Effects of PEMFC Operational History under Dry/Wet Conditions on Additional Voltage Losses due to Ionomer Migration

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Over its lifetime in a fuel cell electric vehicle, a polymer electrolyte membrane fuel cell inevitably suffers from certain duration of dry operational conditions, where significant performance losses of the fuel cell take place. In this study, we investigate the activity changes of the fuel cell after a prolonged degradation protocol under dry operational condition, followed by various recovery procedures under wet conditions. The utilization of diluted air on the cathode side is found to be advantageous for the recovery due to the superior heat and water management. This more efficient recovery protocol allows the deconvolution of reversible and irreversible losses after dry operations. A subsequent mechanistic study reveals an irreversible decrease of the effective ionomer coverage on the catalyst particles, while the proton conductivity of the catalyst layer drops. These observations point towards ionomer structural changes caused by the dry conditions. This is confirmed by post-mortem analysis via scanning electron microscope, showing clearly that ionomer redistributes and migrates, an additional mechanism which leads to the performance losses. Overall, the degradation mechanisms seem to be mitigated by higher ionomer content in the catalyst layer, while the investigated surface modification of carbon support shows minor sensitivities.

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The global aim of reducing greenhouse gas emissions calls for electromobility in the automobile sector.1 Over the last couple of years, fuel cell electric vehicles (FCEVs) have been gathering increasing attention due to their long driving range and short refueling time compared to full battery alternatives. Currently, commercialization of FCEVs are being led by Toyota, Honda and Hyundai.1–5 However, high costs of the polymer electrolyte membrane fuel cell (PEMFC) stacks have become one of the main bottlenecks towards further development, with a significant cost contribution coming from the precious metal, usually Pt, in the catalyst layers (CLs).6

To fulfill the requirement of lowering the Pt loading while maintaining the fuel cell performance, research has been focusing on further development of individual CL components towards decrease of oxygen mass transport resistance and increase of catalyst mass activity.6–10 The oxygen mass transport is proposed to be strongly influenced by the ionomer thickness and its distribution,9 and the ideal situation would be a conformal thin film covering the catalyst homogeneously.11 This could be achieved by surface modification of the carbon support to promote a more homogeneous ionomer distribution in the CL, as shown recently by Orfanidi et al.9 and Ott et al.12 The catalyst activity, on the other hand, is affected by multiple factors such as Pt particle size, the structure of carbon support and the location of the Pt nanoparticles on or within the carbon primary particle, to name a few.13–16

Among the multiple influential factors, the location of the Pt particles is among one of the most critical due to its effect on both oxygen transport and catalyst activity. It has been shown that locating a higher proportion of the Pt particles externally (on the surface of the carbon primary particles) could be advantageous towards better mass transport in the CL. However, this location ensures that the Pt surface is in contact with the ionomer, leading to adsorption of sulfonic acid groups and poisoning effects.17 Based on such observations, Harzer et al.18 suggested that an ideal catalyst ought to have most of the Pt particles outside for good mass transport, while having a small fraction of internal Pt to increase total mass activity. Similar results have also been obtained by other researchers.8,15 Yarlagadda et al.10 pointed out the alternative of accessible carbon mesopores to protect Pt particles from direct ionomer adsorption while allowing reasonable access of O2 and protons. It is currently accepted that controlling the proportion of Pt particles inside and outside the carbon primary particle is a viable route to thrift the loading of Pt group metals to levels that will help mass commercialization for automotive applications, i.e. cathode loading < 0.15 mgPt cm−2 and power densities of 1.8 W cm−2.17

Experimentally, external and internal Pt particles can be distinguished on catalyst powders with the use of scanning transmission electron microscopy (STEM), as shown by Park et al.9 The particle locations in CLs can also be estimated in situ, either electrochemically or in the gas phase, with CO as a probe molecule, as shown by Yarlagadda et al.10 and Iden et al.14

While further increase of cathode catalyst activities is essential and extensive research has been conducted over the past decade, the activity must also be sustained during the full operational life of an FCEV over about 5000 h.19,20 Degradation of CL components and the corresponding fuel cell performance losses, therefore, have to be prevented or kept to a minimum. Here, one may distinguish reversible losses from irreversible ones, where the former can be reversed by altering operational conditions or by shutdown and restart of the cell.21–23 The reversible voltage decays are often higher than the irreversible ones24,25 and may develop into irreversible ones over time,26 thus necessitating proper recovery protocols at the right intervals. In the literature, one may find various recovery procedures aimed at mitigating different reversible losses, including steps like shutdown/interruption,25,26 increasing gas humidity,28,29 lowering the cell potential,30–33 and switching the cathode gas to N2.28,32,33 to name a few.

Over the lifetime of the FCEVs, certain periods of operation under elevated temperatures and low relative humidity (RH), as well as cycling between high and low RH conditions, are unavoidable.
Under these conditions, it is known that the CL degrades, with the major part of degradation being reversible. The issue could be mitigated by operational strategies in an FCEV, e.g. by strictly reducing its operation time under dry conditions, yet the methodology brings additional constraint and cost for constructional elements. Therefore, CL optimization in terms of degradation resistance is a more attractive choice to tackle the issue. However, this requires a better understanding of the degradation mechanisms, the recoverability of the corresponding voltage losses, and the influence of certain CL components. From the literature, one of the main degradation mechanisms was identified to be the specific adsorption of ionomer sulfonic groups onto the Pt catalyst surface, where the number of adsorbed groups was shown to increase under dryer conditions. For instance, Kodama et al. gave clear experimental evidence of ionomer poisoning on Pt(111) in the voltage window of 0.6–0.85 V with a clear reduction in the activity for oxygen reduction reaction (ORR). Jomori et al. proposed that the adsorbed sulfonate ions might alter the electronic state of the Pt particles, rendering them inactive for oxygen reduction. This effect was presumed to be stronger at higher potentials and under dryer conditions. To explain the increase of O$_2$ mass transport resistances during their detailed degradation studies, two possibilities were postulated: the reduction in active sites on the Pt surface due to adsorption, and/or additional resistance due to changes in ionomer structure at the Pt/ionomer interface.

In this experimental study, we utilize a prolonged degradation protocol under low RH, followed by a high RH recovery step, to investigate the changes in a PEMFC cathode electrode with non-alloyed Pt. First, we evaluate various recovery strategies in the literature, with the aim to develop an optimal protocol for the present experimental setup. This allows us to deconvolute the contributions of the reversible and irreversible voltage losses accurately. With the recovery step defined, we conduct electrochemical characterizations at various stages of the stress protocol as well as post-mortem analysis to gain further insights into the degradation phenomena and the additional voltage losses. Based on our experimental findings, we suggest other possible mechanisms, namely ionomer migration and distortion of proton conductive pathways, apart from the known mechanisms of sulfonic group poisoning and degradation of the Pt/ionomer interface described in the literature. Additionally, we investigate whether the state-of-the-art surface modification of the carbon support and the ionomer content of the CL shows any sensitivity on the present studied phenomena.

**Experimental**

Membrane electrode assembly preparation.—All membrane electrode assemblies (MEAs) used in this study were prepared by the decal transfer method. Catalyst inks were prepared in-house according to Orfanidi et al. Catalyst inks were prepared by mixing first the catalyst powder with water, followed by solvent 1-propanol and last the ionomer dispersion containing water-solvent (725 EW 3 M dry powder dispersed in 40% H$_2$O/60% 1-propanol, resulting in a 18 wt% ionomer solution) in a 15 ml HDPE capped bottle containing 26.5 g of 5 mm ZrO$_2$ beads. In order to obtain an appropriate viscosity for the coating process, the solids content of the ink was set to 0.03 g mL$^{-1}$ and the water content was adjusted to 16 wt%. The inks were mixed by placing the bottles onto a roller bed (60 rpm) for 18 h at room temperature. Thereafter, the inks were coated onto virgin PTFE using a Mayer bar coater (coating speed: 10 mm s$^{-1}$). The coated decals was left at room temperature for a couple of minutes until it was visibly dry. Thereafter, it was placed on a pre-heated vacuum table (≥40 °C) to remove any remaining solvent or water. For the cathodic electrodes, two ionomer to carbon weight ratios (I/C) of 0.65 and 0.82 were used, while for the anodic electrodes, the I/C was set at 1.0. Three types of Pt/C catalysts, supplied by Johnson Matthey, were used for the cathodic electrode: a 35 wt% Pt-out/KB (carbon support Ketjen EC300J with around 70% of the Pt particles located outside the carbon porous structure), a 50 wt% Pt/KB (carbon support Ketjen EC300J with around 50% of the Pt particles located outside the carbon porous structure) and a 50 wt% Pt/KB-mod (Nitrogen surface modified carbon support Ketjen EC300J with around 30% of the Pt particles located outside the carbon porous structure). Particle location was determined by transmission electron microscopy (TEM) using a similar method as Park et al. All of the anodic electrodes comprised 30 wt% Pt on graphitized Ketjen Black (abbreviation in this study: gKB, TEC10EA30E purchased at Tanaka Kikinzoku).

The real Pt loading of the cathode electrodes was approximately 0.12 mgPt cm$^{-2}$geo (see details in Table I). The nominal thickness of the CLs comprising 35 wt% Pt-out/KB was about 5 μm, whereas for the ones comprising 50 wt% Pt/KB or 50 wt% Pt/KB-mod, it was about 3 μm (measured stacking density of 24 μm2/mgC cm$^{-2}$), see Supporting Information). All the anodes had loadings between ∼0.03 and ∼0.05 mgPt cm$^{-2}$geo (see details in Table I). The Pt loadings of the electrodes were determined by weighing the decal before and after the catalyst layer transfer.

The 8.25 cm$^2$ MEAs were assembled by hot-pressing a 10 μm membrane (Gore MX20.10) placed between the anode and cathode decals at 155 °C for 3 min with an applied force of 0.24 kN cm$^{-2}$. The MEAs were thereafter laminated between two subgaskets (200 × 200 mm, 25 μm PEN-foil CMC 61325 coated with a heat activated adhesive (∼15 μm thick) from CMC Klebetechnik, Germany), leaving an actual MEA active area of 5 cm$^2$ (50 × 10 mm). Figure S1 (available online at stacks.iop.org/JES/167/144513/mmedia) shows a picture of a laminated framed MEA. In Table I, MEA 1–3 were used for the investigation of the recovery steps conditions. We chose the cathode catalyst which has approximately 70% of Pt outside carbon porous structure (denoted by Pt-out), since it is known that a high fraction of external Pt particles enhances the adsorption of ionomer sulfonic groups. This should help in defining the most efficient recovery steps due to the higher degree of performance losses.

MEAs 4–9 were used for the mechanism study as well as to evaluate the effect of various carbon supports and I/C ratios on the voltage losses. The cathodic carbon support is either a surface modified Ketjen Black (denoted by KB-mod) or a plain reference KB. For each MEA, two independent fuel cell measurements were conducted; the average value of the measurements is depicted in the corresponding figures, while the error bars correspond to their standard deviation.

**Fuel cell operation.**—The electrochemical measurements were performed using a modified single-cell hardware (Tandem Technologies Ltd), fitted with 14 serpentine channel graphite

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**Table I.** MEA specifications: catalyst types, Pt loadings and I/C mass ratios of the anode and cathode electrodes.

| MEA | Anodic electrode | I/C | Pt loading [mgPt cm$^{-2}$geo] | Cathodic electrode | I/C | Pt loading [mgPt cm$^{-2}$geo] |
|-----|------------------|-----|--------------------------------|-------------------|-----|--------------------------------|
| 1–3 | 30 wt% Pt/gKB    | 1.0 | 0.037 ± 0.009                   | 35 wt% Pt-out/KB  | 0.65 | 0.123 ± 0.008               |
| 4–5 | 30 wt% Pt/gKB    | 1.0 | 0.047 ± 0.004                   | 50 wt% Pt/KB     | 0.65 | 0.126 ± 0.006               |
| 6–7 | 30 wt% Pt/gKB    | 1.0 | 0.049 ± 0.001                   | 50 wt% Pt/KB-mod | 0.82 | 0.116 ± 0.004               |
| 8–9 | 30 wt% Pt/gKB    | 1.0 | 0.049 ± 0.005                   | 50 wt% Pt/KB     | 0.65 | 0.125 ± 0.009               |
composite flow fields (50 cm$^2$ geo active area), similar to Baker et al.$^{38}$ ($\approx 0.5$ mm lands/channels; purchased by Nisshinbo). The clamping force of the cell was set to 15.2 kN and the compression of the gas diffusion media (SGL 29BC in both anode and cathode) was set to 20% by using incompressible fiber-glass PTFE sub-gaskets (Fiberflon). As shown in Fig. S2, the MEA was placed at the end of the flow channels (similar to Baker et al.$^{38}$), while the rest of the flow field was masked, thus preventing cross-channel convection. This assembly ensures that under all operating conditions, the maximum pressure drop is below 1 kPa over the entire active area (5 cm$^2$) and that mass transport of the reactant gases occurs only via diffusion and not via convection.

All tests were performed on a HORIBA FuelCon GmbH (Germany) single cell test station equipped with dynamical humidification with direct water injection. Pure hydrogen (99.999% purity) was used as anode reactant and compressed air as cathode reactant. To control the cell potential, a potentiostat as well as a booster (ZAHNER-Elektrik GmbH & CoKG) were used. The latter ensures accuracy at low total currents, which is required because of the small active area.

Two test protocols were used (see Fig. 1): one for the evaluation of the various recovery steps (Fig. 1a, protocol A) and one for the evaluation of the voltage losses under our low RH stress test (Fig. 1b, protocol B). Test protocol A started with an MEA conditioning, followed by a beginning-of-test (BoT) characterization. The test item was then held at low humidity and high operating temperature (20% RH and 90 °C) under 0.8 V cell voltage for 12 h, followed by an activity measurement (end-of-degradation, EoD). Thereafter a recovery step was employed (details in following section Recovery steps) and a final evaluation of the activity conducted (after-recovery, AR) to determine the effectiveness of each recovery step.

In test protocol B, the MEA was first conditioned, followed by a shortened recovery step (2 h) to ensure that the beginning-of-test (BoT) performance was not influenced by any reversible voltage losses. The BoT characterizations then started with a polarization curve, while H$_2$/air electrochemical impedance spectroscopy (EIS) was performed at certain cell voltages. Thereafter, CO stripping took place at 90% and 30% RH, followed by limiting current measurements and EIS in H$_2$/N$_2$, ending the characterization cycle. The MEA was then subjected to 12 h low RH operation. Afterwards (end-of-degradation, EoD), the whole characterization block was repeated (polarization curve, CO stripping, limiting current and EIS H$_2$/N$_2$). The full recovery step (selected from prior experiments) was then utilized, followed by another characterization block after the recovery (AR).

In the following, we elaborate every single testing procedure within the test protocols A/B. It shall be noticed that all given values of cell pressure refer to the absolute pressure (in kPa).

**Conditioning.**—All MEAs were conditioned at the beginning of each test protocol using the same voltage-controlled activation procedure under constant H$_2$/air flows of 1000/2000 nccm at 80 °C, 100% RH and 170 kPa$_{outlet}$. The sequence following was repeated 10 times: 45 min at 0.55 V, 30 s at open-circuit voltage (OCV), and 10 min at 0.85 V.

**Activity measurement.**—The activity measurements were performed using a similar experimental procedure as reported by Jomori et al.$^{28}$ We made small adjustments of the operating conditions, setting 80 °C, 90% RH and 170kPa$_{outlet}$ on both anode and cathode side. Additionally, the cell voltage was set to 0.85 V instead of 0.9 V (as reported by Jomori et al.) during the activity assessment, since the activity of Pt differs from that of Pt/Co used in the aforementioned publication. Figure S3 shows a schematic description of the activity measurement process. In short, the anode flows were kept constant at 1000 nccm H$_2$, while the cathode was being purged with 2000 nccm N$_2$, during which the cell voltage was set to 0.15 V for 180 s to ensure the reduction of the Pt surface before the measurement. Thereafter, cathode inlet gas was switched to air and held for 180 s. Lastly, the cathode potential was set back to 0.85 V and held for 350 s. The value that was taken as activity corresponds to the measured current density after 200 s at 0.85 V.

**Polarization curve.**—Polarization curves were measured at 80 °C, 90% RH and 170kPa$_{outlet}$ under constant differential flows of

![Figure 1](https://example.com/image1.png)

**Figure 1.** Summary of the two fuel cell measurement protocols for the evaluation of recovery steps (test protocol A) and voltage losses during the dry operation (test protocol B).
H₂/air at 1000/2000 nccm, respectively (at a current density of 2 A cm⁻², it would correspond to a stoichiometry of 14.2 for H₂ and 12.1 for air). The polarization curve was acquired similar to the EU harmonized test protocol: first ramping down the cell voltage towards high current densities (2.0 A cm⁻²), and thereafter recording the performance while ramping the cell voltage up from high current densities to low. Each current density point was held for 10 min (except 0.05, 0.1 and 0.2 A cm⁻², where the holding time was reduced to 30 s) and the resulting voltage was averaged over the final 30 s. Alternating current (AC) impedance spectra were collected at each current density to determine the respective high frequency resistance (HFR).

CO stripping (cyclic voltammetry).—CO stripping was performed at 80 °C cell temperature with 30% and 90% RH to determine the electrochemical active surface area (ECSA). The measurements were conducted under ambient pressure in both anode and cathode cell compartment. In the first step, the cathode was purged with 2000 nccm N₂ to remove all traces of O₂ for 30 min, whereas H₂ flow remained constant at 1000 nccm at the anode. Thereafter, CO (0.1% in N₂) was adsorbed for 30 min while the cell voltage was held at 0.1 V, followed by an additional 30 min of N₂ purging to remove any remaining CO from the gas phase. Subsequently, cyclic voltammetry (CV) measurement was conducted to oxidize the adsorbed CO by ramping the cathode cell potential from 0.053 to 1 V with a scan rate of 50 mV s⁻¹. Two additional sweeps were recorded in order to verify the complete CO oxidation from the electrode and gas phase. The ECSA was obtained by integrating the area in the voltammogram between the first anodic CO cycle and the subsequent cleaning cycle using a specific charge of 420 μC cm⁻².

Limiting current.—The total mass transport resistance was evaluated from limiting current measurements at a cell temperature of 80 °C and at two different RHs (30% and 90% RH). The flows were kept constant at 1000 nccm H₂ and 1235 nccm diluted air (4% O₂, 235 nccm air + 1000 nccm N₂). The cell was held at 0.3 V for 5 min and thereafter at 0.2 V for 2 min. The total mass transport current was kept to a minimum in order to avoid surface recovery, a similar protocol as in Jomori et al. The procedure was run at 170 kPa at both respective RHs. The total transport resistance (R²O₂) at a measured limiting current density (iₘₚ) can be obtained according to Eq. 1.

\[ i_{\text{lim}} = \frac{4F}{R^{\text{O}_2}} \left( \frac{\text{CO}_\text{ads}}{\text{O}_2 \text{channel}} \right) \]

Electrochemical impedance spectroscopy (EIS) in H₂/N₂.—The proton conduction resistance in the cathodic electrode during the various operating points was determined by AC impedance under H₂/N₂ (anode/cathode at 1000/2000 nccm) at 0.5 V with peak-to-peak perturbation of 20 mV (similar protocol as Liu et al.39,40). Frequencies were varied between 100 kHz and 0.3 Hz with 20 points per decade (<66 Hz: 5 periods, >66 Hz: 20 periods). Three sequential spectra were collected at each time to confirm reproducibility. Proton conduction resistances (R²H⁺,ca) were determined at 30% RH at 80 °C while maintaining the gas partial pressures constant. EIS spectra were also recorded at 90% RH, though deconvolution and fitting the transmission line model proved a challenge due to the electrode thickness (~3 μm) under these wet conditions.

From the proton conduction resistance, the specific proton resistivity (ρH⁺,ca) in Ω cm was obtained via Eq. 2, where the cathode electrode thickness was determined by the carbon loading (Lc) and the stacking density (24 μm/mg C cm⁻²), see Supporting Information.

\[ \rho_{H^+,ca} = \frac{R_{H^+,ca} 24 \mu \text{m}/(\text{mg C/cm}^2) \cdot L_c}{L_{\text{total}}} \]

Low humidity operation.—During the low humidity operation, the cell voltage was kept constant at 0.8 V, while the cell temperature and RH were set to 90 °C and 20%, respectively. The flows remained constant at 1000 nccm H₂ on the anode and 2000 nccm air at the cathode, while an outlet pressure of 170 kPa was kept in both sides. The duration of this operation was set to 12 h.

It should be mentioned that, due to the applied voltage, the resulting current density was below 0.1 A cm⁻². The little amount of produced water and the excess of the reacting gas ensured that the cell RH was the same as the outlet RH (also by taking into consideration the pressure drop over the active area, which is ~1 kPa).

The low RH operation at high cell temperature led to an accelerated performance loss (combination of reversible and irreversible losses) of the MEA, especially focusing on the cathodic electrode. These conditions were chosen as they would represent the conditions seen at the inlet of an automotive cell, where it is expected to suffer from the most voltage losses due to lower inlet RH. It is estimated that an automotive fuel cell stack, over its lifetime, will operate in total for around 200 h at temperatures above 90 °C and with cathode inlet RH between 20% and 30%. Although a continuous operation under these extreme conditions is unlikely for a real stack, by holding the experimental cell for a total of 12 h continuously in the present study, we were able to investigate the low RH effect in an accelerated environment. As the focus of the study is the catalyst layer, the total measuring time was also restricted to 12 h to avoid any structural change originating from the membrane.

We note that degradation protocols at OCV are also commonly applied in the literature, differing from the 0.8 V cell voltage applied here. It can be expected that greater reversible/irreversible losses will take place under OCV conditions, giving the possibility of membrane degradation as well as the higher overpotential towards adsorption reactions of ionomer sulfonic groups. The complete absence of water production under OCV will also possibly lead to slightly lower local RH within the cathode catalyst layer, compared to the currently applied 0.8 V. This might lead to further increase of the interfacial resistances on the Pt/ionomer interface.

Recovery steps.—Table II presents a summary of all three recovery steps that were investigated in the present study. The conditions for recovery step I were taken from the study of Jomori et al., where N₂ was fed to the cathode. Based on the knowledge that low applied cathode potential and high RH benefit recovery, the cell voltage was set to 0.2 V and cathode inlet RH to 120% for

| Recovery conditions | H₂/N₂ | H₂/Air | H₂/8.6% O₂ |
|---------------------|-------|--------|------------|
| Anode flow [nccm]   | 1000  | 1000   | 500        |
| Anode RH inlet      | 100%  | 100%   | 100%       |
| Cathode flow [nccm] | 2000  | [N₂] 2000 [Air] | 1700 [8.6% O₂] |
| Cathode RH inlet    | 120%  | 100%   | 100%       |
| Cell temperature [°C]| 80    | 45     | 45         |
| Cell voltage        | 0.2 V | 0.2 V  | 0.1 V      |
| Back pressure [kPa] | 170   | 170    | 230        |
| Duration [h]        | 2     | 4      | 4          |

Table II. Summary of recovery steps (I–III) investigated in this study. Anode gas is always H₂. Recovery step I applies N₂ on the cathode, whereas steps II and III air or diluted air.

[2]
recovery step I. Cell temperature was set at 80 °C and the recovery lasted 2 h, a duration which was deemed sufficient by the aforementioned publication.

Recovery step II took the principle from Owejan et al. and Harzer et al., introducing air as the cathode gas during the recovery. Cathode inlet humidity was set at 100% as in the publications, while cell temperature was reduced to 45 °C. The duration was prolonged to 4 h (instead of 2 h as in the publications) to ensure the completeness of the recovery. Applied cell voltage was kept at 0.2 V. This accounts for the high electric resistance of the graphite composite monopolar plate used, which elevates the local cathode potential to over 0.3 V (details will be given further on in Results and Discussions, Fig. 4a), similar to the cathode potential in the publications (0.3 V cell voltage, while using graphite monopolar plate with low electric resistance).

Recovery step III is a fusion of recovery step I and II. The cathode air was diluted with N₂ (air:N₂ = 7:10, which gives 8.6% O₂). Cell voltage was further lowered to 0.1 V with the aim to improve recovery efficiency, while the cathode back pressure was increased to 230 kPa.

Post mortem analysis using scanning electron microscope (SEM).—Images with high contrast and high resolution were obtained by use of HR-SEM (Zeiss SUPRA 55 VP with field emission electron gun and variable pressure) with a secondary electron detector, which serves to evaluate the ionomer distribution in the macropores of the catalyst layer. In order not to damage or alter the ionomer structure/morphology during image acquisition, the gentle beam mode was used with a low acceleration voltage of 1 kV. Working distance was adjusted depending on the geometry of each sample.

Imaging was performed at the back side of the decal of used and pristine MEAs: for the used MEAs, the gas diffusion layer (GDL) was carefully removed prior to imaging; for the pristine MEAs as a reference, the decals were transferred onto the membrane via a hot pressing procedure, and the back side of the electrode (after removal of the PTFE transfer film) was imaged (i.e. the side of the electrode that would be facing the GDL after cell assembly).

In addition, micrographs were obtained from pristine and used GDLs (after detach the GDL from the cathodic electrode), where an accelerating voltage of 1.5 kV was applied.

Results and Discussion

Effectiveness of recovery steps.—The percentage of activity loss that is regained during the recovery defines the effectiveness of the recovery steps. In Fig. 2, we compare the activity of the MEA after conditioning (beginning-of-test, BoT), after 12 h of low RH operation (end-of-degradation, EoD) and after various recovery steps (after recovery, AR). The activities are normalized to the BoT activity, which allows a better quantification of the percentages of the voltage loss and the voltage gain during each protocol. For all three experiments, the EoD mass activity is around 60% of the one at BoT, indicating degradation of the MEA after 12 h of low RH operation. This activity decrease is expected to be mainly caused by the increased anion adsorptivity of sulfonic groups upon drying of the CL in PEMFCs, which further induces change in ionomer structure and Pt/ionomer interfacial resistances.

From Fig. 2, however, it is surprising that under our experimental conditions, only recovery step III leads to an effective recovery. Recovery step I, suggested by Jomori et al., actually leads to a further degradation of the MEA, as the normalized AR activity only amounts to 0.3. On the other hand, recovery step II does not lead to an effective recovery either, showing less than 1% of recovery based on the obtained activities. In contrast, recovery step III using dilute air (8.6% O₂) at 0.1 V results in an activity recovery, reaching slightly above 80% of the BoT value. The missing ~20% of the BoT activity is due to irreversible losses that will be thoroughly explained in the following section.

According to Jomori et al., either liquid water presence or low potential at the cathode electrode would be sufficient for the recovery from low RH operations. Our results obtained from recovery steps I with H₂/N₂, however, suggest that even with both measures (high saturation at 100% in the CL, combined with cell voltage of 0.2 V), a successful recovery is not achieved. One plausible explanation is that the degradation by ionomer adsorption to the Pt surface is more severe in our case than in Jomori’s due to the higher fraction of external Pt particles (70% of the Pt particles are located on the external surface area, as opposed to Jomori et al. where most of the PtCo particles are located inside the primary pores of the high surface area carbon support). In addition, one has to consider the effects of ionomer type (backbone, side chain length and equivalent weight) in combination with the ink and electrode manufacturing process, which are known to affect the ionomer coverage of Pt and carbon, thus possibly contributing to the observed differences. It should be mentioned, though, that a prolongation of the recovery step I unlikely leads to any improvement, since a decline in activity was observed during the 2 h duration (Fig. 2).

Figure 3 illustrates another plausible explanation of the issue during recovery steps with H₂/N₂ (Fig. 3a) and compares it with steps utilizing H₂/air (Fig. 3b). Over-saturation in the flow field might not directly lead to over-saturation locally in the electrode, since water transport in the GDL is driven by capillary forces and may, in most cases, only occur in the direction away from the CL as a result of pore size distribution and their wetting characteristics. With air fed on the cathode inlet, recovery steps II and III have direct water production on the electrode as a result of oxygen reduction reaction (ORR). At cathode inlet humidity of 100%, this ensures that the electrode is over-saturated, which should result in a more effective recovery from dry operations.

However, recovery step II does not lead to efficient performance recovery, as opposed to recovery step III with dilute air (Fig. 2). To understand the different results with steps II and III, one has to compare the electric potentials, as well as heat and water management of both cases, shown in Fig. 4. It shall be emphasized that the cathode potential locally on the CL is always higher than the applied cell voltage, where their difference is mainly caused by the HFR of the cell. Under the high RH present during the recovery step (> 100% RH), the contribution of membrane resistance (10 μm thickness) to the HFR is expected to be small (less than around 0.015Ω·cm²), whereas the finite electric resistivity of the GDLs and the monopolar plates (MPPs) plays a more significant role. This becomes more evident due to the graphite composite monopolar plates used in our experimental step, which have a relatively high
electric resistance (0.0345 Ω·cm²). For recovery step II, where air is fed and the applied cell voltage is lowered to limiting current range at 0.2 V, the current density is up to ≈3 A cm⁻². An approximate profile of the electric potentials can be taken from Fig. 4a, where it can be observed that the actual cathode potential is elevated to around 0.34 V. In the case of both Owejan et al. and Harzer et al. graphite monopolar plates (low electric resistance) were used and a cell voltage of 0.3 V applied, hence their cathode potential ought to be similar to ours. According to Jomori et al., this cathode potential (>0.3 V) may be too high for an effective recovery within 4 h. However, this criterion might only apply for Pt/Co catalysts. Hanawa et al. estimated that above 0.2 V, sulfonic groups specially adsorb on Naion/Pt/Co (with Pt skin layer); whereas for Naion/Pt, the potential has been reported to be 0.4 V. This value was confirmed by Kodama et al. It would mean that when using Pt based electrodes in a fuel cell, any voltage below 0.4 V would eventually desorb the ionomer sulfonic groups and restore the electrode activity. Based on the results obtained from recovery step II, it is likely that the 0.34 V cathode potential is close to the adsorption/desorption equilibrium (around 0.4 V) and therefore the desorption process is too slow to be effective. A prolongation of the recovery step II is, however, not feasible due to the possibility of H₂O₂ formation at these low potentials, which could lead to irreversible degradation of the carbon support and detachment of ionomer.

Using diluted air (8.6% O₂) during recovery step III, the current density is reduced to <2 A cm⁻² for an applied cell potential of 0.1 V. As a result, the local cathode potential amounts to ≈0.18 V (see Fig. 4a). This gives a relatively large “driving force” towards desorption, which likely explains the successful recovery. In addition, the lower current density results in a lower heat production within the electrode and thus a lower temperature, which consequently amounts to a higher local RH. Figure 4b shows the estimated temperature and humidity profile for both cases based on the current produced (100% inlet RH is used in both cases, same as...
our experimental conditions). The calculations are done with the well-known down-the-channel flow model, details of which can be found in the Supporting Information.

Based on the above, it is evident that the combination of both low local potential (<0.2 V) and high local RH (>130%) leads to the high effectiveness of recovery step III compared to step II. By comparing to conventional recovery steps found in the literature, the advantages of the presented recovery step III are:

1. Direct water production via ORR and liquid water presence on the cathode electrode;
2. Relatively low current density (1.5–2 A cm\(^{-2}\)), which leads to relatively low cathode potential at constant cell voltage while producing sufficient amount of liquid water in the electrode;
3. High local RH due to low heat production.

We used the recovery step III for the second part of our study regarding the catalyst layer degradation mechanism and the influence of carbon support and I/C ratios.

**Overview of voltage losses.**—In the following section, we present the behavior of MEAs subjected to 12 h of low RH operation and the effect of the irreversible and reversible losses under these operating conditions. As also described in the experimental section, 5 cm\(^2\) MEAs were fabricated to determine the influence of the catalyst layer composition (carbon support with and without surface modification, as well as the I/C ratio) on the performance losses. The cathode catalyst layers of all MEAs have very similar loadings (overall 0.122±0.008 mgPt cm\(^{-2}\), see Table I), which ensures comparability between the different measurements (refer to Table I for details of each MEA).

Figure 5a depicts the performance at beginning of test (BoT) and after 12 h of low RH operation, denoted as end of degradation (EoD). The MEA performance at BoT for all three types of MEAs does not exhibit any significant difference despite the distinction between the CL composition and catalyst type (with and without surface modification).

It can be seen that the total voltage loss during the 12 h of low RH operation is substantial, amounting to around 100 mV at a current density of 1 A cm\(^{-2}\). This high voltage loss is expected due to the strong adsorption of ionomer sulfonic groups on the Pt surface under dry conditions, which results in a significant reduction of the Pt activity, in combination with ionomer structural changes (increase in interfacial resistance, mass transport and proton resistivity of the ionomer film). The loss of active sites is already evident in the low current density region (below 0.1 A cm\(^{-2}\)) due to the increased ORR overpotential. The MEAs consisting of the modified carbon support, independent of I/C ratio, exhibit higher performance losses than the ones with reference carbon. A plausible explanation is that the CLs with modified carbon support, having more homogeneous ionomer distribution, also exhibit a higher ionomer coverage over the Pt particles. This would inevitably result in stronger sulfonic group adsorption and loss of activity compared to CLs with non-modified carbon support.

As shown in Fig. 5b, after the recovery step (AR), part of the voltage losses is regained and thus can be characterized as reversible voltage loss. In contrast, the remaining counterpart even after the recovery step defines the irreversible losses over the low RH operation. For a better illustration, the total voltage losses (BoT performance minus EoD performance), as well as their deconvolution into reversible and irreversible losses, are depicted in Fig. S4 as a function of current density. There, it can be seen that within error bars, both the reversible voltage losses (also difference of respective bars in Figs. 5a and 5b) and the irreversible ones (also shown in Fig. 5b) are similar for all three types of MEAs studied. Based on the average voltage losses in Fig. S4, the irreversible voltage losses seem to be slightly higher for the CLs with I/C ratio of 0.65 compared to 0.82. This might suggest that the predominant origin of the irreversible performance loss is the ionomer detachment from the catalyst and support surface. It might still maintain a fairly high ionomer coverage of external Pt particles even after this ionomer movement. In addition, irreversible losses can take place due to ionomer degradation under dry operating conditions, where the ionomer decomposes to its fragments, sulfate or atomic sulfur. Adsorption of sulfur may further block Pt active sites. Nonetheless, due to the relatively large error bars of the voltage losses (refer to Fig. S4), we cannot derive concrete conclusions at this stage yet.

Lastly, it shall be mentioned that the H\(_2\) crossover was confirmed in situ to be constant at 0.6 mA cm\(^{-2}\) in all three test stages, thus having no influences on the polarization performances. Despite this, it can be observed in Fig. 5 at current density zero that the OCV of all three types of MEAs decreases from BoT to EoD and recovers from EoD to AR. This shall be explained by the decreased activity at EoD and is further discussed in the Supporting Information.
different MEAs. Under these conditions, the observed voltage losses (see Fig. 5) cannot be rationalized to have originated from any major ohmic changes in the CL.

Nevertheless, proton resistances increase significantly with lower RH, which also corresponds to significantly reduced measurement error. Thus, proton conductivity measurements recorded at 30% RH were used for the evaluation of the changes in proton conductive pathway in the different cathode catalyst layer types.

Figure 6 depicts the specific proton resistivity in the cathode catalyst layer from various MEA types during degradation and recovery at 30% RH. Under the same I/C ratio of 0.65, the MEAs comprising catalyst supported on reference KB (grey bars) show overall higher proton resistances than the ones with modified carbon (green bars). This is expected since surface modification of carbon support is known to lead to a more uniform ionomer distribution.\textsuperscript{9,13} Unsurprisingly, between the two modified based CLs, the one with higher ionomer content also exhibits slightly lower proton resistivity. The observed proton resistivity, especially for the MEA comprising the reference carbon, is in good agreement with the values observed in literature for high surface area carbons using low equivalent weight ionomers with similar I/C.\textsuperscript{13}

For all three types of CLs, it was observed that the resistance increases slightly during low RH operation (BoT to EoD) and returns to its original position after the recovery steps have been conducted (EoD to AR). Although the differences are relatively small and comparable to error bars, the same trend is observed for all MEAs and should be convincing. Such small changes in the proton conductivity might be due to distortion of proton conductive pathways, which could be caused by ionomer movement over the carbon surface during the low RH operation as a result of dehydration (shrinking of ionomer). The extent of this distortion is the highest for the reference carbon (grey bars in Fig. 6), as the ionomer is less constrained by carbon surface modification.\textsuperscript{9,12} MEAs with I/C = 0.82 (blue bars) show the lowest extent of degradation, which is likely the result of a thicker ionomer layer, where the same extent of distortion would have a less significant influence on proton conduction. The return of the proton conductivity during the recovery step (AR) to its original value (BoT) does not necessarily mean that the ionomer is being redistributed to its original state. Orfanidi et al.\textsuperscript{37} showed that the homogeneity of the ionomer on the catalyst surface cannot necessarily be deduced from proton resistivity measurements, as electrodes with the same tortuosity but different ionomer distributions might still result in the same value of CL proton conductivity. As it will be discussed later on, the ECSA reflects this change in the ionomer distribution more accurately.

**Kinetic losses.**—The increased kinetic losses caused by dry operation may partially be reflected by the decrease in electrochemical surface area (ECSA) of the cathode electrode.

Figure 7 shows the ECSA with the three tested MEAs at different stages during the measurement. The effect of the RH on the ECSA is also compared. Generally speaking, the evaluation of the ECSA via CO stripping (see Experimental) provides an estimation of the surface area of the Pt particles that are accessible to water and hence protons. The water accessibility allows the presence of adsorbed oxygenated groups (such as \(-\text{OH}\)) which are required for the electrochemical oxidation of CO to \(\text{CO}_2\). Therefore, for CO oxidation at low RH (e.g. \(\leq 30\%\)), the charge observed during the anodic scan not only comes from those particles located at the surface of the primary carbon particle, but also from Pt particles inside pores with \(> 3 \text{ nm}\) in diameter that still allow some ionomer penetration and hence water adsorption. Internal Pt particles (located deep inside the micropores of \(< 2 \text{ nm}\) diameter), on the other hand, are electrochemically inactive under these conditions due to in-accessibility of the ionomer through the pore opening and lack of proton conduction pathway under low RH. Contrary, under high RH (\(> 80\%\)), capillary condensation occurs within primary pores, granting access of protons also to internal Pt particles. As a result,
The decrease of the ECSA at 90% RH from $\sim 50$ m$^2$/gPt to $\sim 40$ m$^2$/gPt would correspond to a theoretical kinetic voltage loss of $\sim 6$ mV at 1.0 A cm$^{-2}$. This is estimated by applying the kinetic calculation by Neyerlin et al.$^{52}$ (Eq. 11 in the publication) and a specific current density ($i_{\text{kin}}^{0.9 \text{V}}$) of 250 $\mu$A cm$^{-2}$. This is taken as constant for the comparison, $i_{\text{kin}}^{0.9 \text{V}}$ and the corresponding mass activity at 0.9 V (125 A g$^{-1}$) agree well with the literature$^{12,13}$ on surface modified Pt/KB catalysts. This theoretical voltage loss will be slightly different for the reference KB with somewhat different $i_{\text{kin}}^{0.9 \text{V}}$. Overall, however, this theoretical loss of $< 10$ mV is too small to explain the irreversible voltage losses observed in the polarization curves (Fig. 5b) in the order of over $\sim 30$ mV. This suggests that the ECSA decrease is not the only origin of performance losses, as will be thoroughly discussed in the next section. Nonetheless, it has to be stated that it is very challenging to assign all the voltage losses based on the measurement technique itself.$^{5,13}$

**Concentration losses.**—To evaluate whether the observed additional performance losses at high current densities are influenced by concentration losses, the total oxygen mass transport resistances were evaluated via limiting current method. Measurements were conducted at 30% and 90% RH and the results are shown in Fig. 8. A relative humidity of 90% (instead of 100%) was used in order to avoid measurement artifacts due to water condensation in the GDL.$^{29,38}$ In addition, we conducted the limiting current experiments in the same manner as described by Jomori et al.$^{28}$ to minimize the measurement time, thus avoiding any reconstruction of the Pt/ionomer interface that might lead to a partial recovery during the measurement.

As shown in Fig. 8a, all three different CLs exhibited almost identical total oxygen mass transport resistance at 90% RH over the duration of degradation and recovery protocols (BoT, EoD and AR). This is in contrast to a previous study by Orfanidi et al.$^9$ where it was shown that surface functionalization of a Vulcan carbon support resulted in reduced mass transport resistance for the same I/C. The discrepancy can be explained by considering the different type of carbon used in this study, namely Ketjen Black. Harzer et al.$^{11}$ also showed that surface modification when using a KB carbon support for an I/C = 0.65, similar like in our case, did not result in any benefit with respect to the mass transport resistances. This was rationalized based on the effective ionomer film thickness: a significant fraction of the ionomer is being absorbed into the carbon nanofibers,$^{54}$ resulting in a very thin ionomer film over the high surface area KB carbon support$^{11}$ ($\approx 1.7$ times thinner ionomer coverage on the outer surface of the KB compared to the Vulcan$^\text{C}^\text{3}^\text{d}$). Therefore, inhomogeneous ionomer distribution in the CL would not result in any significant difference in the total mass transport resistance due to the very thin ionomer film thickness. The same rational can be used for not observing any mass transport increase for the CLs with I/C = 0.82.

From Fig. 8a, it is apparent that the mass transport resistances measured at 90% RH do not change during our testing protocol. Therefore, they do not contribute to any additional voltage losses observed in the polarization curves (Fig. 5).

Figure 8b depicts the development of mass transport resistances measured at 30% RH. By lowering the humidity, we are able to identify more clearly the changes in the CL with respect to ionomer distribution and its effect on the mass transport resistance. As expected, the absolute values of the resistances are significantly higher compared to the ones at 90% RH.$^{37,53}$ Additionally, CLs comprising of modified KB with I/C = 0.82 show a significant lower mass transport resistance compared to the same carbon support with I/C = 0.65. This on a first glimpse seems counter-intuitive, as it is well known that higher I/C would lead to a thicker ionomer film over the catalyst and higher mass transport resistances.$^9$ Instead, one also has to account for the roughness factor of each CL and its influence on the mass transport resistance.$^{29}$ Since for the CL with I/C = 0.82, the ECSA at 30% RH is $\sim 30\%$ higher than the CL with I/C = 0.65 (Fig. 7), it can be expected that the measured mass transport resistance is lower.

![Figure 7](image-url) Comparison of electrochemical active surface area (ECSA) at beginning-of-test (BoT), end-of-degradation (EoD, after low RH operation) and after recovery step (AR) for MEAs No. 4–9 (listed in Table I) with various I/C ratios (0.65, 0.82) and with/without carbon support surface modification, measured at (a) 30% and (b) 90% RH. The ECSAs are measured via CO stripping method. Error bars represent the mean absolute deviation from two independent measurements.

The ratio of the surface area obtained from wet to dry RH can be used as a projection of catalyst accessibility at a given RH value.

Under 30% RH (Fig. 7a), both types of CLs with I/C = 0.65 exhibit the same ECSA at BoT, which is in both cases significantly lower compared to the CL with I/C = 0.82. This indicates that for the case of I/C = 0.65, the ionomer is not covering the catalyst surface entirely. This is not surprising as a significant fraction of the ionomer is known to be absorbed into the carbon nanofibers,$^{54}$ possibly rendering the remaining amount insufficient to fully cover the external surface of the KB and to grant access to all Pt particles. The latter hypothesis is confirmed after comparing the ECSA of the different catalyst layer at BoT under 90% RH (Fig. 7b), where considering the error bars, the ECSA appears to be very similar for all cases.

At 30% RH, no decrease in ECSA can be observed throughout our testing protocol (from BoT to EoD and AR). This would suggest that the Pt particle size and the ionomer coverage with respect to the catalyst external surface did not significantly change. On the other hand, the ECSA under 90% RH decreases considerably over the subsequent recovery (AR). Based on the results with 30% RH, where the electrochemical accessibility of the external Pt particles did not change, it is highly likely that the internal Pt particles become inaccessible also for protons under high RH.

Additionally, it can be observed from Fig. 7b that the ECSA losses at 90% RH seem to be less for the MEAs comprising KB-mod I/C = 0.65, compared to the other two types. This may serve as evidence towards ionomer rearrangement, since a high ionomer content (I/C = 0.82) or weaker ionomer interaction with the support (reference KB, no functional groups to interact with the ionomer) would both lead to stronger rearrangement statistically.

The decrease of the ECSA at 90% RH from $\sim 50$ m$^2$/gPt to $\sim 40$ m$^2$/gPt would correspond to a theoretical kinetic voltage loss of $\sim 6$ mV at 1.0 A cm$^{-2}$. This is estimated by applying the kinetic
Interestingly, the mass transport resistance after 12 h operation at 90 °C and 20% RH increases significantly for all types of CLs (Fig. 8b). This increase is completely reversible by the subsequent recovery steps. Jomori et al. explained the similar phenomenon by proposing two possibilities for the degradation of Pt/ionomer interface, namely by a decrease in effective Pt surface area, or by structural changes of ionomer near to the Pt surface which lowers O2 permeability locally. However, since we did not observe a decrease in the ECSA at 30% RH (Fig. 7), we believe that the dominating degradation mechanism in our case is the disruption of Pt/ionomer interface.

Additionally, it is highly plausible that a change in proton conductivity (Fig. 6) is an additional contributing factor in the increase of the mass transport resistance. In order to understand the origin of this, one has to go back to the basic principles of the measurement itself. Two transport phenomena limit the measured current: a. O2 mass transport through Pt/ionomer interface; and b. proton transport that delivers the necessary protons for the ORR to the Pt active sites. Nonoyama et al. reported that proton conduction resistance in the CL is low enough, so that the measured current is primarily limited by the O2 mass transport resistance, as is the case in a standard limiting current measurement.

When conducting limiting current measurement at 70%–100% RH, the proton conduction resistance in the CL is low enough, so that the measured current is primarily limited by the O2 mass transport resistance, as is the case in a standard limiting current measurement (Fig. 7a, right). On the other hand, when conducting the measurement at 30% RH, both factors may play a role (Fig. 7b, right) as the proton resistivity in the CL increases significantly (by a factor of ∼4–7, see Fig. 6 vs Fig. S8). As a result, it is plausible that the observed increase in the proton conductivity at EoD (Fig. 6), due to a decrease in the recorded current density, contributes “artificially” in the rise of the mass transport resistance.

In addition, as both types of catalyst (with and without surface modification) were synthesized in the same manner, such that both had the same percentage of external vs internal Pt particles with respect to the carbon surface, all types of electrodes are expected to exhibit the same contribution of the Pt location on the local mass transport resistance. Hence, the difference observed at 30% RH can solely be attributed to the difference in Pt/ionomer interface (ionomer film thickness and distribution) and proton conductivity change in the CL and not due to the Pt location.

Post-mortem analysis: results from SEM.—In order to verify the hypothesis of ionomer re-distribution in the CL, SEM micrographs of the cathodic electrodes were obtained for all samples subjected to test protocol B. The same analysis was also applied to pristine MEAs as a reference state. Generally, the ionomer in the electrode is hardly visible via SEM due to significant shrinkage in the dry vacuum environment, in addition to the weak contrast between ionomer and carbon. Nevertheless, secondary ionomer aggregates or ionomer fibers that are large enough in size can possibly be visualized under specific conditions (see experimental section).

Figure 9 shows representative micrographs for two pristine electrodes (before operation), made from two catalyst types (different carbon support: Ketjen Black with and without surface modification as well as different I/C ratios). Thin ionomer fibers are visible only at high magnifications on the CL surface for both types of electrodes (Figs. 9b, 9c, and 9f where the fibers are indicated by white arrows). For the MEA with an I/C ratio of 0.82, additional thin nm-sized patches of ionomer (∼400 × 200 nm, see Fig. 9c marked by white arrows) were observed to cover parts of the CL surface. As expected, the extent to which ionomer patches and fibers appear increases with the CL ionomer content. The presence of ionomer patches on the back side of the CL (facing the GDL) is known to block macropores under high RH operating conditions, causing mass transport hindrance and thus resulting in lower MEA performance.

However, we do not observe any hindrance of the MEA performance by comparing their respective polarization curves under 90% RH (Fig. 5). This is due to the significantly smaller size of these ionomer patches compared to those in literature.
Figures 10a–10d depict the SEM micrographs of the cathodic CLs (GDL facing surface) after operation. In all cases, we observe ionomer fibers with length scale in microns covering large parts of the surface. It should be mentioned that these fibers, as also seen when comparing with Fig. 9, were not present before operation of the MEA, which serves as a first indication of ionomer movement.

Furthermore, the extent of coverage and amount of these ionomer fibers differ with respect to the I/C ratio in the CL. More specifically, it is apparent from Fig. 10 that the CL surface is covered to a much higher extent with micron-scale ionomer fibers for the case of I/C = 0.82 compared to I/C = 0.65 (refer to Figs. 10a, 10b and Figs. S12–S14). In contrast to the catalyst layer with I/C = 0.82, the electrodes with I/C = 0.65 (Figs. 10a and 10c) had large areas were these ionomer fibers were absent (Figs. S13a and S14a). The above stated observations agree with our hypothesis of the ionomer “displacement,” as one would expect that this would be more prominent with a higher ionomer content in the CL. The ionomer displacement and redistribution, as well as loss of total ionomer fraction in the CL with operation time, were also observed by Morawietz et al. They reported that the ionomer displacement and redistribution resulted in a growth of bigger ionomer agglomerates after prolonged operation. Similar in our case, after operation, we observe the increase in amount and size of the ionomer fibers that are present in the CL/GDL interface.

For additional proof that the observed ionomer fibers were not generated by the detachment of the GDL from the CL during sample preparation for SEM imaging, we conducted an additional experiment. A fresh MEA, with the same specifications as MEAs No. 6–7 (50 wt% Pt/KB-mod with I/C = 0.82) was subject to normal fuel cell operation with no RH changes nor increased operating temperature (see details of experimental conditions and discussions in the Supporting Information section “Additional SEM section and SEM micrographs”). From the obtained SEM micrographs in Fig. S11, we conclude that the operation history could affect the
presence of the ionomer fibers on the CL/MPL interface, and that the sample preparation (detachment of GDL from cathode CL) for the SEM imaging is not responsible for the presence/formation of these ionomer fibers. Although all CLs have been prepared under identical conditions, these observations regarding ionomer rearrangement are intrinsic to the experimental protocol used in this work in terms of ink composition and catalyst layer drying. These conditions define the strength of ionomer/support interaction.

One may argue whether the observed fibers could also have originated directly from the additives or binders in the microporous layer (MPL) in the GDL. In fact, if this had been true, the extent of the increase of these fibers would have been independent of the I/C ratio in the CL. Nonetheless, for additional confirmation, GDLs were also subjected to the SEM analysis. During the sample preparation, it was observed that detaching the GDLs did not require a lot of forces (see Supporting Information). Nevertheless, for MEAs of I/C = 0.82, slightly more effort was required compared to the lower I/C based cathodic electrodes. By comparing Figs. 10c and 10f (as well as Figs. S15–S16), it becomes clear that the surface of the MPL was also covered with ionomer fibers of the same nature and length as those present on the cathode catalyst surface. As shown in Fig. S16, the ionomer fibers were only present in the upper surface of the MPL, while no fibers were seen to originate from within MPL cracks. In Supporting Information, we have added more micrographs at different magnifications in order to depict our observations. Based on this, we can exclude the possibility that the observed fibers (Figs. 10a, 10b) originate from the GDL. Instead, the fibers observed on the MPL are rather being transferred from the catalyst layer onto the MPL during the sample preparation of used MEAs, where the GDL has to be detached from the catalyst layer.

Figure 10. SEM micrographs of cathodic electrodes and GDLs after operation (with test protocol B): (a), and (c), cathodes comprising 50 wt% Pt/KB with I/C = 0.65; (b), and (d), cathodes comprising 50 wt% Pt/KB-mod with I/C = 0.82; (e), pristine GDL; (f), used cathodic GDL.
Discussion of degradation mechanisms.—It is known that the nanostructure of ionomer perfluorosulfonic acids (PFSA) is not stationary, but it adapts according to its operating history and related changes in humidity, temperature and pressure.36 This nature of PFSA ionomers makes the investigation of ionomer degradation mechanisms in the CL challenging. Based on the data presented in this study, we propose the following degradation mechanism and plausible origin of the performance losses.

The degradation of the Pt/ionomer interface starts during the 12 h operation at low RH. Prolonged operation at elevated temperatures (90 °C) and low RH leads, as it is widely known and also discussed in previous sections of this paper, to stronger adsorption of ionomer SO3− groups on the Pt surface, which disrupts the Pt/ionomer interface and possibly induces ionomer restructuring/reorganization.28 This results in changes in both mass transport resistance and proton conductivity in addition to interfacial resistances. All of the above have contributed, each to a different degree, to the observed performance losses (BoT to EoD) accounting for both reversible and irreversible losses.

In addition, the loss of interfacial and/or bulk water during the 12 h holding under 90 °C and 20% RH would result in shrinking of the ionomer film that is covering the Pt/C.57 This might lead to local delamination of the ionomer from the carbon support. Furthermore, the higher operating temperature is known to induce a flow of ionomer from positions around the Pt/C particles to the mesopores.55

Directly after the low RH and high temperature operation, the recovery step takes place (holding at 0.1 V under high RH), where the low cathode potential results in desorption of the ionomer SO3− groups, while liquid water is generated at the Pt/ionomer interface. This induces hydration and regeneration/restructuring of the ionomer, leading to recovery of proton conductivity48,49 (as observed in Fig. 6) and mass transport resistances28 (Fig. 8). These mechanisms represent the reversible losses during the low RH operation.

Furthermore, during the recovery step (> 120% RH), the presence of liquid water in the CL likely facilitates ionomer solving while creating micelles.55 It is widely known that short side chain low EW ionomer have the propensity for dissolution and flow, compared to the high EW ionomers, which has been rationalized by the comparable higher ionomer water uptake.55 Thus, the ionomer variant in the present study (725 EW), together with the ink composition and catalyst layer drying protocol used in this work, is prone to such ionomer flows and would irreversibly alter the ionomer distribution in the CL. While liquid water is generated in the CL and flows towards the GDL (typical water removal process within a fuel cell), the micelles are likely dragged by the water flow in the same direction. As a result, the ionomer is partially rearranged/redistributed inside the CL, probably causing partial blockage of the porous structure. This change of ionomer distribution is a possible explanation for the additional irreversible ECSA loss (as illustrated in Fig. 7b) observed after the recovery step, which also represents the irreversible voltage losses.

Due to structural hindrance of the CL porous structure, it is unlikely for the ionomer to move across the entire catalyst layer. Based on the analysis above, it is most likely that the ionomer fibers visible at the CL/GDL interface (observed in the SEM, Figs. 9 and 10) have originated from the CL region that is closer to the GDL.

Lastly, it shall be noted that the mechanism of ionomer redistribution is not to be considered as a result of only the water-producing recovery step, since any further normal fuel cell operation (or the electrochemical characterizations in the present study at > 90% RH) would lead to similar water production and hence ionomer migration. A recent study from Yin et al. has shown that microstructural change in CL are related to ionomer migration, which occurs under conditions of high humidity during periodic RH cycling.59 The ionomer displacement, induced by operations under low RH conditions and sequentially high RH, not only causes irreversible ECSA losses directly, but inevitably induces further irreversible losses when the fuel cell returns to its normal wet operational conditions. Therefore, routes that lead to an increase in the strength of ionomer interaction are highly desired in order to mitigate irreversible losses that can occur during fuel cell operation.

Conclusions

The degradation of the MEA, being reversible and/or irreversible in its nature, lowers the performance of a PEMFC and inhibits its commercialization. In this paper, performance losses after prolonged dry operation and subsequent recovery of a PEMFC were experimentally studied, with focus on recovery step effectiveness and degradation mechanisms. We show that a recovery protocol with full-humidified diluted air is more beneficial towards efficient activity recovery due to its privileges in water and heat management.

With the help of electrochemical characterizations and post-mortem SEM imaging, we identified ionomer detachment from the catalyst and ionomer redistribution within the CL as an additional mechanism for the performance losses, besides the known mechanism of sulfonic group poisoning and degradation of Pt/ionomer interface. While the poisoning effect and degradation of interface are mostly recoverable, the ECSA loss that is caused by the ionomer movement highly probably results in irreversible voltage losses. A comparison between MEAs with different carbon support reveals that this surface modification alters the beginning-of-test electrochemical characteristics to a certain extent, yet has limited influence on the performance degradation throughout our measurement protocol.

On the other hand, it turns out that a higher ionomer content may lead to some mitigation of the voltage losses occurring during the low humidity operations. These mechanistic insights serve as valuable inputs for future operational strategies and MEA development towards higher durability of PEMFCs.

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