15}Ru_{0.85}O_x-MH shows slightly higher cell voltage (~14 mV) than the MEA with RuO₂-MH at the beginning of the stability test (time = 0 h) in Figure 12c. The higher cell voltage of the MEA with Ti_{0.15}Ru_{0.85}O_x-MH, which is due to the higher anode potential, would accelerate ruthenium dissolution and result in a faster degradation of the anode catalyst than the MEA with RuO₂-MH. It should be noted that the cell voltage difference between the MEAs with the RuO₂-based catalysts at the beginning of the stability test at 1 A cm⁻²_{MEA} in Figure 12c (~14 mV) is slightly higher than the cell voltage difference recorded at 1 A cm⁻²_{MEA} in the polarization curves in Figure 12b (~4 mV). This might be due to the faster degradation of Ti_{0.15}Ru_{0.85}O_x-MH than RuO₂-MH that already occurs during recording the data at 1.5 and 2 A cm⁻²_{MEA} at the end of recording the polarization curves in Figure 12b,

where the MEA with $\text{Ti}_{0.15}\text{Ru}_{0.85}\text{O}_x\text{-MH}$ shows ~ 9 mV higher HFR-free cell voltage than the MEA based on $\text{RuO}_2\text{-MH}$. The higher HFR-free cell voltage for the MEA with $\text{Ti}_{0.15}\text{Ru}_{0.85}\text{O}_x\text{-MH}$, which is due to the higher anode potential, would result in the higher degradation of $\text{Ti}_{0.15}\text{Ru}_{0.85}\text{O}_x\text{-MH}$ compared to $\text{RuO}_2\text{-MH}$ prior to the stability test in Figure 12c. Based on the data presented in this study, RuO_2 in a solid solution phase has a higher reduction resistance than the pure RuO_2 , however, the lower OER activity of the solid solution catalyst exerts higher potentials to the electrode during OER which accelerates the dissolution and loss of the catalyst. Therefore, the future research on developing reduction resistant RuO_2 catalysts should focus on improving the stability of these catalysts at high potentials during OER.

Conclusions

In this study, an unprecedented approach was introduced for the preparation of reduction resistant RuO_2 - and IrO_2 -based anode co-catalysts for mitigating cell voltage reversal damages in PEMFCs. The approach is based on the formation of a solid solution phase between RuO_2 or IrO_2 and Nb_2O_5 or TiO_2 . The procedure to make a high surface area solid solution catalyst is composed of three steps: i) a high temperature heat treatment step for the formation of the solid solution phases; ii) a ball milling step of the solid solution samples to reach specific surface area of $> 25 \text{ m}^2 \text{ g}^{-1}$; iii) a quick heat treatment step of the ball milled samples at 400°C to partially recover the compromised reduction resistance of the samples during the ball milling step. Based on the TGA data in 3.3 vol.% H_2/Ar atmosphere, RuO_2 or IrO_2 dissolved in the solid solution phases have higher reduction

resistance than the pure RuO_2 or IrO_2 catalysts prepared through the same thermal/mechanical treatment route. The reduction resistance improvement of the solid solution catalysts is attributed to the stabilization effect of TiO_2 or Nb_2O_5 in the solid solution phases, as these transition metal oxides are not reduced by H_2 at low temperatures. However, the OER activity of the solid solution catalysts is shown to be lower than that of the parent RuO_2 or IrO_2 catalysts. Since RuO_2 is typically not considered as a stable OER catalyst due to its dissolution at high potentials, it was further investigated whether the RuO_2 -based solid solution catalysts prepared in this study have higher stability than RuO_2 when used as an OER catalyst. OER stability tests using MEAs in a PEMWE showed that the lower OER activity of the solid solution catalysts exerts higher potentials to the electrode during OER compared to the pure RuO_2 catalyst, which results in a faster dissolution and loss of solid solution catalysts. Therefore, the future research on developing reduction resistant RuO_2 catalysts should focus on improving the stability of these catalysts at high potentials during OER.

Acknowledgments

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Appendix

This section provides the XPD patterns of the ball-milled and healed samples in Figure A-1.

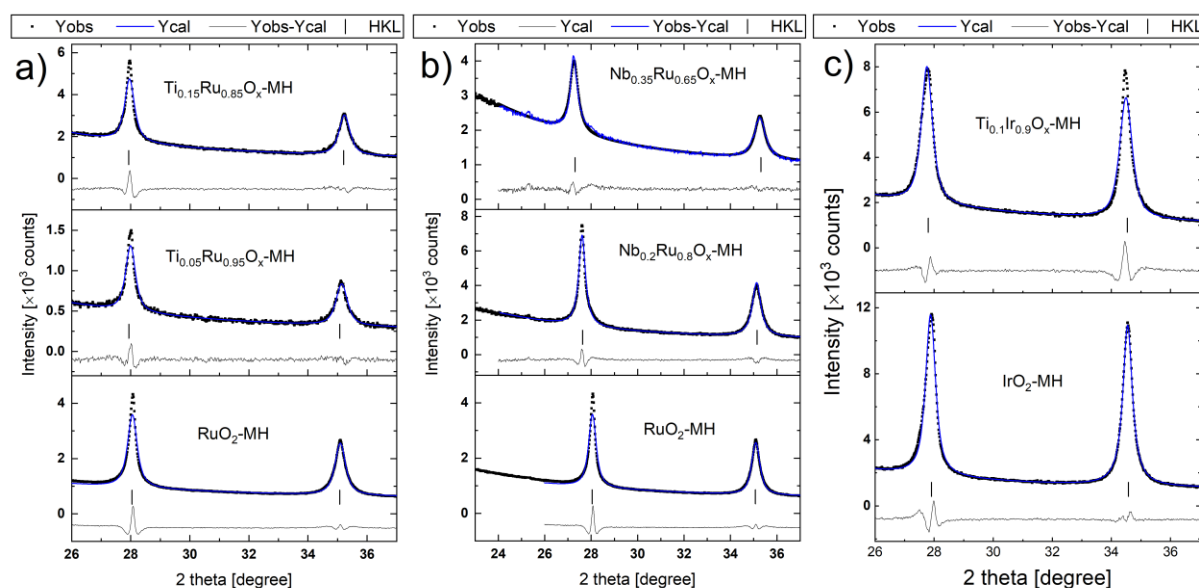


Figure A-1. X-ray powder diffraction results of the a) $\text{Ti}_{0.15}\text{Ru}_{0.85}\text{O}_x\text{-MH}$, b) $\text{Nb}_{0.35}\text{Ru}_{0.65}\text{O}_x\text{-MH}$, and c) $\text{Ti}_{0.1}\text{Ir}_{0.9}\text{O}_x\text{-MH}$ powders. The data were collected at our in-house Cu-diffractometer ($\lambda = 1.54059 \text{ \AA}$) at $2\theta = 20\text{-}90^\circ$ and then the whole diffractograms were refined in the $P42/mnm$ space group according to the Le Bail method. However, the plots only show the strongest crystalline reflections at low 2θ region for a better representation. The observed (black points), calculated (blue lines), and difference diffraction profiles (black lines) are shown. The position of Bragg peaks of RuO_2 - and IrO_2 -rich phases with $P42/mnm$ space group are marked with the black ticks, and the detailed fitting parameters of these phases can be found in Table 2.

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4 Conclusions

This PhD thesis focused on the performance and durability of oxygen evolution reaction (OER) (co-)catalysts for proton exchange membrane fuel cells (PEMFCs) and proton exchange membrane water electrolyzers (PEMWEs). Hereby, the main focus was put on evaluating and developing measurement methods to determine OER catalyst activity and stability, on elucidating the degradation mechanisms of anode OER co-catalysts in a PEMFC, and on developing OER catalysts that are not reduced under the conditions of a PEMFC H₂ anode. Fig. 4.1 shows an overview of the scope of this thesis.

In the field of OER catalyst development, quick screening tools such as the rotating disk electrode (RDE) technique are required to assess the activity and stability of newly developed catalysts. In section 3.1 and 3.2 of this thesis, challenges of OER catalyst activity and stability measurements using the RDE technique were discussed and the results were compared to measurements of the catalysts incorporated into membrane electrode assemblies (MEAs) that were then measured in a single-cell PEMWE. RDE-based OER catalyst stability measurements predict significantly shorter lifetimes than those measured in an MEA in a PEMWE.^{13, 131} While there are several hypotheses in the literature to explain this discrepancy, it was shown in section 3.1 that shielding of the catalyst active sites by microscopic oxygen bubbles is one of the major reasons for the rapid OER performance decay observed during the RDE experiments. It was shown that OER catalyst stability measurements of an iridium disk electrode by potential cycling and constant current experiments lead to a significant loss in performance within minutes. However, once ultrasonication was applied, the performance remained relatively constant throughout the experiments,

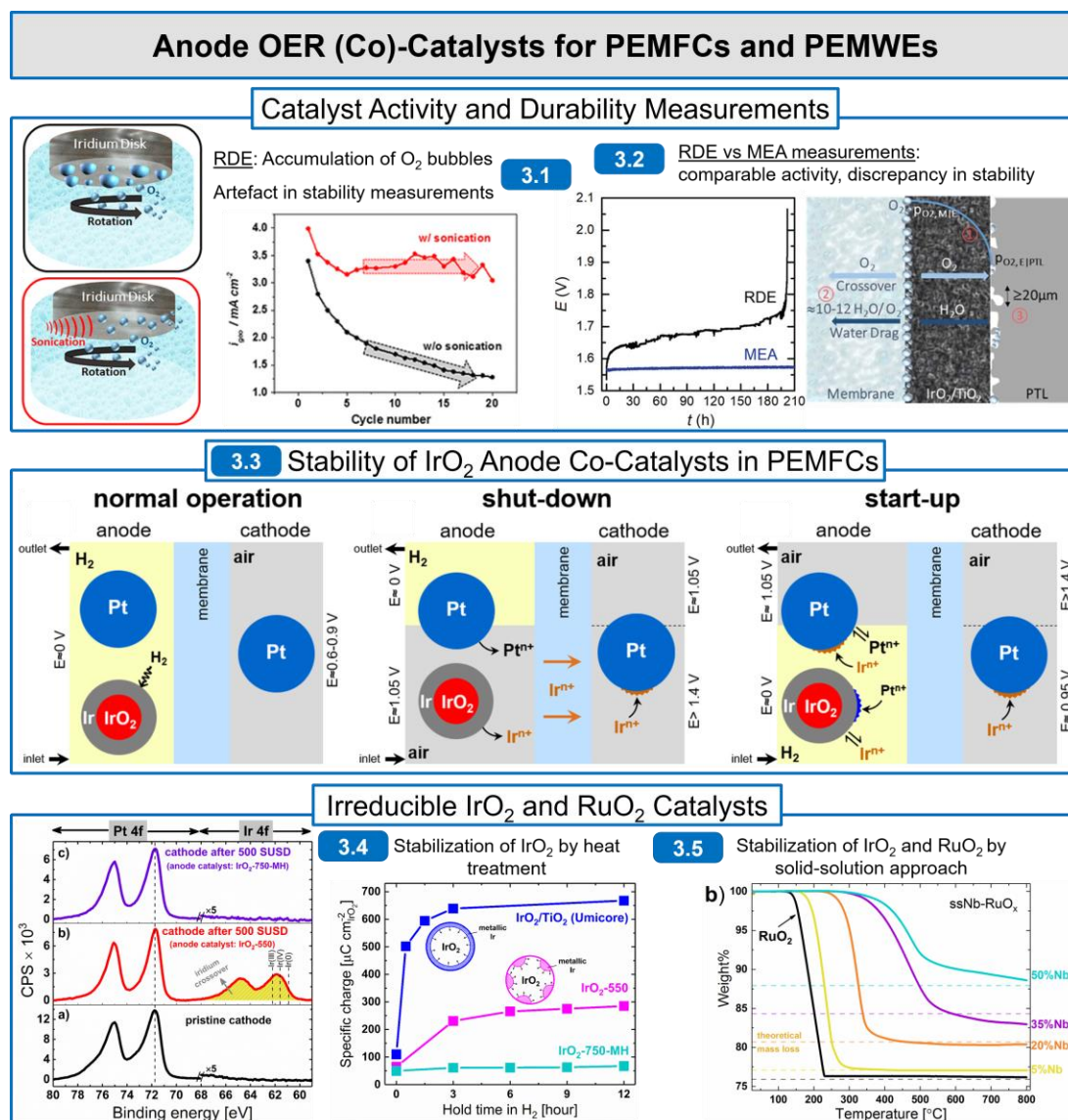


Figure 4.1. Graphical summary of the key findings of this PhD thesis. The numbers in the blue boxes refer to the respective sections in the Results chapter. OER catalyst activity and durability measurements were the subject of sections 3.1 and 3.2. It was shown that RDE-based OER activity measurements result in comparable activity values to those measured in an MEA in a PEMWE. However, RDE measurements are not reliable for estimating OER catalyst lifetime due to the accumulation of microscopic oxygen bubbles in/on the catalyst layer, which result in orders of magnitude shorter lifetimes for RDE-based vs MEA-based measurements. In section 3.3., the degradation mechanism of an IrO₂ anode co-catalyst was investigated under start-up/shut-down (SUSD) events in a PEMFC, showing that a reduction resistant catalyst is required to prevent this degradation mode. In section 3.4, a reduction resistant IrO₂ catalyst was prepared by a heat treatment approach, and in section 3.5 reduction resistant IrO₂- and RuO₂-based catalysts were prepared by forming a solid-solution phase of these PGM-oxides with other metal oxides.

concluding that the high degradation rates observed during RDE-based catalyst stability measurements are due to the shielding of catalyst active sites by microscopic oxygen bubbles.

The effect of O₂ bubbles was further investigated in section 3.2, comparing the stability of an IrO₂ catalyst deduced from various commonly used accelerated degradation tests (at constant current, at constant potential, potential cycling) either based on RDE measurements or on MEA-based measurements in a PEMWE. This revealed that the accumulation of microscopic oxygen bubbles in/on the catalyst layer during OER takes place in both measurement configurations, but is much more significant in RDE measurements, where the shielding of almost all of the catalyst active sites by gas bubbles leads to a rapid performance deterioration. It thus does not allow for a meaningful projection of a catalyst lifetime in an actual PEMWE, nor does it allow for a reliable ranking of the durability of different OER catalysts. Therefore, although RDE-based OER activity measurements result in activity values that are comparable to those measured in an MEA in a PEMWE, RDE measurements are not reliable for OER catalyst lifetime estimation due to the artefact created by the accumulation of microscopic oxygen bubbles.

Extending the application of OER catalysts to PEMFCs, the addition of an OER co-catalyst such as IrO₂ and RuO₂ to the anode electrode of a PEMFC is a common strategy to mitigate the damages due to cell reversal events which are caused by H₂ starvation.³⁷ The OER activity of a co-catalyst, typically determined by RDE measurements, usually correlates with the effectiveness of the catalyst for mitigating cell reversal damages in a PEMFC.^{46, 53} This has led to numerous studies in the literature which focus on improving the OER activity of co-catalysts. However, section 3.3 in this thesis revealed a hitherto unnoticed challenge in the development of anode OER co-catalysts for PEMFCs. It is related to the here made observation that the near-surface layer(s) of a conventional IrO₂ anode co-catalyst can be completely reduced to metallic Ir upon exposure to H₂, e.g., under the typical operating conditions of a PEMFC H₂ anode. The formation of

metallic Ir on the catalyst surface drastically affects its stability upon the anode potential transients which occur during start-up/shut-down (SUSD) events, leading to the enhanced dissolution of metallic Ir and the subsequent cross-over of the dissolved Ir^{n+} species through the membrane to the cathode electrode, as evidenced by X-ray photoelectron spectroscopy (XPS) of the cathode electrodes after SUSD cycling. The deposition of cross-over iridium on the Pt nanoparticles of the cathode catalyst deteriorates its ORR activity and results in a significant performance loss during the normal operation of the fuel cell. At the same time, SUSD transients also cause an OER activity loss of the anode co-catalyst, which was shown to be mainly due to the redeposition of Pt dissolved from the Pt/C-based hydrogen oxidation reaction (HOR) catalyst at the anode onto the reduced IrO_2 anode co-catalyst, blocking its OER active sites. These findings suggested that the reduction stability of IrO_2 -based anode co-catalysts in H_2 -containing atmosphere should be carefully assessed, for which a new methodology was proposed for screening anode co-catalysts prior to their use in a PEMFC. It is based on thermogravimetric analysis (TGA) experiments around the operational temperatures of PEMFCs and under a dilute H_2 atmosphere, where the reducibility of the OER co-catalyst can be reliably and quantitatively examined. Since the above-mentioned degradation mechanisms are caused by the chemical reduction of the OER co-catalysts in the PEMFC anode, it was suggested that a reduction resistant OER catalyst should eliminate these degradation mechanisms. The preparation of such catalysts was the subject of sections 3.4 and 3.5.

Section 3.4 introduced a novel and industrially scalable approach to produce IrO_2 catalysts which are not reduced in the PEMFC H_2 anode environment. Such irreducible IrO_2 catalysts ("irr- IrO_2 ") were produced via a three-step procedure consisting of a high-temperature (650-1000 °C) heat treatment step, followed by a ball-milling and a post annealing step to prepare catalyst powders with specific surface areas of $> 20 \text{ m}^2 \text{ g}^{-1}$. TGA experiments in 3.3% H_2/Ar showed that the formation of metallic Ir is hindered in the near-surface layer(s) of such irr- IrO_2 catalysts at PEMFC operating temperatures. The high reduction stability of the

synthesized irr-IrO₂ catalysts was due to their intrinsic structural distinctions from the typically synthesized IrO₂ catalysts that are heat-treated at low temperatures, which was also reflected by the different activation energies for the reduction of these catalysts by H₂. It was shown that anode potential transients, caused by SUSD cycles, do not lead to the dissolution of iridium from the irr-IrO₂ anode co-catalysts and the associated iridium poisoning of the ORR activity of Pt/C-based cathode catalysts, evidenced by Ir 4f XPS spectra of the cathode electrodes after SUSD cycling.

Section 3.5 introduced a novel strategy to prepare IrO₂- and RuO₂-based catalysts which are irreducible in PEMFC anode environment. Such irreducible IrO₂- and RuO₂-based catalysts were prepared by forming a solid-solution phase of these platinum group metal (PGM) oxides with other transition metal oxides, namely TiO₂ or Nb₂O₅. The preparation of the solid-solution phase catalysts is based on a high-temperature heat treatment step to form the solid-solution phase, followed by a ball-milling and a post-annealing step to prepare catalyst powders with specific surface areas of > 25 m² g⁻¹. TGA experiments in 3.3% H₂/Ar showed higher reduction stability for the solid-solution phase catalysts than the pure RuO₂ or IrO₂ catalysts prepared by the same procedure. The observed reduction stability improvement was attributed to the stabilizing effect of TiO₂ and Nb₂O₅ in the solid-solution phases, as these transition metal oxides are not easily reduced by H₂ at temperatures < 800 °C.^{142, 143, 154} As mentioned in section 1.3.2.2, RuO₂ is typically not considered as a stable OER catalyst due to its unacceptably high corrosion rate at the high OER potentials. It was further shown by PEMWE experiments in section 3.5 that the RuO₂-TiO₂ solid-solution phase catalyst do not have an improved stability at the high OER potentials compared to the RuO₂ catalyst, and further strategies are required to stabilize RuO₂ catalysts at high potentials so that it would be used as an anode catalyst in a PEMWE.

In summary, this PhD thesis has contributed to a better understanding of how to assess the performance and durability of OER (co-)catalysts for PEMFCs and

PEMWEs. The OER catalyst activity and stability measurements showed that while OER activity measurements by the RDE technique result in comparable activity values to those measured in an MEA in a PEMWE, RDE measurements are not reliable for OER catalyst lifetime estimation due to the artefact caused by microscopic oxygen bubbles. The detailed investigation of the degradation mechanism of an IrO₂ anode co-catalyst under the transient operating conditions of a PEMFC showed that the origin of such degradation is the chemical reduction of the OER co-catalysts in the PEMFC H₂ anode, and that a reduction resistant catalyst is required to prevent this degradation. The preparation of such reduction resistant catalysts was the subject of the last two studies in the results section. The novel approaches to produce irreducible OER catalysts introduced in this thesis have the potential to significantly improve the long-term durability of PEMFC systems. While the stability of RuO₂-based solid-solution phase catalysts at the high OER potentials is still a remaining challenge for their practical applications as OER catalysts in real systems, further stabilization approaches can be investigated, such as the formation of ternary RuO₂-IrO₂-TiO₂ solid-solution phases. If such a solid-solution phase can be synthesized, one might expect a perhaps synergistic combination of the properties of the three metal oxides in one catalyst: the high OER activity of RuO₂, the high stability of IrO₂ at high OER potentials, and the high reduction resistance of TiO₂.

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List of Figures

Figure 1.1. Schematic representation of a 3-layer MEA (or CCM), with the membrane sandwiched between the anode and cathode electrodes. The insets are the schematic representations of the anode and cathode electrode components, including platinum nanoparticles (black dots) supported on a high surface area carbon black (gray spheres) and a well-connected network of a proton-conducting ionomer coating (blue film). 5

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the accumulation of microscopic oxygen bubbles in/on the catalyst layer, which result in orders of magnitude shorter lifetimes for RDE-based vs MEA-based measurements. In section 3.3., the degradation mechanism of an IrO₂ anode co-catalyst was investigated under start-up/shut-down (SUSD) events in a PEMFC, showing that a reduction resistant catalyst is required to prevent this degradation mode. In section 3.4, a reduction resistant IrO₂ catalyst was prepared by a heat treatment approach, and in section 3.5 reduction resistant IrO₂- and RuO₂-based catalysts were prepared by forming a solid-solution phase of these PGM-oxides with other metal oxides. 136

Scientific Contribution

PUBLISHED PATENT APPLICATIONS

- 1) **Fathi Tovini, M.**; Suchsland, J.-P.; Elsayed, H.; Damjanovic, A. M.; Hasché, F.; Gasteiger, H.; Speder, J.; "Oxygen Evolution Catalyst, Production and Use Thereof, Membrane Electrode Assembly, and Fuel Cell or Electrolysis Cell"; International Application WO/2022/078874 A1; published: April 21, **2022** (filed: October 7, 2020).
- 2) **Fathi Tovini, M.**; Elsayed, H.; Damjanovic, A. M.; Gasteiger, H.; Speder, J.; Alessandro, G.; Suchsland, J.-P.; "Oxygen Evolution Catalyst, Production and Use of Same, Membrane Electrode Arrangement and Fuel Cell or Electrolytic Cell"; International Application WO/2022/078873 A1; published: April 21, **2022** (filed: October 7, 2020).

PUBLISHED SCIENTIFIC ARTICLES

- 1) **M. Fathi Tovini***, A. M. Damjanovic, H. A. El-Sayed, B. Strehle, J. Speder, A. Ghielmi, H. A. Gasteiger, "Irreducible IrO₂ Anode Co-catalysts for PEM Fuel Cell Voltage Reversal Mitigation and Their Stability Under Start-up/Shut-down Conditions", *J. Electrochem. Soc.*, **2024**, 171, 074510.
- 2) **M. Fathi Tovini***, A. M. Damjanovic, H. A. El-Sayed, J. Speder, C. Eickes, J.-P. Suchsland, A. Ghielmi and H. A. Gasteiger, "Degradation Mechanism of an IrO₂ Anode Co-Catalyst for Cell Voltage Reversal Mitigation under Transient Operation Conditions of a PEM Fuel Cell", *J. Electrochem. Soc.*, **2021**, 168, 064521.
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- 4) **M. Fathi Tovini**[‡], A. Hartig-Weiß[‡], H. A. Gasteiger and H. A. El-Sayed*, "The Discrepancy in Oxygen Evolution Reaction Catalyst Lifetime Explained: RDE vs MEA - Dynamicity within the Catalyst Layer Matters", *J. Electrochem. Soc.*, **2021**, 168, 014512.
- 5) A. Hartig-Weiß[‡], **M. Fathi Tovini**[‡], H. A. Gasteiger and H. A. El-Sayed*, "OER Catalyst Durability Tests Using the Rotating Disk Electrode Technique: The Reason Why This Leads to Erroneous Conclusions", *ACS Appl. Energy Mater.*, **2020**, 3, 10323.
- 6) M. Bernt*, A. Hartig-Weiß, **M. Fathi Tovini**, H. A. El-Sayed, C. Schramm, J. Schröter, C. Gebauer, H. A. Gasteiger, "Current Challenges in Catalyst Development for PEM Water Electrolyzers", *Chem. Ing. Tech.*, **2020**, 92, 31.
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SCIENTIFIC ARTICLES IN PREPARATION

- 1) **M. Fathi Tovini***, F. Friedrich, C. Schramm, H. A. El-Sayed, H. A. Gasteiger, "A Solid Solution Route to Prepare Irreducible IrO₂ and RuO₂ Anode OER

Co-catalysts for PEM Fuel Cell Voltage Reversal Mitigation”, *to be submitted*.

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ORAL PRESENTATIONS

- 1) **M. Fathi Tovini**, A. M. Damjanovic, H. A. El-Sayed, F. Friedrich, B. Strehle, J. Speder, A. Ghielmi, H. A. Gasteiger, “Irreducible IrO₂ Anode Co-Catalysts for PEM Fuel Cell Voltage Reversal Mitigation and Their Stability Under Transient Operation Conditions”, *241st ECS Meeting*, May 29-June 2, **2022**, Vancouver, Canada (presented by A. M. Damjanovic due to the delayed visa issuance to M. Fathi Tovini).
- 2) **M. Fathi Tovini**, E. Yilmaz, “The Effects of RuO₂ Catalyst on Na-O₂ Battery Electrochemistry”, *E-MRS Spring Meeting*, May 22-26, **2017**, Strasbourg, France.

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