


Current Challenges in Catalyst Development for PEM Water Electrolyzers

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This work addresses current challenges in catalyst development for proton exchange membrane water electrolyzers (PEM-WEs). To reduce the amount of iridium at the oxygen anode to levels commensurate with large-scale application of PEM-WEs, high-structured catalysts with a low packing density are required. To allow an efficient development of such catalysts, activity and durability screening tests are essential. Rotating disk electrode measurements are suitable to determine catalyst activity, while accelerated stress tests on the MEA level are required to evaluate catalyst stability.

Keywords: Accelerated stress test, Catalyst, Iridium, Oxygen evolution reaction, PEM electrolysis

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1 Introduction

With its high power density and excellent load-following capability, proton exchange membrane water electrolysis (PEM-WE) presents a promising technology for sustainable hydrogen production in the context of large-scale energy storage [1–3]. However, due to the harsh environment (low pH, potential > 1.5 V and high oxygen concentration on the anode) in a PEM-WE, the choice of electrocatalysts is limited to platinum group metals (PGMs). Typically, carbon supported platinum (Pt/C) is used for the hydrogen evolution reaction (HER) on the cathode, while iridium (Ir) based catalysts are used for the oxygen evolution reaction (OER) on the anode. Even though high catalyst loadings are commonly applied (≈ 0.5 – $1.0 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$ on the cathode and $\approx 2 \text{ mg}_{\text{Ir}} \text{ cm}^{-2}$ on the anode [4]), catalyst materials account for only $\approx 5\%$ of the total cost in today's relatively small (kW range) systems [5]. However, for larger systems (MW range), the contribution of balance-of-plant costs and other stack components will be much lower, so that catalyst costs are expected to become a major cost contributor [6]. Additionally, the limited availability of Ir will become a concern when PEM-WE installation capacities reach the GW-scale. For this scenario, a recent study by our group shows that a significant reduction of the Ir loading from currently $\approx 2 \text{ mg}_{\text{Ir}} \text{ cm}^{-2}$ to only $\approx 0.05 \text{ mg}_{\text{Ir}} \text{ cm}^{-2}$ would be required to enable a large-scale application of PEM-WEs [3, 7].

A reduction of the Pt loading on the cathode was shown to be possible without any impact on performance due to the extremely fast HER kinetics of Pt in acidic electrolytes [2, 7–9]. For the Ir catalyst, on the other hand, the OER kinetic penalty of a reduction in Ir loading for an IrO₂ based OER catalyst is illustrated in Fig. 1. The solid red line presents the measured data for an MEA (membrane elec-

trode assembly) with a Nafion[®] 212 membrane ($\approx 50 \mu\text{m}$), a Pt loading of $\approx 0.35 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$ on the cathode, and an Ir loading of $\approx 2 \text{ mg}_{\text{Ir}} \text{ cm}^{-2}$ on the anode at a temperature of 80 °C and ambient pressure (taken from Fig. 4a in reference [10]). Due to the thin membrane and the optimized electrode structure, a cell voltage efficiency with respect to the lower heating value of hydrogen (LHV) of 70 %_{LHV} (corresponding to a cell voltage of 1.79 V) can be reached at a current density of 4 A cm^{-2} [10], equating to a cell energy consumption of $\approx 48 \text{ kWh kg}_{\text{H}_2}^{-1}$. Based on the typically observed Tafel kinetics for IrO₂ based OER catalysts with a Tafel slope of $\text{TS} \approx 50 \text{ mV decade}^{-1}$ [10], the kinetic OER overpotential increase ($\Delta\eta_{\text{OER}}$) when the catalyst loading is reduced from 2 to $0.05 \text{ mg}_{\text{Ir}} \text{ cm}^{-2}$ would equate to a cell voltage increase of $\approx 80 \text{ mV}$ (from $\Delta\eta_{\text{OER}} = \text{TS} \log[2/0.05]$). Assuming that all other voltage losses are not affected by the reduction of OER catalyst loading, the voltage vs. current density curve would simply be shifted upwards by 80 mV, as is shown by the red dashed line in Fig. 1.

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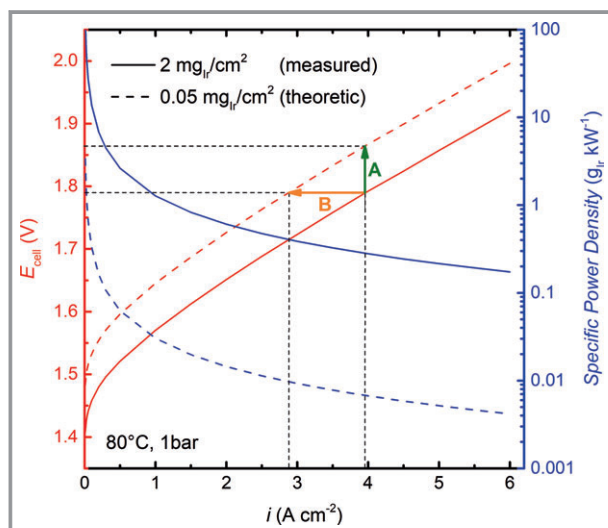


Figure 1. Ambient pressure PEM-WE performance curves measured for an MEA with a 50 μm thick Nafion[®] 212 membrane and catalyst loadings of $\approx 2 \text{ mg}_{\text{Ir}} \text{ cm}^{-2}$ and $\approx 0.35 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$ at a temperature of 80 $^{\circ}\text{C}$ (solid red line; 5 cm^2 single-cell data taken from reference [10]). The dashed red line gives the projected performance curve for an Ir loading of 0.05 $\text{mg}_{\text{Ir}} \text{ cm}^{-2}$, calculated based on the OER kinetics of the IrO_2 catalyst and the assumption that all other voltage losses are not affected by the reduction of OER catalyst loading. The blue lines represent the Ir-specific power density as a function of current density for Ir loadings of 2 $\text{mg}_{\text{Ir}} \text{ cm}^{-2}$ (solid line) and 0.05 $\text{mg}_{\text{Ir}} \text{ cm}^{-2}$ (dashed line). The arrows illustrate the consequence of lowering the Ir loading while keeping either the current density constant (path A) or while keeping the cell voltage (i.e., the efficiency) constant (path B).

With regards to the Ir-specific cell power density (i.e., the Ir loading divided by the cell power density, in units of $\text{g}_{\text{Ir}} \text{ kW}^{-1}$), the projected performance loss when reducing the Ir loading by a factor of 40 (i.e., from 2 to 0.05 $\text{mg}_{\text{Ir}} \text{ cm}^{-2}$) would still result in a ≈ 30 -fold reduction of the Ir-specific power density (see solid vs. dashed blue line in Fig. 1). In other words, the performance metrics projection for this 40-fold lowering of the Ir loading can be viewed in either one of two ways: i) if keeping the current density constant, the cell voltage at 4 A cm^{-2} would increase by $\approx 80 \text{ mV}$ to 1.87 V, which corresponds to an increase of the cell energy consumption by $\approx 4\%$ to $\approx 50 \text{ kWh kg}_{\text{H}_2}^{-1}$ ($\equiv 67\%_{\text{LHV}}$ efficiency), but the Ir-specific power density would be reduced from $\approx 0.3 \text{ g}_{\text{Ir}} \text{ kW}^{-1}$ to $\approx 0.007 \text{ g}_{\text{Ir}} \text{ kW}^{-1}$ (see path A marked in Fig. 1); or, ii) when keeping the efficiency constant at 70 $\%_{\text{LHV}}$, the current density would have to be decreased by $\approx 27\%$ to $\approx 2.9 \text{ A cm}^{-2}$, but the Ir-specific power density would still be substantially reduced to $\approx 0.01 \text{ g}_{\text{Ir}} \text{ kW}^{-1}$ (see path B in Fig. 1). Both strategies would lead to a reduction of the Ir-specific power density to the $\leq 0.01 \text{ g}_{\text{Ir}} \text{ kW}^{-1}$, which would be required for GW-scale applications of PEM-WEs [7]. It also should be noted, however, that the voltage efficiencies of $\geq 70\%_{\text{LHV}}$ at current densities $> 2 \text{ A cm}^{-2}$ shown in Fig. 1 can only be achieved with thin membranes [11, 12] ($\approx 50 \mu\text{m}$ here vs. $\approx 200 \mu\text{m}$ in today's

commercial electrolyzers), which in turn requires special mitigation strategies to prevent the formation of explosive H_2/O_2 mixtures in the anode compartment [13].

The analysis presented above suggests that the requirements for a large-scale application of PEM-WEs could be met by reducing the Ir loading to 0.05 $\text{mg}_{\text{Ir}} \text{ cm}^{-2}$. However, such a drastic reduction of Ir loading is not possible with today's commercial catalyst materials. In case of the titanium oxide supported IrO_2 ($\text{IrO}_2/\text{TiO}_2$) catalyst (Elyst Ir75 0480 from Umicore, Germany) that was used at an Ir loading of 2 $\text{mg}_{\text{Ir}} \text{ cm}^{-2}$ for the performance curve shown in Fig. 1 (solid red line), the catalyst layer becomes very thin and inhomogeneous when its loading is reduced to $< 0.5 \text{ mg}_{\text{Ir}} \text{ cm}^{-2}$, resulting in a much higher performance loss than expected based simply on the OER kinetics losses [7]. That analysis shows that while the OER activity of today's commercial Ir based catalysts would be sufficient to allow a drastic reduction in iridium loading at only minor performance losses, high-structured catalysts, i.e., catalysts with a much reduced iridium packing density in the electrode, will be required to enable the fabrication of a homogeneous catalyst layer at such low Ir loadings. For example, the iridium packing density of the here used $\text{IrO}_2/\text{TiO}_2$ catalyst in the anode electrode is $\approx 2.3 \text{ g}_{\text{Ir}} \text{ cm}^{-3}$ (corresponding to a layer thickness of $\approx 4.3 \mu\text{m} (\text{mg}_{\text{Ir}} \text{ cm}^{-2})^{-1}$ [7]), which is ≈ 30 -fold larger than that of a typical carbon supported platinum catalyst used in fuel cells or in the electrolyzer cathode ($\approx 0.08 \text{ g}_{\text{Pt}} \text{ cm}^{-3}$ or $\approx 125 \mu\text{m} (\text{mg}_{\text{Pt}} \text{ cm}^{-2})^{-1}$ for a 15 wt % Pt/C catalyst [7]). In the following section, different concepts to develop such a high-structured catalyst will be discussed.

2 Concepts for Ir-Based OER Catalyst Development

In state-of-the-art PEM-WEs, unsupported Ir or IrO_2 based catalysts are used for the OER on the anode [4]. There are different possible approaches to create a high-structured catalyst which would enable the fabrication of electrodes with ultra-low Ir loadings and with sufficient thickness ($\approx 4\text{--}8 \mu\text{m}$ [7]). One strategy is to maximize the noble metal dispersion by supporting thin films or nanoparticles of Ir or IrO_2 on high-surface area support materials, a concept similar to the Pt/C catalyst used for the electrolyzer cathode or for PEM fuel cell electrodes. The high electrochemical potential on the anode side of $> 1.4 \text{ V}$, however, precludes the use of carbon supports which would get oxidized to CO_2 under these conditions [14, 15]. On the other hand, titanium dioxide (TiO_2) is a stable, commercially available, and inexpensive material [16], and is frequently used as a catalyst support for Ir [17, 18]. However, a relatively high amount of Ir or IrO_2 ($> 40 \text{ wt}\%$) is required to generate sufficient electric conductivity by forming a contiguous network/film of Ir or IrO_2 nanoparticles [19, 20], since TiO_2 itself is not conductive. A conductive and stable support material would eliminate the need for a percolating

network of Ir or IrO₂ to provide sufficient conductivity across the catalyst layer and, hence, enable lower Ir loadings. Antimony doped tin oxide (ATO) [21–24] and niobium doped titanium oxide (NTO) [25] have been proposed as potential support materials, but their long-term stability for PEM electrolysis still needs to be verified. Another promising support option are titanium suboxides that have a higher intrinsic conductivity compared to ATO [26, 27], but further research is required to show if this high conductivity can be maintained during prolonged electrolyzer operation. Tungsten doped titanium oxide (W_xTi_{1-x}O₂) has been presented as another potential support material and high performance and sufficient stability over 1000 h at an Ir loading of 0.2 mg_{Ir} cm⁻² has been demonstrated [28]. In the absence of a suitable support material, alternative catalyst structures, such as Ir based nanowires [29], nanostructured thin films (NSTFs) [30], or core-shell structures [6, 22] along with improved catalyst layer manufacturing techniques, like reactive spray deposition [6], present another pathway to achieve lower Ir loadings.

Within the Kopernikus P2X project [31], different approaches to reduce the iridium loading were investigated by the project partners Greenery GmbH, Heraeus Deutschland GmbH & Co.KG, the Ludwig-Maximilians-University Munich (LMU), and the Technical University of Munich (TUM), which yielded a new high-structured catalyst with reduced iridium packing density ($\approx 0.46 \text{ g}_{\text{Ir}} \text{ cm}^{-3}$), which at a loading of $\approx 0.3 \text{ mg}_{\text{Ir}} \text{ cm}^{-2}$ still enables a sufficiently thick electrode of $\approx 6.5 \mu\text{m}$. Its performance at this loading and thickness is compared in Fig. 2 (green line) to that of the commercial IrO₂/TiO₂ catalyst at the higher loading of 2.5 mg_{Ir} cm⁻² with an electrode thickness of $\approx 11 \mu\text{m}$ (red line). Even though the catalyst loading was reduced by a factor of ≈ 8 , a slightly higher performance was obtained for the new catalyst. This presents an important first step to a significant reduction of the Ir loading required for a large-

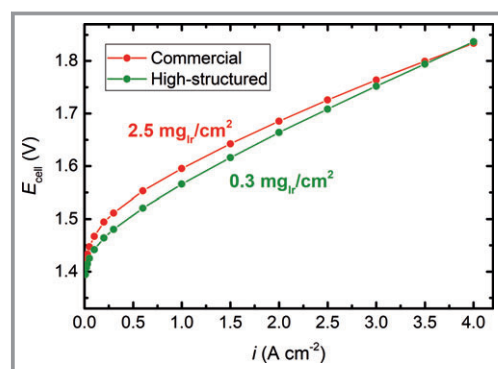


Figure 2. Ambient pressure electrolyzer performance (5 cm² single cell) at 80 °C for an MEA with a commercial catalyst (IrO₂/TiO₂, Umicore) with an anode Ir loading of 2.5 mg_{Ir} cm⁻² (red) compared to a new high-structured catalyst material with an Ir loading of $\approx 0.3 \text{ mg}_{\text{Ir}} \text{ cm}^{-2}$ (green). MEAs were prepared with $\approx 50 \mu\text{m}$ Nafion® 212 membranes and a cathode Pt loading of 0.3 mg_{Pt} cm⁻²; the cell hardware and the other cell components are as described in reference [10].

scale application of PEM-WE. At a cell voltage of 1.79 V corresponding to a cell voltage efficiency of 70%_{LHV}, the current density for both catalysts is $\approx 3.4 \text{ A cm}^{-2}$, which would correspond to Ir-specific power densities of $\approx 0.41 \text{ g}_{\text{Ir}} \text{ kW}^{-1}$ and $\approx 0.05 \text{ g}_{\text{Ir}} \text{ kW}^{-1}$ for the 2.5 mg_{Ir} cm⁻² and the 0.3 mg_{Ir} cm⁻² anode, respectively. For this new Ir-based OER catalyst, the projected Ir-specific power density would already be within a factor of 5–10 of the above stated target of 0.01 g_{Ir} kW⁻¹. However, the development of such new OER catalysts requires fast and reliable screening methods to identify promising materials within a reasonable time scale. Possible methods and the associated challenges will be discussed in the following section.

3 Screening of OER Catalyst Activity and Stability

In order to evaluate the activity/stability of novel OER catalysts, screening tests based on rotating disk electrode (RDE) or flow-channel configurations [18, 32, 33] are commonly used. Typically, RDE measurements are performed in a three-electrode cell using a reversible hydrogen electrode (RHE) as a reference electrode, a high surface area gold (Au) mesh as a counter electrode, and a disk working electrode with a polycrystalline gold disk embedded in a PTFE body (Pine Research Instrumentation, USA). Often, diluted sulfuric acid is used as a liquid electrolyte and, in contrast to MEA measurements, only a few milligrams of catalyst are needed to assess the OER activity as well as the catalyst stability. The small amount of catalyst needed is one main advantage of using the RDE technique. New synthesis routes often yield only a few milligrams of catalyst material, and prescreening the OER activity along with the catalyst stability is beneficial for pre-selecting promising materials before a lot of effort is taken to produce several grams of catalyst which are required for MEA preparation and testing in an electrolyzer.

Fig. 3a shows the high-frequency resistance (HFR) corrected cell voltage vs. the logarithm of the mass-normalized current density (a so-called Tafel plot), often used to assess OER activity and kinetics, for the IrO₂/TiO₂ catalyst (Umicore) measured at 40 °C, both with the RDE technique in argon-purged 0.1 M H₂SO₄ and in a PEM electrolyzer at $\approx 1 \text{ bar}_{\text{abs}} \text{ O}_2$. The observed Tafel slope is quite similar for these two different measurement configurations ($\approx 50 \text{ mV dec}^{-1}$), indicating that the prevailing OER reaction mechanism is similar in both environments. When referencing the OER activity at an HFR-corrected voltage of 1.5 V vs. the reversible hydrogen reference electrode potential, the activity of the Umicore (IrO₂/TiO₂) catalyst measured by the RDE technique (21 A g_{Ir}⁻¹) is roughly twice as high as when measuring the same catalyst in an MEA (10 A g_{Ir}⁻¹). While this difference of a factor of two is unclear at the moment, the obtained OER mass activities are still close enough to provide a reasonable prediction of

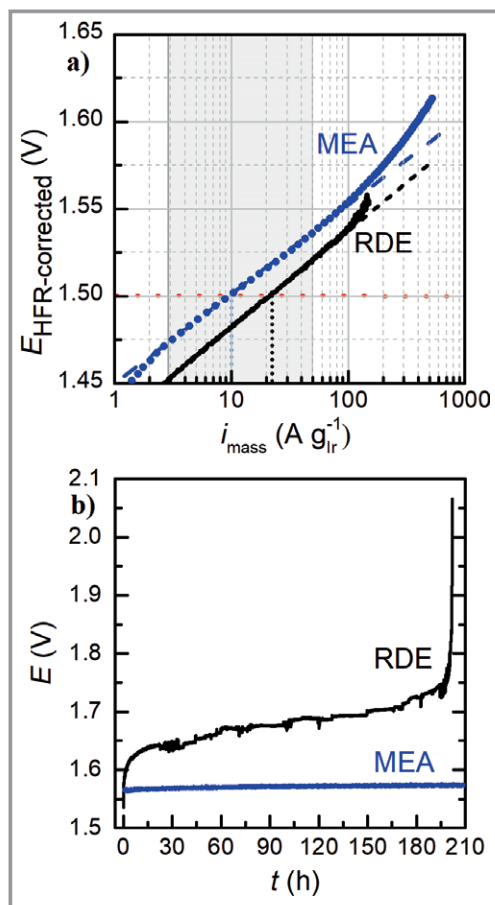


Figure 3. Evaluation of the OER activity and the stability of the Umicore catalyst ($\text{IrO}_2/\text{TiO}_2$) by the RDE technique (in 0.1 M H_2SO_4 at 10 mV s^{-1} , purged with pure argon) and in a 5 cm^2 single-cell PEM-WE (also at 10 mV s^{-1} and at $\approx 1 \text{ bar}_{\text{abs}}$ O_2 pressure) at 40°C : a) Tafel-plots of HFR-corrected cell voltage vs. the logarithm of the mass-normalized current density obtained by the RDE technique (black line) or by measuring an MEA in a single-cell PEM-WE (blue circles); b) chronopotentiometry at the same mass-specific current density of $70 \text{ A g}_{\text{Ir}}^{-1}$ for an RDE (black) at a loading of $0.4 \text{ mg}_{\text{Ir}} \text{ cm}^{-2}$ and a geometric current density of 28 mA cm^{-2} and for an MEA measurement (blue) at a loading of $2.0 \text{ mg}_{\text{Ir}} \text{ cm}^{-2}$ and a geometric current density of 139 mA cm^{-2} .

the performance of a new OER catalyst in an electrolyzer on the basis of RDE data.

Other than estimating the OER activity of novel catalysts, obtaining an estimate for their long-term stability is of crucial importance for a successful implementation in a real system. Research groups synthesizing new OER catalysts often use a chronopotentiometric (CP) RDE experiment, as it can be conducted with only mg-quantities of catalyst. There, a constant current is applied and the corresponding increase in potential is correlated with catalyst stability. Fig. 3b shows the resulting potential transient for a constant mass specific current density of $70 \text{ A g}_{\text{Ir}}^{-1}$ applied to the commercial $\text{IrO}_2/\text{TiO}_2$ catalyst whose performance was shown in Fig. 2 (red line), both using the RDE technique (at a loading of $0.4 \text{ mg}_{\text{Ir}} \text{ cm}^{-2}$ and a geometric current density

of 28 mA cm^{-2}) and MEA measurements in a 5 cm^2 single-cell (at a loading of $2.0 \text{ mg}_{\text{Ir}} \text{ cm}^{-2}$ and a geometric current density of 139 mA cm^{-2}). In case of the RDE measurements, the potential increases significantly within the first $\approx 200 \text{ h}$, until it finally jumps to $> 2 \text{ V}$. On the contrary, measuring the catalyst stability in the MEA shows a constant performance over the same time period, which is consistent with previous studies, where it was shown that a PEM-WE can operate for thousands of hours at constant current without any significant loss in performance [34]. In the literature, the increasing potential observed in RDE measurements is ascribed to the dissolution of active material until its complete loss, at which point the potential jump occurs [35]. However, it was recently shown by our group that the increase in potential is caused by the shielding of active sites due to the accumulation of oxygen bubbles trapped within the catalyst layer and that it cannot be correlated to catalyst degradation [36]. The accumulation of oxygen in the catalyst layer and partial shielding of the active sites results in a lower effective catalyst surface area. To provide the same total current the effective current density at the remaining active sites will increase leading to the observed increase in potential. Thus, the rising potential and the accompanied degradation of the catalyst is a result of the partial shielding of active sites by oxygen bubbles and cannot be related to the intrinsic stability of the catalyst. In general, filling the catalyst layer with oxygen bubbles would be a relatively fast process. However, we believe that some of the formed oxygen bubbles recombine and get removed by rotation leading to a slower accumulation of oxygen in the catalyst layer. Other occurring mechanisms, like changes of the wettability or the hydrophobicity of the catalyst might play an important role and have to be studied in more detail. In summary, we have to conclude that RDE measurements as well as iridium dissolution experiments in liquid electrolyte based electrochemical cells [32] are not a reliable predictor for the lifetime of newly developed OER catalysts, since trapped oxygen bubbles within the catalyst layer decrease the apparent stability of the catalyst by orders of magnitude compared to MEA measurements.

Nevertheless, degradation protocols are necessary to assess the long-term stability of newly developed OER catalysts in real PEM-WE systems. As already mentioned, under constant current operation the detected performance losses in PEM-WEs are rather small ($< 4 \mu\text{V h}^{-1}$) [34], so that at least 1000 h of testing would be required to obtain a voltage loss of only $\approx 4 \text{ mV}$. Since other non-catalyst related variables such as temperature variations or membrane thinning can mask such small changes even longer test durations on the order of several thousands of hours would be required which is not feasible and would slow down the development and implementation of new OER catalysts dramatically. Therefore, accelerated stress tests (ASTs) are required to mimic operation and trigger certain degradation mechanisms on a shorter time-scale. One such example would derive from the need to couple water electrolysis with

fluctuating renewable energy sources, in which case the intermittent power supply would result in PEM-WE operation alternating between hydrogen generation when power is available and idle periods, where no current is supplied. In a recent study by our group, a test protocol was developed, where the cell was operated at 80 °C and an H₂/O₂ pressure of 10/1 bar_{abs}, at which condition it was cycled between high (3 A cm⁻²) and low current densities (0.1 A cm⁻²), followed by idle periods where no or almost no current was supplied [37]. During the idle period, the cell was either left at open circuit voltage (referred to as OCV-AST) or was polarized at 1.3 V_{RHE} (referred to as reference test).

Fig. 4a depicts the voltage profile during one cycle for both the reference test (blue circles) and the OCV-AST (black line). During the reference test, a cell potential of 1.3 V was maintained during the idle period, requiring an applied current of $\approx 1 \text{ mA cm}^{-2}$ [37], while during the OCV-AST no current/voltage was applied to the electrolyzer cell during the idle period, resulting in a drop of the cell voltage to $\approx 0 \text{ V}$ within a couple of minutes. This observed decrease in cell voltage is caused by an accumulation of hydrogen in the anode compartment due to hydrogen crossover through the membrane from the cathode side, where a hydrogen pressure of 10 bar_{abs} was maintained [11]. This H₂-rich gas-phase at 80 °C leads to the reduction of the surface of the crystalline IrO₂ of the catalyst (IrO₂/TiO₂, Umicore) to metallic iridium, accompanied by a concomitant drop of the anode potential to $\approx 0 \text{ V}_{\text{RHE}}$ [37, 38]. Upon resuming operation, the anode potential will again increase to $\approx 1.4\text{--}1.8 \text{ V}_{\text{RHE}}$ (depending on the current density, Fig. 4), where metallic iridium will be oxidized to an amorphous hydrous Ir(OH)_x that is more active towards the OER [38, 39]. Thus, during the OCV-AST the cell voltage is continuously cycled between $\approx 0 \text{ V}_{\text{RHE}}$ and $\approx 1.4\text{--}1.8 \text{ V}_{\text{RHE}}$, resulting in a repetitive transition of the surface of the iridium catalyst between high and low iridium oxidation states, which we ascribe to be the cause of the iridium dissolution into the membrane observed by post-mortem transmission electron microscopy (TEM) [37], analogous to what occurs during the voltage-cycling induced platinum dissolution in a PEM fuel cell [40]. Note that the here advanced hypothesis is different from that proposed by Cherevko et al. [41], who on the basis of half-cell experiments in an aqueous sulfuric acid electrolyte proposed that the intrinsic dissolution rate of hydrous iridium oxide is higher than that of crystalline IrO₂. Owing to the high iridium loading in the here shown OCV-AST, the effect of iridium dissolution on the OER activity is very small ($< 20 \text{ mV}$ [37]) and the vast majority of the observed performance losses after 718 OCV-AST cycles (red diamonds Fig. 4b) are due to an increase of the HFR (red diamonds Fig. 4c). On the other hand, no loss of performance and no increase of the HFR is observed for the reference test after 500 cycles (blue circles in Fig. 4b), where the anode potential was always kept positive of 1.3 V_{RHE}. Both the increase

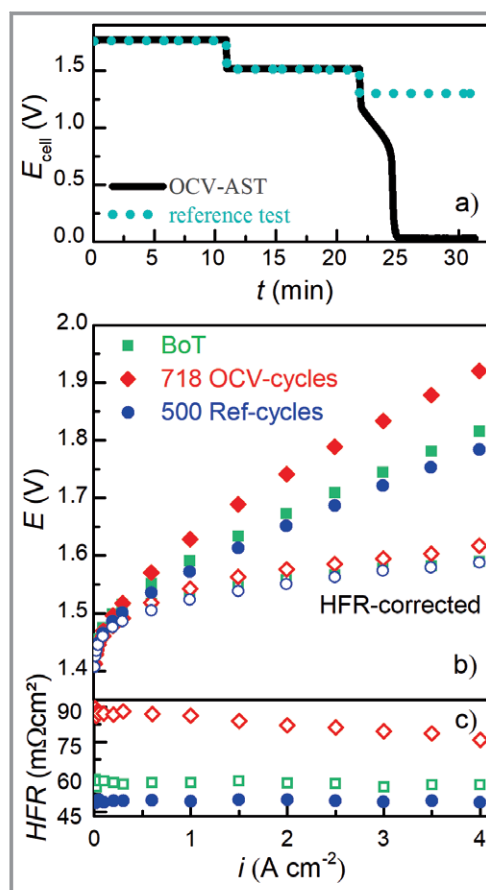


Figure 4. a) Cell potential during the accelerated stress test (AST) at 80 °C and 10:1 bar_{abs} H₂/O₂ to mimic an intermittent power supply of a PEM-WE, with periods of low and high current density followed by OCV (“OCV-AST”, black solid line), and of a reference test in which the potential is held at 1.3 V during idle periods (“reference test”, blue dotted line). b) Ambient pressure PEM-WE E_{cell} vs. i performance (filled symbols) and HFR-free performance data (hollow symbols) conducted at 80 °C at beginning-of-test (BoT, green symbols), and after either 718 OCV-cycles (red symbols) or after 500 cycles of the reference test (blue symbols) recorded during the AST shown in Fig. 4a. c) Corresponding HFR values. MEA specifications: anode loading of 1.75 mg_{Ir} cm⁻² (IrO₂/TiO₂; Umicore); 50 μm thick Nafion® 212; cathode loading of 0.2 mg_{Pt} cm⁻² (45.8 wt % Pt/C, Tanaka); for details see reference [37].

in HFR as well as the formation of a hydrous Ir(OH)_x phase clearly shown by cyclic voltammetry [37] are both related to cycling the anode potential between $\approx 0 \text{ V}_{\text{RHE}}$ during the OCV-periods and high potentials when current is applied to the electrolyzer. The main cause for an increasing HFR along with the observed performance decrease over the course of the OCV-AST can be related to the formation of an additional interfacial resistance on the anode side of the MEA. This additional resistance is the result of a higher contact resistance due to the passivation of the Ti-PTL (porous transport layer) in combination with the less electrically conductive Ir(OH)_x [37]. In summary, significant degradation of an electrolyzer MEA can occur during

extended OCV periods during which the anode potential is allowed to decay to $\approx 0 V_{\text{RHE}}$, a situation which should be avoided in a PEM-WE, at least when using non-coated Ti-PTLs.

4 Conclusions

In this work, an overview of the current challenges in catalyst development for PEM-WEs is given. Due to the limited availability of iridium which is currently the only viable option as an oxygen evolution reaction (OER) catalyst, a reduction of the iridium loading from currently $\approx 2 \text{ mg}_{\text{Ir}} \text{ cm}^{-2}$ to only $\approx 0.05 \text{ mg}_{\text{Ir}} \text{ cm}^{-2}$, i.e., by a factor of 40 is required in order to enable a large-scale application of PEM-WEs. While the activity of current Ir-based catalysts would generally be sufficient to achieve the proposed target values for Ir loading at only minor performance losses (only 4 % increase of the cell energy consumption to produce 1 kg of H_2), the development of catalyst structures with a much lower iridium packing density compared to current catalyst materials is absolutely required to realize homogeneous catalyst layers at very low Ir loadings. Several pathways to develop such high-structured catalysts (i.e., catalysts with a low iridium packing density) have been proposed in the literature. Here we show first results that demonstrate that for a high-structured catalyst a reduction of the Ir loading by a factor ≈ 8 is possible, even with a slightly improved efficiency compared to a commercial Benchmark catalyst. With this new OER catalyst developed by Heraeus, the Ir-specific power density at an efficiency of 70%_{LHV} ($\equiv 1.79 \text{ V}$) of $\approx 0.05 \text{ g}_{\text{Ir}} \text{ kW}^{-1}$ can be achieved at $> 3 \text{ A cm}^{-2}$ with a 50 μm thick Nafion[®] membrane.

To make the development of new catalyst materials more efficient, activity and durability screening methods are required to allow a fast identification of promising materials. The rotating disk electrode (RDE) method which is commonly used to evaluate catalyst performance is shown to be suitable for a characterization of catalyst activity, while OER catalyst stability tests are affected by measurement artefacts and, hence, do not give meaningful information about catalyst lifetime. Consequently, accelerated stress tests (AST) on the membrane electrode assembly (MEA) level are required to evaluate catalyst stability at realistic operating conditions. A test protocol simulating an intermittent power supply by cycling between open circuit voltage (OCV) and operating potentials is presented as an example for such an AST. Here, the recurring transition between reducing and oxidizing conditions leads to the dissolution of Ir and the formation of a contact resistance between electrode and PTL resulting in a much higher degradation rate compared to a reference experiment without OCV periods. The information gained from this experiment helps to identify harmful operating conditions that need to be avoided in real PEM-WE systems.

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Abbreviations

AST	accelerated stress test
ATO	antimony doped tin oxide
CP	chronopotentiometry
HER	hydrogen evolution reaction
LHV	lower heating value
NSTF	nanostructured thin film
NTO	niobium doped titanium oxide
OCV	open circuit voltage
OER	oxygen evolution reaction
PEM-WE	proton exchange membrane water electrolysis
PGM	platinum group metal
Pt/C	carbon supported platinum
RDE	rotating disc electrode
RHE	reversible hydrogen electrode

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