The Key to High Performance Low Pt Loaded Electrodes

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The effect of ionomer distribution on the oxygen mass transport resistance, the proton resistivity of the cathode catalyst layer, and the H2/air fuel cell performance was investigated for catalysts with surface modified carbon supports. By introducing nitrogen containing surface groups, it was shown that the ionomer distribution in the cathodic electrode can be optimized to decrease mass transport related voltage losses at high current density. The in-house prepared catalysts were fully characterized by TEM, TGA, elemental analysis, and XPS. Thin-film rotating disk electrode measurements showed that the carbon support modification did not affect the oxygen reduction activity of the catalysts, but exclusively affects the ionomer distribution in the electrode during electrode preparation. Limiting current measurements were used to determine the pressure independent oxygen transport resistance – primarily attributed to oxygen transport in the ionomer film – which decreases for catalysts with surface modified carbon support. Systematically lowering the ionomer to carbon ratio (I/C) from 0.65 to 0.25 revealed a maximum performance at I/C = 0.4, where an optimum between ionomer thickness and proton conductivity within the catalyst layer is obtained. From this work, it can be concluded that not only ionomer film thickness, but more importantly ionomer distribution is the key to high performance low Pt loaded electrodes.

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Since 2015, proton exchange membrane fuel cell (PEMFC) electric vehicles (FCEVs) are emerging in the market. Despite the major breakthroughs in achieving the durability and performance targets for automotive applications, the cost of fuel cell stacks is still higher compared to the competing internal combustion engines, which is partly related to the cost and supply constraints of the platinum based catalysts, especially for the air cathode (the fast kinetics of the hydrogen oxidation reaction allow for low anode Pt loadings without compromising performance). For large-scale commercial viability, it has been estimated that the Pt loading, especially at the cathode needs to be reduced below 0.1 mgPt/cm².[2,3]

Over the past decade there have been numerous studies focusing on the optimization of the cathode layer and seeking to gain fundamental insights into the various kinetic and transport resistances, which limit the performance of air cathodes, particularly at low Pt loadings.[4-8] While several methods were developed to quantify the voltage losses, there still remain unexplained voltage losses at high current density, particularly in the case of low Pt loading cathodes.[9-14] These have been rationalized by suggesting more complex oxygen reduction reaction (ORR) kinetics with variable Tafel slope,[5] by an interfacial resistance at the ionomer/platinum interface,[9,15] and/or by unusually high oxygen transport resistances through an assumed homogeneous thin ionomer film covering the Pt particles.[16,17] However, recent high-resolution transmission electron microscopy studies suggested that the ionomer coverage in the electrode may be rather inhomogeneous[18] and that the solvents used for preparing catalyst inks for electrode preparation influence the ionomer distribution in the final electrode, which in turn affects MEA (membrane electrode assembly) performance.[19] Therefore, one of the challenges in preparing MEAs is to achieve catalyst layers with a homogeneous ionomer distribution. This is not only expected to lead to maximum MEA performance, but also to allow for a more quantitative assignment of the transport related voltage losses, as all transport resistance measurements and voltage loss corrections are based on assuming uniform ionomer distribution in the electrode.

In the following, we will show that a modification of the carbon support of the platinum catalyst and an optimization of the ionomer content of the cathode catalyst layer result in a significant improvement of the MEA performance with ultra-low Pt loadings (ca. 0.07 mgPt/cm²). We hypothesize that this is due to achieving a more homogeneous ionomer coverage on the carbon support (Vulcan XC72) which we functionalized with amide/imide/factam groups (–NH2), which are known to ionically interact with the ionomer’s sulfonic acid groups (–SO3H).[20,21] This hypothesis is consistent with a very recent conference report[22] and with our finding that the unassigned MEA voltage losses, i.e., after correction for the measured proton and oxygen transport resistances, are reduced to unprecedentedly low values in MEAs based on NH2-functionalized carbon supports.

Experimental

Carbon functionalization with NH2 surface groups.—2 g of commercially available Vulcan XC72 (Tanaka Kikinzoku Kogyo K.K.) was mixed with 100 ml of 70% HNO3 (Sigma Aldrich, ACS reagent) and then immersed into a pre-heated oil bath (70 °C, reflux conditions) for 30 min. The carbon (further on referred to as “V-Ox”) was filtrated and washed with hot water until neutral filtrate pH; then it was dried in a vacuum oven for 12 h at 80 °C. Thereafter, 1 g of the sample was placed in a tube furnace (Carbolite Gero GmbH & Co KG, Germany) for 4 h at 200 °C under pure NH3 gas with a flow rate of 1 l/min to prepare aminated Vulcan carbon (further on referred to as “V-NH2”). This procedure closely follows that described by Jansen et al.[23]

Synthesis of ca. 20 wt% Pt/V-NH2.—300 mg of the aminated Vulcan support, 200 ml of ethylene glycol, 100 ml of deionized water, and 1.54 ml of H3PtCl6 (8 wt% H3PtCl6 in H2O (≡ 0.25 mol/l) from Alfa Aesar) were placed in a round-bottom flask and stirred for 18 h at 25 °C. Thereafter, the flask was immersed in a pre-heated oil bath at 120 °C and stirred for 2 h. The catalyst was separated by filtration and washed with hot water until the filtrate was pH neutral and chloride free; subsequently, the catalyst was dried in a vacuum oven at 70 °C for 12 h.[24] The final platinum loading was quantified by both TGA and elemental analysis.

Microstructure of carbon.—The surface areas of the commercial and aminated Vulcan carbon were evaluated by N2 physisorption at 77 K using a Autosorb-iQ instrument (Quantachrome, UK). All samples were degassed under vacuum at 90 °C for 15 h prior to physisorption measurements. Adsorption and desorption isotherms of all sam-

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samples were recorded in the relative pressure range of \(10^{-5} \leq (p/p_0) \leq 0.995\), where \(p\) represents the gas pressure and \(p_0\) the saturation pressure. This specific relative pressure range was chosen in order to ensure high resolution in the micro and mesopore region; to ensure high accuracy, the sample weight was adjusted to have a minimum absolute surface area of \(>10 \text{ m}^2\). The specific surface area and pore volume distribution were calculated by the Brunauer-Emmett-Teller (BET) method and by the quenched solid density functional theory (QSDFT) method, respectively (using the ASiQwin program). The adsorption branch was used for the BET surface area (best fit within 0.01 \(\leq (p/p_0) \leq 0.25\)) using a multipoint fit. In addition, a slit/cylindrical pore and adsorption QSDFT kernel was used for the characterization of the nanopore size distribution (small mesopores and micropores with <30 nm) of the carbons. It should be noted that QSDFT is more accurate than other theories or non-local density functional theory (NLDFT), as it takes into consideration the heterogeneity of the carbon surface and thus gives a more realistic estimate of the micro and mesopores contribution.

**Transmission electron microscopy.**—Transmission electron microscopy (TEM) was used to evaluate the Pt distribution on the carbon support. Samples for TEM analysis were prepared by dispersing a very small amount of the catalyst in deionized water and then depositing a few drops of the suspension onto carbon-coated Cu400 TEM grids (Science Services, Germany). Imaging was performed using a CM100 EM (Philips, Netherlands) operated at 100 kV and a resolution of 0.5 nm. For the evaluation of the average Pt particle size distribution, 230 individual particles were measured manually using ImageJ.

**Thermogravimetric analysis.**—Thermogravimetric analysis (TGA) of the carbons (V, V-Ox, and V-NH\(_x\); all without platinum) was performed with a TGA/DSC 1 (Mettler Toledo, Switzerland) in pure argon at 5 K/min in order to quantify the amount of functional groups on the pristine, oxidized, and aminated carbons. The Pt content was also evaluated by TGA from the residual sample weight after burning the carbon by heating the sample to 1000 °C. The Pt content was determined by subtracting the weight of the carbon from the total weight of the sample. This specific relative pressure range was chosen in order to quantify the amount of functional groups on the carbon surface and thus gives a more realistic estimate of the micro and mesopores contribution.

**Elemental analysis.**—CHNS analyses were done using a EURO EA analyzer (Hekatek, Germany), which is based on the dynamic flash combustion technique. The Pt content was analyzed photometrically using a UV 160 photometer (Shimadzu, Japan).

**X-ray photoelectron spectroscopy.**—Surface chemical analysis was accomplished by X-ray photoelectron spectroscopy (Leybold–Heraeus LHS 10 XPS with a non-monochromatized Mg K\(_a\) source). The powder samples were pressed and fixed onto a vacuum-compatible copper foil adhesive tape. The spectra were recorded at a constant pass energy of 100 eV, corresponding to an energy resolution of \(\approx 1.11\) eV. The measured C 1s peak at a binding energy of 284.5 eV indicates the absence of sample charging. All spectra were recorded at a pressure below \(5 \times 10^{-9}\) mbar. The core level spectra were fitted by Voigt functions after subtraction of a linear background.

**Rotating disk electrode.**—Electrochemical characterization of the catalysts was done by the thin-film rotating disk electrode (RDE) technique, comparing the intrinsic activities of commercial Vulcan XC72 supported platinum catalyst (19.6 wt% Pt/V from TKK) with that of the here synthesized Pt/V-NH\(_x\) catalyst (20.3 wt% Pt). The catalyst inks were prepared by mixing 7.8 mg of Pt/V in 5.57 ml of DMF and 7.0 mg of Pt/V-NH\(_x\) in 5.0 ml of DMF (both equating to 1.4 mgPt/ml ink). The suspensions were sonicated at 25 °C for 15 min. No Nafion was added to the inks in order to ascertain the true mass and specific activities of catalysts without any poisoning caused by Nafion. 5 μl of the ink was drop-cast onto a polished (0.05 μm aluminia, Büehler, Germany) and pre-cleaned stationary 5 mm diameter GC electrode (Pine, USA), resulting in a catalyst loading of 36 μg/cm\(^2\). The electrode was coated with a beaker and the catalyst film was dried overnight at room temperature in order to yield a homogeneous film. All electrochemical measurements were conducted in a home-made three-electrode jacketed glass cell. The electrode was attached to a rotator (Pine, USA), which was connected to a potentiostat (Autolab, Germany). A reversible hydrogen electrode (RHE) was used as a reference electrode, which was calibrated at the beginning of each experiment. All measurements were done at 25 °C in 0.1 M HClO\(_4\), which was prepared from 18 M ClO\(_4\)·cm Milli-Q water (Merck Millipore, Germany) and HClO\(_4\) (60%, analytical grade, Kanto Chemical, Japan). All gases (Ar, O\(_2\), and H\(_2\)) were of 6.0 grade (Westfalen, Germany). The reported potentials are referenced to the RHE scale and are iR-free. ORR activities were extracted at 1600 rpm from 20 mV/s anodic scans. Mass and specific activities are extracted after applying the mass transport correction for RDE.

**Membrane electrode assembly preparation.**—All 5 cm\(^2\) membrane electrode assemblies (MEAs) were fabricated using the decal transfer method. Catalyst inks were prepared by mixing the catalyst with a low-EW ionomer containing water-solvent dispersion (Asahi Kasei, Japan, 700 EW (EW ≡ 8polyene/moleH\(_2\))). The ink components were added into a 8 ml HDPE capped bottle containing 16.5 g of 5 mm ZrO\(_2\) beads in the following sequence: catalyst, water, 1-propanol, and finally the ionomer dispersion. The water concentration in the inks was 10 wt%, while the solid content was 0.03 g/ml in order to obtain a suitable viscosity for the coating process. Three ionomer to carbon weight ratios (I/C) were used: 0.65, 0.40, and 0.25. The inks were mixed by placing the bottles onto a roller-mill (60 rpm) for 18 h at room temperature. Thereafter, the inks were coated onto virgin PTFE using a mayer rod coater.

The noble metal loading of the cathode electrodes was ca. 0.07 mg/cm\(^2\) (see details in Table III) for all cases. The loading of the electrodes was determined by weighing the decals before and after the catalyst layer transfer. The same anodes were used for all measurements: 0.1 mg/cm\(^2\) consisting of 19.6 wt% Pt/V (TKK) with an I/C ratio of 0.65. The MEAs were assembled by hot pressing a 15 μm membrane (Asahi Kasei) placed between the anode and cathode decals at 155 °C for 3 min with an applied force of 0.11 kN/cm\(^2\). All inks and decals were manufactured twice to verify reproducibility. For each MEA type, two independent fuel cell measurements were conducted; the average value of the measurements with error bars corresponding to the standard deviation are depicted in all figures.

**Fuel cell operation.**—The electrochemical measurements were performed using a single-cell hardware purchased from Fuel Cell Technologies Inc., fitted with 5 cm\(^2\) active area graphite flowfields (0.5 mm lands/channels; made by Poco Graphite). The assembling torque applied was 12 Nm and the compression of the gas diffusion media (Freudenberg H14C7) was set to 20% by using incompressible fiber-glass PTFE sub-gaskets. Fuel cell tests were performed on an automated Greenlight Innovation fuel cell test station (type G60). All MEAs were conditioned before each test using the same voltage-controlled ramp-in procedure (H\(_2)/\text{air flows of 1390/3320 nccm at 80 °C, 100% relative humidity, and 150 kPa}_{\text{abs, inlet}};: 0.6 V for 45 min, 5 min at OCV, and 10 min at 0.85 V). This sequence was repeated 10 times, after which constant performance was reached. Differential-flow polarization curves were recorded in current-control mode at 80 °C, 170 kPa\(_{\text{abs, inlet}}\) controlled pressure, 100% relative humidity (RH) for both reactants, and constant flows of 2000 nccm of H\(_2\) and 5000 nccm of air or O\(_2\) (at these conditions, the inlet to outlet pressure drop in anode and cathode are 2 and 22 kPa, respectively). Prior to recording a polarization curve from
low to high current densities, MEAs were conditioned at 0.75 V for 15 min; each current density point was held for 10 min, and the resulting voltage was averaged over the final 30 s. AC impedance spectra were collected at each current density to determine the respective high frequency resistance (Gamry Ref3000 potentiostat).

**Fuel cell diagnostic measurements.**—The electrochemically active surface area (ECSA) of the cathode electrode was evaluated via cyclic voltammetry, averaging the H-desorption and H-adsorption charge and using a reference value of 210 μC/cm². The counter/reference electrode was fed with 200 nccm of fully humidified 5% H₂ in nitrogen, while the working electrode was first flushed with dry N₂, the flow of which was stopped during recording the CVs. The potential was cycled at 150 mV/s between 0.03 and 1.0 V (vs. RHE) at 40 C and ambient pressure. The charging resistance and the H₂ cross-over currents were measured with H₂/air at 170 kPaabs, 80 °C, and 100% RH.

The proton conduction resistance in the cathode electrode was determined by AC impedance (Gamry Ref3000 potentiostat) under H₂/N₂ (anode/cathode) at 0.2 V, following previous work (peak-to-peak perturbation of 3.5 mV between 500 kHz and 0.2 Hz, with 20 points per decade). Three spectra were collected at each condition to verify reproducibility. Proton conduction resistances (RiH+/cat) were determined at 100, 70, 50, and 30% RH at 80 °C under differential flow conditions (H₂/N₂ at 1000/1000 nccm), maintaining constant gas partial pressures (i.e., at cell pressures of 270, 255, 246, and 236 kPaabs, respectively). Under these operating conditions the pressure drop over the flow field was negligible (<2 kPaabs), which resulted in no change in the RH between the inlet and outlet of the cell.

The effective proton resistance RH+/cat (in units of Ω·cm²) was calculated by using Equation 10 from Liu et al. and was used to correct for the proton conduction resistance induced voltage loss. The proton resistivity RH+/cat (in units of Ω·cm) was calculated by dividing the proton resistance (RH+/cat) by the cathode electrode thickness (calculated from the well-known packing density of Vulcan carbon based electrodes of 28 (μg/mg-C/cm²)).

The total mass transport resistance was derived from limiting current measurements at 80 °C cell temperature and at 70% RH under differential conditions (2000 nccm of H₂ and 5000 nccm of O₂/N₂ mixtures). The dry mole fraction of oxygen was altered from 0.5 to 24% O₂ in N₂, while the cell potential was set to 0.3, 0.15, 0.1, and 0.05 V for 2 min each. To quantify pressure-independent and pressure-dependent oxygen transport resistances, limiting current measurements were conducted at 170, 270, 350, and 500 kPaabs,inlet. Under these experimental conditions there was no significant change of the RH over the whole active area of the MEA. To be more precise, the RH in the inlet of the cell was set at 70% for all cases, while the resulting RH at the outlet was 68%, 70%, 71%, and 73% for the 170, 270, 350, and 500 kPaabs,inlet, respectively, based on the measured pressure drop at a given flow rate and pressure as well as a water production corresponding to 4 A/cm²geo.

**Results**

**Carbon and catalyst characterization.**—CHNS elemental analysis (see Table I) was conducted in order to determine the functionalization degree of the pristine Vulcan XC72 carbon (V), after its oxidation (V-Ox), and after its subsequent amination (V-NHx). It is well known that oxidation of carbon in concentrated HNO₃ leads to a surface functionalization with carboxylic, hydroxyl, and NOₓ groups. Accordingly, the N-content of the oxidized Vulcan support is significantly higher than that of the pristine carbon (see Table I). It further increases after the heat-treatment in NH₃ to 0.9% (see V-NHₓ in Table I), owing to the formation of amidic/imide/lactams upon reaction with NH₃. With the increase in N-content, a simultaneous increase in the C-content is also seen (from 95.1 to 96.8 wt%), which is due to the loss of less stable O-containing functional groups during heat-treatment. The carbon content determined by CHNS analysis (see Table I) is in excellent agreement with that determined by TGA analysis (see Figure S1).

The presence and nature of the N-containing functional groups on the V-NHₓ support was examined by X-ray Photoelectron Spectroscopy (XPS). The broad peak at 399.8 eV (see Figure 1) is consistent with the presence of imides/lactams/amides; while it is not possible by XPS to distinguish between the different groups. The pristine Vulcan XC72 carbon was also subjected to the same analysis and, as expected, no N-containing surface groups could be detected (Figure 1).

The microstructure of the pristine (V) and functionalized carbon (V-NHₓ) was investigated via N₂ adsorption isotherm, seeking to determine any potential changes in the microstructure of the support by the amination treatment, as this could affect the performance of the catalyst in low Pt loaded electrodes. Table II depicts the results from the BET and the QSDFT analysis. The total surface area estimated by BET (first row in Table II) and QSDFT (i.e., the sum of micro and mesopore areas from QSDFT analysis) are in perfect agreement. QSDFT determines the contribution of the micropores and mesopores to the total area (see experimental for more details). Using the IU-PAC classification, the contribution of the micropores (<2 nm) and the mesopores (>2 nm) to the total surface area was quantified (see Table II and Figure S2). The area of the micropores is commonly referred to as internal surface area, while the one of the mesopores is referred to as external area of a carbon support. Functionalization of the Vulcan carbon with NHₓ groups clearly results in a decrease of the internal porosity of the carbon support (from 127 to 74 m²/g).

![Figure 1. XP spectra of V and V-NHₓ carbons in the N 1s region.](image)

<table>
<thead>
<tr>
<th>Sample</th>
<th>C [%]</th>
<th>H [%]</th>
<th>N [%]</th>
<th>S [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>V</td>
<td>98.8 ± 0.3</td>
<td>0.0</td>
<td>0.2 ± 0.3</td>
<td>0.5 ± 0.3</td>
</tr>
<tr>
<td>V-Ox</td>
<td>95.1 ± 0.3</td>
<td>0.1 ± 0.3</td>
<td>0.4 ± 0.3</td>
<td>0.5 ± 0.3</td>
</tr>
<tr>
<td>V-NHₓ</td>
<td>96.8 ± 0.3</td>
<td>0.2 ± 0.0</td>
<td>0.9 ± 0.0</td>
<td>0.5 ± 0.0</td>
</tr>
</tbody>
</table>

**Table II. Surface area analysis of pristine Vulcan carbon (V) and aminated carbon (V-NHₓ).** 1st row: total surface area determined by BET; 2nd and 3rd row: meso and micropore areas determined by QSDFT.
without, however, affecting the external surface area of the carbon and the mesopore size distribution (see Figure S2). The observed decrease in micropore area was previously suggested to be due to the blocking of micropores by functional groups.\(^{39}\)

TEM micrographs of the commercial Pt/V and the here prepared Pt/V-NH\(_x\) catalyst were obtained to determine their Pt particle size distribution. Representative micrographs and the corresponding particle size distribution histograms are shown in Figure 2. It is clear that both catalysts exhibit a similar and reasonably narrow Pt distribution over the carbon support (see also Figure S3), as well as similar average Pt particle diameters of 2.4 \(\pm\) 0.6 nm for the 19.6 wt% Pt/V catalyst and of 2.2 \(\pm\) 0.4 nm for the 20.33 wt% Pt/V-NH\(_x\) catalyst (see Table S4).

No changes of the surface functionalization are expected to occur during the Pt deposition procedure used in the present work, as was demonstrated by XPS measurements in an earlier work.\(^{24}\)

**Evaluation of the ORR activity by RDE.**—Thin-film RDE ORR activity measurements were performed on the catalysts with functionalized and non-functionalized carbon support. These were done on a Nafion-free thin-film in order to avoid any poisoning of Pt due to Nafion and to exclude any interaction of Nafion with the functionalized catalyst. The obtained mass and specific activities are in good agreement with the literature for Nafion-free films.\(^{27}\) Table III shows that the ORR mass activity of the catalyst with the functionalized support (Pt/V-NH\(_x\)) is the same as that of the non-functionalized support (Pt/V), both also displaying the same Tafel slope (see Table III and Figure S5). The specific activity of the Pt/V-NH\(_x\) catalyst is slightly higher than that of the Pt/V catalyst due to the difference in the ECSA (see Table III). This clearly confirms that both catalysts have essentially identical ORR activity and that the functionalization does not significantly influence the ORR activity. Thus, any of the below shown differences in the MEA performance of Pt/V vs. Pt/V-NH\(_x\) can be unambiguously attributed to the interaction between the ionomer and the support.

**Fuel cell characterization.**—All cathode electrodes had similar Pt loading (68–78 mgPt/cm\(^2\)_geo) and their detailed specifications, including their electrochemically active surface area (ECSA) are summarized in Table IV. The ionomer to carbon weight ratio (I/C) was altered to highlight the role of the ionomer film thickness on the mass transport resistance, as will be discussed further on. The uncorrected H\(_2\)/O\(_2\) differential flow performance curves at 80°C, 100% RH, and 170 kPa\(_{abs}\) inlet pressure as well as the corresponding HFR values are depicted in Figure 3a. Figure 3b shows the H\(_2\)/O\(_2\) performance vs cathode Pt-mass normalized current density (in units of A/gPt), corrected for the HFR, the effective cathode proton transport resistance (R\(_{\text{cath}}\)) calculated from p\(_{\text{H2,cath}}\) in Figure 6a), and the H\(_2\) crossover (4 \(\pm\) 0.5 mV/cm\(^2\)_geo), i.e., an analogous correction which had been applied previously.\(^{11}\) For each catalyst, two MEAs were prepared and tested to check for reproducibility, with the error bars corresponding to the standard deviation between those two measurements.

The ORR mass activity values (im) for the 19.6 wt% Pt/V and 20.3 wt% Pt/V-NH\(_x\) based cathodes were extracted from Figure 3b and are summarized in Table IV. As can be seen, the mass activities of the Pt/V and the Pt/V-NH\(_x\) catalysts are essentially identical, consistent with the identical mass activities determined by RDE (see Table III). In addition, to facilitate a better comparison with the literature, the here obtained ORR mass activities at a total pressure of 170 kPa\(_{abs}\) (i.e., O\(_2\) and H\(_2\) partial pressures of 123 kPa\(_{abs}\)) were also converted to those ORR mass activities (im\(*\)) which are obtained at a cell pressure of 150 kPa\(_{abs}\) (i.e., O\(_2\) and H\(_2\) partial pressures of 103 kPa\(_{abs}\)) using Equation 12 from Ref. 38. The ORR mass activity of all MEAs are in good accordance with literature values reported for 20 wt% Pt/V\(^{39}\) and other carbon supported catalysts.\(^{30}\) Tafel slopes were determined from Figure 3b between 50 and 800 mA/cm\(^2\) (\(\sim\)850 and \(\sim\)12500 A/gPt in Figure 3b), following the approach by Neyerlin et al.,\(^{38}\) to only use current densities greater than 10 times the H\(_2\) crossover current density and up to below 1 A/cm\(^2\). The Tafel slopes of all electrodes range between 72 and 76 mV/dec. (see Table IV),

![Figure 2](https://example.com/figure2.png)

**Figure 2.** TEM micrographs and their corresponding Pt size distribution for: a. 19.6 wt% Pt/V and b. 20.3 wt% Pt/V-NH\(_x\).

### Table III. Electrochemically active surface area (ECSA), ORR mass (im), and specific (i\(_s\)) activity at 0.9 V, and Tafel slope (TS) determined by RDE measurements (from the anodic going scan at 20 mV/s and 1600 rpm in O\(_2\) saturated 0.1 M HClO\(_4\) at 25°C). All data are corrected for IR and oxygen mass transport; the errors represent the standard deviations from 3 independent experiments.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>ECSA [m(^2)/gPt]</th>
<th>im [mA/mgPt]</th>
<th>i(_s) [(\mu)A/cm(^2)_Pt]</th>
<th>TS [mV/dec.]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/V</td>
<td>74 ± 2.4</td>
<td>548 ± 37</td>
<td>828 ± 26</td>
<td>56 ± 3</td>
</tr>
<tr>
<td>Pt/V-NH(_x)</td>
<td>60 ± 0.5</td>
<td>614 ± 36</td>
<td>1036 ± 65</td>
<td>56 ± 2</td>
</tr>
</tbody>
</table>

### Table IV. Cathode electrode Pt loadings (LPt) and I/C mass ratios, their electrochemically active surface area (ECSA) determined by cyclic voltammetry, and their ORR mass activity at 0.9 V, 80°C, and 100% RH at the experimentally used H\(_2\) and O\(_2\) partial pressures of 123 kPa\(_{abs}\) (im\(*\)) as well as extrapolated to H\(_2\) and O\(_2\) partial pressures of 103 kPa\(_{abs}\) (im\(*\)). The last column shows the Tafel slopes. Mass activities and Tafel slopes were obtained from Figure 3b, \(\sim\), after correction for the HFR, the effective proton conduction resistance in the electrodes, and H\(_2\) crossover correction. The indicated variation represents the standard deviation from two independent measurements.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>LPt [mgPt/cm(^2)_geo]</th>
<th>ECSA [m(^2)/gPt]</th>
<th>im [mA/gPt]</th>
<th>i(_{\text{H}2}/\text{O}2) [% A/gPt]</th>
<th>TS [mV/dec.]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/V</td>
<td>0.65</td>
<td>68 ± 1</td>
<td>52 ± 2</td>
<td>119 ± 2</td>
<td>93 ± 2</td>
</tr>
<tr>
<td>Pt/V-NH(_x)</td>
<td>0.65</td>
<td>58 ± 2</td>
<td>55 ± 1</td>
<td>110 ± 6</td>
<td>86 ± 6</td>
</tr>
<tr>
<td>Pt/V-NH(_x)</td>
<td>0.40</td>
<td>74 ± 2</td>
<td>56 ± 3</td>
<td>127 ± 2</td>
<td>100 ± 2</td>
</tr>
<tr>
<td>Pt/V-NH(_x)</td>
<td>0.25</td>
<td>68 ± 4</td>
<td>59 ± 4</td>
<td>146 ± 8</td>
<td>105 ± 8</td>
</tr>
</tbody>
</table>

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Figure 3. H2/O2 (2000/5000 nccm) differential flow performance of MEAs with ultra-low Pt cathode loadings (68–78 μgPt/cm2geo; see Table IV) at 80°C, 100% RH, and Pcell = 170 kPaabs,inlet for the 19.6 wt% Pt/V cathode catalyst at an I/C mass ratio of 0.65 (orange curves) and for the 20.3 wt% Pt/V-NHx cathode catalyst at I/C mass ratios of 0.65 (purple), 0.40 (green), and 0.25 (light blue): a. uncorrected performance curves (left y-axis) with their corresponding HFR (right y-axis); b. performance curves referenced to the Pt-mass normalized current density corrected for HFR, H+ conduction resistance in the cathode (ReffH+), and the H2 crossover current. Anode Pt loading were 0.1 mgPt/cm2geo and the error bars correspond to the standard deviation between two independent measurements on two different MEAs.

Figure 4. Differential flow polarization curves at 80°C and 100% RH of 19.6 wt% Pt/V (orange) and 20.3 wt% Pt/V-NHx (purple) cathodes with I/C of 0.65 with 21% O2 (dashed lines) and 10% O2 (solid lines) in the cathode gas feed at a cell pressure of 170 kPaabs,inlet. Cathode Pt loadings were 68 ± 1 and 78 ± 2 μgPt/cm2geo for the Pt/V and the Pt/V-NHx electrodes, respectively. The error bars correspond to the standard deviation for repeat measurements with two different MEAs. Schemes: sketch of the hypothesized ionomer distribution on the different carbon supports.

and are thus quite close to their theoretical value of 70 mV/dec. (i.e., based on a transfer coefficient of α = 1), as reported by Neyerlin et al. Larger Tafel slopes of ~80 mV/dec. for 0.05 mg/g cathodes were observed by Owejan et al. (evaluated from their transport-corrected H2/O2 polarization curves between 40 and 800 mA/cm2geo). Considering that residual and/or not accurately corrected for transport resistances always lead to higher apparent Tafel slopes, the slightly higher Tafel slopes in their study to unaccounted transport losses, possibly due to not fully optimized electrodes (e.g., inhomogeneous ionomer distribution), which were shown to yield higher Tafel slopes.

To estimate H2/air performance of MEAs by differential flow experiments, the stack inlet conditions and the stack outlet conditions are commonly simulated by using 21% and 10% O2, respectively (the latter corresponds to an air stoichiometry of ~1.9). Thus, polarization curves were measured under differential flows of 21% and 10% O2 in N2 at 80°C, 100% RH, and 170 kPaabs,inlet. Figure 4 shows the effect of the carbon support functionalization on the MEA performance for 21% O2 (dashed lines) and 10% O2 (solid lines). The performance at 0.6 V for the 19.6 wt% Pt/V catalyst (orange lines) is in excellent agreement with recently published data under essentially identical conditions (differential flow, 80°C, 100% RH, and 150 kPaabs,outlet) for a graphitized carbon supported Pt catalyst at the same loading: 1.4 A/cm2geo (our data) vs 1.3 A/cm2geo at 21% O2 and 0.78 A/cm2geo (our data) vs. 0.83 A/cm2geo at 10% O2. Significantly better performance, however, is observed with our NHx-functionalized catalyst (1.65 A/cm2geo at 21% O2 and 0.91 A/cm2geo at 10% O2). Kongkanand et al. showed that the carbon support surface area (particularly the fraction of surface in micropores) and the location of the Pt particles on the primary carbon particles can significantly influence the local O2 mass transport resistance and in turn the performance of the MEA. Pt particles that are located in the interior of the catalyst (Pt supported on a high-surface area carbon, Pt/MSC-a), versus Pt particles located exclusively on the exterior of the carbon (Pt supported on a graphitized carbon support, Pt/GrC-a) can significantly influence the performance under low O2 partial pressure and low Pt loadings.
In our study, the V-NHx has a surface area of 175 m²/gC, out of which 75 m²/gC are micropores, so roughly 40% less micropores are accessible on the V-NHx compared to the V support. Part of the performance improvement which is observed for the Pt/V-NHx vs the Pt/V could be attributed to the reduced micropores of the carbon support. Nevertheless, by comparing the performance of the GrC-a (100 m²/gC) used in the study by Kongkanand et al. which has no micropores, with the V-NHx supported catalyst, the latter exhibits better performance under the same operating conditions. This indicates that the performance improvement between Pt/V-NHx and Pt/V cannot be solely attributed to the difference of microporosity of the carbon supports.

We hypothesize that this is due to a more homogeneous ionomer distribution on the NHx-functionalized carbon support (illustrated by the sketches in Figure 4), which would result in a homogeneous ionomer film thickness over the whole electrode. This hypothesis is based on the known coulombic interaction between the NHx groups on the carbon support with the SO3⁻ groups of the ionomer.20,21 (Figure 4, purple-framed sketch).

In the case of Pt/V, the ionomer distribution is expected to be more inhomogeneous with a more random ionomer film thickness, which would lead to a high O₂ transport resistance in the regions where the ionomer film is thicker and to high proton conduction resistance in the regions where the ionomer film is thinner (Figure 4, orange-framed sketch). The latter would not only be expected to result in a performance decrease at high current densities and low oxygen concentrations, but also to larger discrepancies between transport resistance corrected performance curves and the kinetically predicted performance curve.

The above hypothesis, namely that the performance difference between the Pt/V and the Pt/V-NHx is related to a difference in ionomer homogeneity and thus improved oxygen mass transport is further supported by the dependence of the performance to the I/C ratio, evaluated in Figure 5 for the 20.3 wt% Pt/V-NHx catalyst: as the I/C is decreased to 0.40 (green lines), the performance at 0.6 V further increases to 1.75 A/cm²geo at 21% O₂ and 1.0 A/cm²geo at 10% O₂, which can only be attributed to the O₂ permeability through the ionomer film.9 As the I/C ratio is further decreased to 0.25, the performance decreases due to poor proton conductivity in the catalyst layer, as will be quantified in the following.

The proton resistivity of the different cathodes was measured according to the method developed by Liu et al.43 As shown in Figure 6a, the cathode proton resistivity strongly depends on RH and the cathode I/C ratio, as what would be expected.43 Comparing the Pt/V and the Pt/V-NHx based MEAs with an I/C ratio of 0.65, the difference between their proton resistivities at the various RH values is identical within the error of the measurement. It is known that the intrusion of the ionomer into the micropores of the primary carbon particles reduces the ionomer film thickness on the external surface of the carbon support.42 Thus, to estimate the average ionomer film thickness at the external carbon surface, it is necessary to determine the effective I/C ratio (I/Ceff) from the overall I/C ratio, as was done by Liu et al.43 Using this approach, we estimated the effective ionomer thickness (dionomer,eff.) by considering the cumulative pore volume in pores smaller than 3 nm, which was obtained from Figure S2 (high-lighted). As shown in Table V, the effective ionomer film thickness at the I/C ratio of 0.65 is similar for the catalyst with the anminated (Pt/V-NHx) and the untreated carbon (Pt/V). In summary, even though one might have expected that a less homogeneous ionomer film at equal average film thickness (i.e., at equal dionomer,eff.) would lead to a higher proton resistivity, this is not the case. However, differences in proton resistivity would also be expected to be negligible for inhomogeneous ionomer films, as long as there exists a continuous ionomer pathway throughout the electrode. Therefore, the homogeneity of the ionomer on the catalyst surface cannot necessarily be deduced from proton

![Figure 5](image_url)  
**Figure 5.** Differential flow polarization curves at 80°C and 100% RH of 20.3 wt% Pt/V-NHx cathodes with I/C mass ratios of 0.65 (purple), 0.4 (green) and 0.25 (blue) with 21% (dashed lines) and 10% O₂ (solid lines) in the cathode gas feed at a cell pressure of 170 kPaabs, inlet. Cathode Pt loadings were 78 ± 2, 74 ± 2, and 68 ± 4 μgPt/cm²geo for the MEAs with ionomer mass ratios of 0.65, 0.40, and 0.25, respectively. The error bars correspond to the standard deviation for repeat measurements with two different MEAs.

![Figure 6](image_url)  
**Figure 6.** The effect of the cathode catalyst layer composition on: a. the cathode proton resistivity (ρHₚ,eff.) at different relative humidities (RH) and different I/C ratios; b. the total oxygen mass transport resistance (Rtotal) = sum of the solid and hatched bars), which can be separated into a pressure dependent term (RPD) and a pressure independent term (RPID). The error bars correspond to the standard deviation between independent measurements with two different MEAs.
The transport-corrected H2/air cell voltage, $E_{\text{cell,tx-corr}}$, is described by:

$$E_{\text{cell,tx-corr}} = E_{\text{cell}} + \eta_{\text{geo}} \cdot \text{HFR} + \Delta E_{O_2-tx} + \eta_{\text{geo}} \cdot R_{\text{H}^+,-\text{cath}}$$

where $E_{\text{cell}}$ is the measured H2/air cell voltage, $\Delta E_{O_2-tx}$ is the total oxygen transport induced voltage loss, and $R_{\text{H}^+,-\text{cath}}$ is the effective proton conduction resistance in the cathode electrode. As shown by Neyerlin et al., the latter is related to the measured proton conduction resistance in the cathode, $R_{\text{H}^+,-\text{cath}}$, by:

$$R_{\text{H}^+,-\text{cath}} = R_{\text{H}^+,-\text{cath}}/(3 + \xi)$$

where $\xi$ is a scaling parameter which depends on ($\eta_{\text{geo}} \cdot R_{\text{H}^+,-\text{cath}}$) divided by the ORR Tafel slope. The voltage loss due to the total oxygen mass transport resistance ($R_{\text{total}}$) is calculated using Equation 3, derived by Zihrul et al.:

$$\Delta E_{O_2-tx} = \frac{RT}{F} \left( \frac{1}{4} + \frac{\gamma}{\alpha} \right) \ln \left( \frac{p_{O_2,\text{channel}} - \gamma \cdot R_{\text{total}} \cdot \eta_{\text{geo}}}{p_{O_2,\text{channel}}} \right)$$

where, $\gamma$ is the ORR reaction order with respect to oxygen partial pressure ($\gamma = 0.54$), $\alpha$ is the transfer coefficient ($\alpha = 1$), $R$ is ideal gas constant, $T$ is the cell temperature, and $p_{O_2,\text{channel}}$ is the partial pressure of O2 in the channel of the flow field. The transport corrected H2/air performance curves calculated from the H2/air performance and HFR data as well as from the measured $R_{\text{total}}$ and $R_{\text{H}^+,-\text{cath}}$ values (for the reader’s convenience, all tabulated in the SI) using Equations 1–3 are shown in Figure 7a for the four different cathodes.

These can now be compared to the purely kinetically limited ORR performance, $U_{OBR}$, obtained from the reversible cell voltage, $E_{\text{rev}}$, and the ORR overpotential, $\eta_{\text{ORR}}$:

$$E_{\text{ORR}} = E_{\text{rev}} - \eta_{\text{ORR}}$$

whereby the reversible cell voltage at the H2/air operating conditions is $E_{\text{rev}} = 1.17$ V (based on Equation 2 in Ref. 38). Under the assumption that the ORR kinetics follow the simple Tafel kinetics with a constant Tafel slope of 2.303 · R · T ($\alpha$ · $F$), $U_{OBR}$ can be related to the ORR mass activity at the reference conditions of 0.9 V, $T^\ast = 80^\circ$C, and $p^\ast_{O_2} = p^\ast_{H_2} = 103$ kPaabs (corresponding to $i^\ast$ in units of A/gPt; see Table IV) by Equation 11 in Neyerlin et al.:38

$$E_{\text{ORR}} = 0.900 \cdot V - \frac{2 \cdot 303 \cdot R \cdot T}{\alpha \cdot F}$$

$$\cdot \log \left( \frac{i^\ast \cdot L_{Pt} \cdot 10^{-3}}{\gamma \cdot \frac{P_{O_2}}{P_{H_2}}} \right)^{1/2} \cdot \exp \left( \frac{E^{(0)}_{\text{OBR}} - \gamma \cdot (1 - \frac{1}{\alpha})}{R \cdot T^\ast} \right)$$

where $\alpha = 1$ ($\approx 70$ mV/sec at 80°C), $L_{Pt}$ is the cathode platinum loading (in mg/cm² $geo$), $p_{O_2}$ and $p_{H_2}$ are the actual O2 and H2 partial pressures, respectively, $m$ is the reaction order with respect to O2 ($m = 0.79$) and $E^{(0)}_{\text{OBR}}$ is the activation energy at 0.9 V (note that this last term in Equation 5 vanishes for $T^\ast = T$). The average of the ORR kinetics limited performance curves derived from Equation 5 using the ORR mass activities and Pt loadings of the different MEAS ($\gamma \cdot \frac{p_{O_2}}{p_{H_2}}$ and $L_{Pt}$, see Table IV) is plotted as black line in Figure 7a, whereby the error bars represent the standard deviation between the calculated ORR curves for each MEA.
Figure 7. a. Transport-corrected H2/air performance curves derived from Equation 1 for the various MEA types (dashed lines) and average value of the purely ORR kinetics limited performance curve derived from Equation 5; b. unaccounted voltage losses for each MEA type; c.-e. schematic illustration of the effect of the ionomer distribution and thickness on proton conductivity and mass transport. The error bars correspond to the standard deviation for repeat measurements with two different MEAs. Measurement conditions: H2/air at differential flow conditions, 80°C, 100% RH, 170 kPaabs,inlet.

We will first discuss the outcome of this analysis by comparing the two different catalysts in cathodes with the same I/C ratio of 0.65 (orange and purple lines in Figure 7a). Quite clearly, the Pt/V-NHx based MEAs exhibit lower unaccounted voltage losses, i.e., their transport-corrected performance curve is closer to the purely kinetically limited ORR performance curve (black line). To more clearly illustrate the extent of unaccounted voltage losses, Figure 7b depicts the unaccounted loss of each MEA, obtained by subtracting the transport-corrected performance curves from the ORR kinetics limited performance of the same MEA. Figure 7b illustrates that the unaccounted voltage losses of the Pt/V-NHx based MEAs (purple line) are substantially smaller than those of the MEAs based on Pt/V (orange line), which we attribute to a more homogeneous ionomer distribution and thus more homogeneous local ionomer film thickness on the former, illustrated schematically in Figures 7d (Pt/V-NHx) and 7c (Pt/V). While for the case of the V-NHx supported catalyst the unaccounted voltage losses decrease as the I/C ratio decreases.

Under the assumption of a homogeneous ionomer distribution, decreasing the I/C ratio would result in thinner ionomer film over the Pt particles, thereby facilitating higher O2 permeability to the Pt/ionomer interface. This is consistent with the lower oxygen mass transport resistance observed for the Pt/V-NHx based cathodes with an I/C ratio of 0.4 (see Figure 6b) and with their much reduced unaccounted voltage losses (see green line in Figure 7b). Therefore, from this analysis we can conclude that the ionomer distribution and thickness is a key factor in controlling oxygen mass transport resistances. On the other hand, for the Pt/V-NHx based cathodes with an I/C of 0.25, which corresponds to an effective ionomer film thickness of ~0.9 nm (see Table V), the proton resistivity increases dramatically (see Figure 6a), which is reasonable considering that this film thickness corresponds to only ~2 monolayers of ionomer (based on a PFSAA side chain thickness of ~0.5 nm). Thus, as the ionomer film thickness becomes very small, the contribution from oxygen mass transport to the voltage loss becomes very small in contrast to the voltage losses due to poor proton conduction in the cathode (Figure 7e). Thus, a delicate balance between good oxygen mass transport and proton conduction has to be achieved in order to obtain the highest possible performance.

In summary, the here prepared MEAs based on cathodes with NHx-functionalized carbon support show the highest cell voltage performance at ultra-low Pt loadings reported in the literature. However, even with the evidence for a more homogeneous ionomer distribution achievable with an NHx-functionalized carbon support, there still remain ~40 mV of unaccounted voltage loss at 2 A/cm2geo (see Figure 7b). In principle, the origin of the unaccounted voltage loss could be due to: i) a not yet optimized MEA design; ii) a deviation from simple Tafel kinetics at low cathode voltages as suggested by Subramanian et al.;8 and/or, iii) an oxygen mass transport resistance higher than that obtained in the currently used limiting current measurements. While we cannot exclude any of these possibilities, we consider the latter to be most probable, due to the fact that the ratio of heat flux to water generation is higher during limiting current measurements at 0.2 V than that during polarization curve measurements in H2/air at 0.5 V, which affects the oxygen mass transport.

Conclusions

We presented a novel concept for tailoring the ionomer distribution in the catalyst layer. We provide evidence that by functionalizing the surface of a commercially available carbon with –NHx groups, the ionomer is homogeneously distributed throughout the catalyst layer, caused by the coulombic attraction between the sulfonate anions of the ionomer and the NHx surface groups on the carbon support. This, to our best knowledge, results in the highest H2/air performance for
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