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Quantification on degradation mechanisms of polymer electrolyte membrane fuel cell catalyst layers during accelerated stress test

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Abstract

Long term durability of the catalyst layers of a low working temperature fuel cell such as polymer electrolyte membrane fuel cell (PEMFC) is of significant scientific interest owing to their operation criteria and high initial cost. Identification of degradation mechanisms quantitatively during an accelerated stress test (AST) is essential to assess and improve the durability of such catalyst layers. In this study, we present a quantitative analysis of the degradation mechanisms such as (i) electronic connectivity loss due to carbon support corrosion, (ii) proton connectivity loss due to ionomer/catalyst interface loss, (iii) catalyst loss due to dissolution or detachment, and (iv) physical surface area loss due to particle growth responsible for the electrochemical surface area (ECSA) loss in Pt-based catalyst layers for PEMFCs during an AST performed through potential cycling (linear sweep cyclic voltammetry) between 0.4 and 1.6 V for 7000 cycles in Ar saturated 1 M H₂SO₄. Using a half membrane electrode assembly (half-MEA), where a gas diffusion electrode with genuine three-phase-boundaries is used as working electrode through solid electrolyte, we have observed the ECSA loss due to ionomer/catalyst interface loss and identified catalyst heterogeneous degradation pattern during AST. Results suggest a significant ECSA loss due to catalyst isolation (~64% of ECSA loss) from loss of electron and proton connectivities respectively by catalyst support corrosion (~45%) and ionomer/catalyst interface loss (~19%), followed by
particle growth (~30%) and dissolution/detachment (6%). Such knowledge and methodology can effectively contribute to catalyst material screening and electrode structure development to advance the PEMFC technology.

**Keywords**

Degradation mechanism, support corrosion, catalyst/ionomer interface, catalyst isolation, heterogeneous degradation, half-MEA

**Introduction**

Despite their high power conversion efficiency, suitability for a broad range of power requirements and environmentally friendly nature, large scale application of polymer electrolyte membrane fuel cells (PEMFCs) is hindered by the high initial cost and low durability of noble metal, especially Pt-based catalyst layers.\(^1\)\(^-\)\(^2\) Significant efforts are being made since long to understand and mitigate the catalyst degradation mechanisms for the development of highly durable PEMFC catalyst layers.\(^3\)\(^-\)\(^6\) Strategies being employed to enhance the catalyst layer durability include mainly (i) the mitigation of catalyst support corrosion by using highly durable support materials such as carbon nanomaterials,\(^7\)\(^-\)\(^10\) carbon-free supports,\(^11\)\(^-\)\(^12\) etc., and (ii) the enhancement of Pt stability through bulk and surface compositional modifications.\(^13\)\(^-\)\(^15\) Noteworthy research with partial success makes the topic more exciting with possibility for improvements.

In heterogeneous catalysis, the functioning of a catalytically active site depends not only on its catalytic activity but also on its interaction with surrounding media responsible for ensuring the accessibility to reaction species and the removal of byproducts. Particularly, in PEMFCs, performance of catalyst layers towards catalysis of oxygen reduction reaction (ORR; \(\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}\)) and hydrogen oxidation reaction (HOR; \(\text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^-\)) depends on the electronic, protonic and reactant gas connectivity values of the active sites.\(^16\) In a state-of-the-art PEMFC
catalyst layer, the catalyst ink consists of a mixture of the polycrystalline Pt-group metal nanoparticles supported on high surface area carbon and the proton conducting ionomer (e.g. Nafion®) in a typical ratio of 70:30 (w/w). The desired connectivity to e− and H+ are achieved through the carbon support and the ionomer, respectively.

The performance degradation of a catalyst layer during operation is essentially due to either the change in the type or the number of active sites accessible for the reaction. Accelerated stress test (AST) based on evolution of the parameters such as electrochemical surface area (ECSA) during a potential cycling between specified potential range, which is a measure of combination of the type and number of the active sites, has been used frequently for experimental evaluation of the durability of such catalyst layers. However, in a state-of-the-art PEMFC catalyst layer, the type of active site may be considered to be unchanged (assuming random orientation of crystallite faces) during AST. Under this assumption, the change in ECSA of a catalyst layer during operation/AST may be assigned to the change in the number of accessible active sites. Performance degradation due to the reduced number of active sites and hence reduced ECSA may be assigned principally to (i) catalyst isolation due to carbon support corrosion (electronic connectivity loss),17-20 (ii) catalyst isolation due to ionomer/catalyst interface loss (proton connectivity loss), (iii) loss of catalyst loading due to dissolution or detachment and (iv) coarsening of catalyst nanoparticles due to mechanisms such as electrochemical dissolution/redeposition (Ostwald ripening), migration, etc.21

Substantial attention has been paid in recent past towards the identification of electrode performance degradation mechanisms, which requires a combination of electrochemical and structural characterization techniques. While the distribution of particle size can be observed directly using transmission electron microscopy (TEM) or be estimated indirectly through X-ray diffraction (XRD), loss due to Pt-dissolution may be estimated through elemental analysis techniques.22-24 Borup et al. have estimated the effect of carbon corrosion on durability by using the
Pt/C XRD signal ratio before and after AST and a decreased carbon signal was attributed to the carbon corrosion. Similarly, identical location TEM (IL-TEM) has been employed to observe various degradation mechanisms such as support corrosion, agglomeration, dissolution and detachment of catalyst particles. Those works focus on the catalyst itself, which is certainly essential, but remain isolated from the electrode level and ignore huge impact from the interface structure; moreover, the estimation of H⁺ connectivity loss for the standard three-electrode AST has not been arguably reported.

Present study attempts to quantify the fractional contributions of the ECSA loss mechanisms of a state-of-the-art PEMFC catalyst layer during an AST performed through potential cycling (linear sweep cyclic voltammetry) between 0.4 and 1.6 V in Ar saturated 1 M H₂SO₄. Despite significant scientific emphasis on development of catalyst layers with improved durability, fractional quantification of ECSA loss among the aforementioned mechanisms has not been arguably presented due to the inherent limitations of the AST using a three-electrode setup measuring ECSA evolution with potential cycling in liquid electrolytes (Fig. 1a). As shown in Fig. 1b, ECSA measurement using liquid electrolyte provides two H⁺ conduction pathways, namely through liquid electrolyte and through solid electrolyte - ionomer. Hence, particles having no H⁺ connectivity through ionomer (type -2) also contribute to ECSA and hence the effect of catalyst isolation due to ionomer/catalyst interface loss/detachment cannot be detected. Moreover, such artificial proton conductivity also leads to false degradation.

In the present study, a modified three-electrode setup consisting of a working electrode in form of half membrane electrode assembly (half-MEA) along with the conventional reference and counter electrodes (Fig. 1d) has been used. As shown in Fig. 1e, the setup avoids the H⁺ conduction pathway through liquid electrolyte and hence enables estimation of the ionomer/catalyst interface loss/detachment. Possible types of e⁻ and H⁺ pathways to Pt particles after AST (owing to particle
growth, migration, detachment, etc.) have been depicted in figures 1c and 1f for standard and half-MEA setups, respectively. Again, the possible e⁻ and H⁺ connectivity combinations for different types of Pt particles of figures 1b-1c and 1e-1f have been summarized in Table 1.

Figure 1: Schematics of the three-electrode cells for AST using (a) standard and (d) half-MEA setups. (b) and (c) respectively depict the types of e⁻ and H⁺ connectivity pathways for standard electrode before and after AST, while (e) and (f) represent the corresponding types for half-MEA.

Table 1: Possible e⁻ and H⁺ pathways for different types of Pt particles subjected to AST in liquid/solid electrolyte using standard/half-MEA setup.

<table>
<thead>
<tr>
<th>Pt nanoparticle type</th>
<th>Type-1</th>
<th>Type-2</th>
<th>Type-3</th>
<th>Type-4</th>
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<tr>
<td>Connectivity type</td>
<td>e⁻ H⁺</td>
<td>e⁻ H⁺</td>
<td>e⁻ H⁺</td>
<td>e⁻ H⁺</td>
</tr>
<tr>
<td>Liquid electrolyte</td>
<td>✓ ✓</td>
<td>✓ ✓</td>
<td>✓ ✓</td>
<td>× ✓</td>
</tr>
</tbody>
</table>
Accelerated stress test, as a mimic of realistic but extreme operation conditions on catalytic structure in a fuel cell can be expensive, complex and high risk due to involvement of many other operation factors. Half-MEA has advantages such as: (i) systematic study of only one electrode at a time (only anode or cathode); (ii) stable and independent counter and reference electrode for reliable measurements; (iii) realistic three-phase-boundary, not restricted to gas diffusion limit; (iv) economic, flexible and open to a variety of parameters of interest. Such approach can be a powerful tool to clarify reaction and/or degradation mechanisms of electrochemical structures and realistically optimize electrode design for energy conversion related technologies.

2. Experimental methods

2.1 Half-MEA cell assembly

To distinguish between the two proton conduction pathways to catalyst particles, electrochemical measurements were performed using two different three-electrode setups, namely the standard setup consisting of working electrode (WE), reference electrode (RE) and counter electrode (CE) in direct contact with liquid electrolyte (1 M H₂SO₄) and the half-MEA setup where dissimilar to RE and CE, the WE was kept in direct contact with a solid electrolyte – proton exchange membrane PEM (Nafion® 212) instead of liquid electrolyte. While both the proton conduction pathways to the catalyst particles at WE were accessible in the standard setup (WE directly in contact with liquid electrolyte), the half-MEA setup (WE in contact with liquid electrolyte through PEM) was used to block the liquid electrolyte pathway.

State-of-the-art catalyst layers were used for both the half-MEA and the standard setups to ensure high utilization, i.e. a negligible fraction of catalyst particles of type-2. The WE for half-MEA
setup, resembling half of the standard MEAs used in a PEMFC was prepared at EWII fuel cells A/S through state-of-the-art process used for the full MEAs. Briefly, an electrode sheet (2.86 cm$^2$) consisting of HiSPEC® 9100 Pt/C (0.6 mgPt cm$^{-2}$) catalyst and 30 wt% Nafion ionomer spray coated on a gas diffusion layer (GDL; BD35 SIGRACET®) was hot pressed with a PEM (Nafion® 212) to form the half-MEA. As shown in Fig. 1d, the half-MEA three-electrode assembly consisted of a stainless steel (SS) bottom plate with gas inlet and outlet, a graphite end plate with serpentine flow channels (2.0 × 2.0 cm$^2$ flow channel area), the half-MEA (GDL side facing the flow channels), and a top plate (~2 cm thick Teflon block) with a central opening of 2.0 × 2.0 cm$^2$ to provide liquid electrolyte access to the half-MEA such that the liquid electrolyte was in direct contact with its PEM side. The cell was tightened using four screws through the holes in the bottom and top plates with a torque of 5.0 cmkp, while the gas/liquid sealing was achieved through appropriate use of o-rings. The WE was connected to outer circuit through the bottom SS plate, while the RE and CE were in direct contact to the liquid electrolyte.

On the other hand, measurements in liquid electrolyte (standard setup) were performed in a Teflon cell of dimensions similar to those of the half-MEA cell. The WE, a 10 mm diameter circular sheet of HiSPEC® 9100 Pt/C (0.6 mgPt cm$^{-2}$) spray-coated on a GDL (BD35 SIGRACET®), was connected to outer circuit through a 0.2 mm thick gold wire.

2.2 Electrochemical measurements

The durability and degradation mechanisms were studied by subjecting the electrodes to linear sweep cyclic voltammetry cycling for 7000 cycles using 1 M H$_2$SO$_4$ electrolyte (prepared using H$_2$SO$_4$; EMSURE® grade, assay > 95 – 97%, Merck, Germany and Milli-Q water; resistivity ≥ 18.2 MΩ·cm at 25 °C) in an inert atmosphere (Ar) within a potential range of 0.4-1.6 V. The wide potential range was selected to enable various degradation mechanisms such as carbon corrosion,
Pt-dissolution/re-deposition, etc. to act simultaneously.\textsuperscript{27} For half-MEA setup, inert atmosphere was created by continuous flow of Ar (humidified by bubbling through Milli-Q water bubbler at room temperature) through the gas flow channels of the end plate while for the standard three-electrode setup, Ar was bubbled directly through the electrolyte. For both setups, a carbon rod worked as the counter electrode while the potentials were measured using Hg/Hg\textsubscript{2}SO\textsubscript{4} reference electrode (REF 601 Radiometer\textsuperscript{®}) and reported w.r.t. RHE. The electrolyte volume was kept constant (4.0 mL) for all the measurements in both types of setups. All the electrochemical measurements were performed using Zahner\textsuperscript{®} IM6e electrochemical workstation. Reproducibility of the electrochemical measurements was confirmed by at least two repeated measurements.

The ECSA and double layer capacitance (DLC) measurements were performed after 0, 20, 100, 200, 300, 400, 500, 600, 800, 1K, 2K, 3K, 4K, 5k, 6K and 7K stress cycles by using the cyclic voltammograms recorded with a potential sweep rate of 10 mV s\textsuperscript{-1} for two cycles within the potential ranges of 0.02-1.2 V and 0.1-1.2 V for standard and half-MEA setups, respectively. The lower limit for half-MEA setup was set to 0.1 V to avoid the observed hydrogen evolution below 0.1 V, due to potential offset from electrolyte resistance. The area under the hydrogen adsorption peak (cathodic scan) of the second cycle was used to calculate the ECSA, while the DLC was measured using the difference between the cathodic and anodic currents in the region away from the faradaic reactions (Fig. S1, in supporting information).

2.3 Structural characterizations

Measurements of Pt-loading on the electrodes before and after AST were performed through X-ray fluorescence spectroscopy (XRF) using a Thermo Scientific Niton XL3t GOLDD+ XRF analyzer. Thermogrametric analysis (TGA) and differential scanning calorimetry (DSC) measurements of the pre-AST and post-AST samples were performed in presence of O\textsubscript{2} (1:3 mixture of O\textsubscript{2} and N\textsubscript{2}) at a
heating rate of 5 °C min⁻¹ using NETZSCH STA449 F3 thermal analyzer. X-ray diffraction (XRD) patterns of the samples to study the crystallite size evolution of Pt nanoparticles were collected through a Rigaku Miniflex 600 X-ray diffractometer using Cu Kα (λ = 1.5418 Å) radiation. Peak fitting and data analysis was assisted by using OriginPro 9.1. The electrode sheets were directly mounted on a glass sample holder with the catalyst layer side facing the X-ray beam. Transmission electron microscope (JEOL JEM-2100, 200 kV) was employed to investigate the pre-AST and post-AST particle size distributions.

3. Results

3.1 Accelerated stress test

Evolution of cyclic voltammograms with stress cycles for the AST using standard setup and half-MEA has been depicted in Fig. 2a and Fig. 2b, respectively. The voltammograms from both the setups show the characteristic peaks corresponding to (i) hydrogen adsorption and desorption for cathodic and anodic scans below 0.4 V, respectively, and (ii) platinum oxidation during anodic scans for potentials higher than 0.8 V and reduction of platinum oxides during cathodic scans in between 0.5 and 0.9 V. After the AST, the hydrogen adsorption-desorption peaks corresponding to weakly (0.12 V) and strongly (0.28 V) bound hydrogen can be observed clearly for the standard setup. However, these components of the hydrogen adsorption-desorption peaks remain unresolved for the post/AST voltammograms from half-MEA possibly due to lower extent of Ostwald ripening and hence lower evolution of crystalline faces responsible for the peaks.

Evolutions of ECSA and DLC with stress cycles (averaged for different measurements; error bars show the standard deviation) for the two setups have been shown in Fig. 2c and Fig. 2d (open symbols), respectively. For 7000 stress cycles, the ECSA loss observed using half-MEA was ~42% as compared to that of ~72% for the standard setup. Again, the DLC for half-MEA shows a
monotonic loss with stress cycles with ~19% loss for 7000 stress cycles. Contrary to this, the DLC variation with stress cycles for the standard setup shows a minimum at 2000 stress cycles followed by a gradual increase. This is attributed to increased contribution from the GDL with potential cycling (dotted curves of Fig. 2a and Fig. 2b). Therefore, the DLC values corrected for the GDL contributions measured using similar AST protocols for standard and half-MEA setups (filled symbols in Fig. 2c and Fig. 2d) have been used for the degradation calculations.

Figure 2: Cyclic voltammograms recorded after different stress cycles in (a) liquid electrolyte (standard setup) and (b) solid electrolyte (half-MEA setup). Dotted curves show the voltammograms for electrodes without catalyst layer (only GDL) Variations of (c) ECSA and (d)
DLC with stress cycles for standard and half-MEA setups. Open and filled symbols respectively represent the values without and with corrections for GDL contributions.

3.2 Microscopy

Particle coarsening during the AST was examined through TEM of the post-AST samples. TEM samples were prepared by dispersing the catalyst layers in an ethanol/miliQ water mixture (1/2 v/v) by ultrasonic agitation (60 s using ultrasonic probe; hielscher up200st). For the sample from standard setup, the catalyst layer was scratched from the GDL mechanically, while for the half-MEA, it was scratched from the PEM and the GDL, after delaminating them.

TEM micrographs of the catalyst before and after durability tests have been shown in Fig. 3. Fig. 3 (a) illustrates morphology of the pristine catalyst. The TEM image of post-AST sample from standard setup (Fig. 3b) shows a clear growth of almost all the particles (homogeneous growth), which along with the fact that no particles with initial shape and size are observable, suggests both e- and H+ connectivity values to all the catalyst particles. On the other hand, the TEM image of Fig. 3c for the post-AST sample from half-MEA shows a mixed particle size distribution (heterogeneous growth). As can be confirmed from the particle size distribution histograms of Fig. 3d, for half-MEA (Image analysis by using ImageJ\textsuperscript{28} for particle size estimation; excluding observable agglomerates), two groups of particle sizes corresponding to the original and the coarsened particles can be clearly distinguished. The particle size distribution looks more similar to that of the TEM images of catalysts after AST using a single PEMFC\textsuperscript{29}.
Figure 3: TEM images of (a) Pristine HiSPEC 9100 catalyst powder, (b) post-AST catalyst layer from standard setup (liquid electrolyte) and (c) post-AST catalyst layer from half-MEA setup (solid electrolyte). (d) Particle size distribution histograms obtained from the TEM images.

3.3 X-ray diffraction

XRD patterns of the electrodes (pre-AST and post-AST) used in standard and half-MEA setups have been shown in Fig. 4. The coarsening of Pt nanoparticles during AST was estimated from the peak broadening of the Pt (111) using Scherer Formula ($\beta(2\theta) = 0.9\lambda/L\cos\theta$; where $\theta$, $\lambda$, $\beta(2\theta)$ and $L$ correspond to the Bragg’s diffraction angle, diffraction wavelength, peak broadening (FWHM) and average crystallite size, respectively) after subtraction of the normalized contribution from GDL for 2$\theta$ values ranging between ~41 and ~48 (Fig. S2, in supporting information). However, other contributions to peak broadening (e.g. stress, instrumental broadening) have been ignored.
assuming their negligible effect on the relative values of crystallite size. The reduction in peak broadening due to coarsening of particles can be observed clearly by comparing the XRD patterns of figures 4a and 4c corresponding to pre-AST and post-AST samples from standard setup (liquid electrolyte). The Pt(111) and Pt(200) peaks at 2θ values of 39.8° and 46.1° (JCPDS# 65-2868)\(^\text{30}\) have been fitted with Lorentz distributions to estimate the peak broadening and hence the average crystallite size. Similarly, XRD patterns of the pre-AST and post-AST samples from half-MEA setup (solid electrolyte), corrected for the GDL and PEM contributions are shown in figures 4b and 4d, respectively. The GDL and PEM contributions have been estimated by subtracting the normalized background of the XRD pattern of a hot-pressed GDL-PEM assembly (resembling to half-MEA without catalyst layer) for 2θ values ranging between ~32 and ~52). Further, the Pt (111) and Pt (200) diffraction peaks of the pre-AST and post-AST samples from the half-MEA have been fitted using Lorentz distributions. As shown in Fig. 4b, the pre-AST diffraction peaks can be fitted using a single Lorentz distribution for each peak. On the other hand, for the post-AST sample, deconvolution of the diffraction peaks in two Lorentz components has been used to attain a reasonably good fitting (Fig. 4d) of the data as compared to that obtained using single Lorentz components (Inset Fig. 4d). This could be attributed to the presence of two types of crystallites with large difference in average crystallite size as confirmed by microscopic study (Fig. 3d). The Pt volume fraction corresponding to a specified size distribution has been assumed to be equal to the fractional area of the Lorentz component. The relative changes in the crystallite sizes with AST have been summarized in Table 2.
Figure 4: XRD patterns of (a) pre-AST standard electrode (b) pre-AST half-MEA, (c) post-AST standard electrode and (d) post-AST half-MEA samples with Pt (111) and Pt (200) peaks corrected for GDL and/or PEM contributions and fitted using Lorentz distributions (Inset: Improper fit with large residues when using single Lorentz components for Pt peaks).

3.4 Thermal analysis

Thermogravimetry (TG), differential TG (DTG) and differential scanning calorimetry (DSC) studies of the pre-AST and post-AST samples were performed to observe the structural modifications during AST. For standard electrode, the thermal analysis has been performed both on the whole electrode consisting of catalyst layer and GDL (Std. electrode) and on the catalyst layer
(Std. cat.) scratched from the standard electrode mechanically. As shown in Fig. 5, the TG, DTG and DSC plots of half-MEA, Std. electrode and Std. cat. show the typical thermal degradation behaviors characteristic to materials with multiple phases/components. The DSC (Figures 5b, 5d, 5f) and more clearly the DTG peaks (Figures 5a, 5c, 5e) at 310, 420, 540, 620, 660 °C may be assigned to the weight losses corresponding respectively to ionomer in catalyst layer, PEM/catalyst support carbon, Teflon of GDL, microporous and mesoporous layer of GDL, respectively.31-34 While no significant difference in the degradation temperatures of the GDL components (Teflon, microporous and mesoporous layers) is observed, the degradation temperatures of the catalyst layer components (ionomer and carbon support) exhibit significant increment for the post-AST samples, as can be observed more clearly in Fig. 5b (Std. cat.). The increased degradation temperatures of catalyst layer components suggest less catalyst/ionomer and catalyst carbon support interactions leading to less catalytic effect of Pt during thermal degradation, as observed in the earlier studies.8, 32

Figure 5: Thermal degradation behavior of pre-AST and post-AST samples. TG and DTG plots corresponding to (a) half-MEA, (b) standard catalyst and (c) standard electrode. DSC plots
corresponding to (d) half-MEA, (e) standard catalyst and (f) standard electrode. Insets of (b), (c),
(d) and (f) show magnified views of some of the less intense peaks.

4. Discussion

4.1 Estimation of catalyst dissolution and physical detachment loss

Estimation of the decrease in catalyst loading during AST due to various processes\textsuperscript{35} such as
chemical dissolution, electrochemical dissolution-redeposition and physical detachment of
catalyst/support is challenging. Solution study with spectroscopy techniques is insufficient as part
of the dissolved Pt may redeposit on surfaces in contact with the electrolyte (cell walls, counter
electrode, etc.). Such a redeposition of Pt on the gold wire used to connect WE in the standard setup
has been observed in the present study. Again, the detachment of Pt-nanoparticles may remain
undetected in case of sedimentation of larger particles, even using the techniques capable of
detecting Pt\textsuperscript{0}. To overcome the challenge, direct measurement of Pt-loading on the electrode was
performed before and after AST through XRF calibrated for electrodes with known Pt-loadings.

4.2 Quantification of ECSA degradation mechanisms

The fractional contribution from ECSA degradation mechanisms during AST can be quantified in
terms of the associated change in active surface area. Based on the $e^-$ and H\textsuperscript{+} connectivity of the
catalyst particles and their physical surface area, the overall ECSA loss can be attributed to various
degradation mechanisms such as (i) fractional loss of $e^-$ connectivity due to corrosion of catalyst
support ($l_{e^-}$), (ii) fractional loss of H\textsuperscript{+} connectivity due to catalyst-ionomer detachment ($l_{H^+}$), (iii)
fractional loss of Pt-loading due to Pt-dissolution and particle detachment ($l_d$) and (iv) fractional
loss of physical surface area due to coarsening of Pt nanoparticles through Ostwald ripening
/migration mechanisms ($A_f/A_i$, where $A_i$ and $A_f$ are respectively the pre-AST and post-AST
specific areas determined from crystalline sizes. Assuming spherical shape of the nanoparticles,
when the mass keeps constant, \( A_f/A_i \) can be expressed as \( R_i/R_f \), with \( R_i \) and \( R_f \) being the pre-AST and post-AST particle radii (averaged), respectively.

The ECSA loss in percentage can be given by (S3, in supporting information)-

\[
(1 - \frac{ECSA_f}{ECSA_i}) \times 100 = \left(1 - \left[l_d + l_{e^-} + l_{H^+}\right]\right) \times \frac{R_i}{R_f} \times 100
\]

where \( l_d = \frac{M_d}{M_i} \), \( l_{e^-} = \frac{M_{e^-}}{M_i} \) and \( l_{H^+} = \frac{M_{H^+}}{M_i} \) are the fractional losses due to dissolution, e-connectivity loss and H\(^+\) connectivity loss, respectively. Moreover, \( M_i, M_d, M_{e^-} \) and \( M_{H^+} \) represent the initial loading of platinum, the mass loss of Pt due to dissolution, the Pt mass electrochemically inactive due to e- connectivity loss, and the Pt mass electrochemically inactive due to H\(^+\) connectivity loss, respectively.

Fractional contribution of the support corrosion (\( l_{e^-} \)) can be estimated through the change in the limiting double layer capacitance (DLC) of the electrode, which, in absence of any Faradaic processes, depends only on the active electrode area.\(^{36}\) Assuming it to be associated mainly to the high surface area carbon support, the reduction in DLC during AST has been associate to equivalent fraction of Pt-nanoparticles losing e’ connectivity. Similarly, the Pt loss due to dissolution and detachment (\( l_d \)) was estimated by measuring the pre-AST and post-AST Pt loadings on the electrode through XRF. Again, physical surface area loss due to particle growth has been estimated from the pre-AST and post-AST crystalline sizes obtained from XRD analysis. As shown in Table 2, the XRD data show comparatively higher values of crystalline size as compared to those from TEM. However, for the calculations in the present study, relative change of particle size are consistent and the heterogeneous degradation (dissimilar growth of different particles during AST using Half-MEA setup) can be confirmed from both the XRD and TEM data. The XRD crystalline size was preferred over TEM as it contains information averaged over a large number of crystallites while the particle size from TEM is based on a few (<100) particles. As shown in Table 2, while the ECSA loss for liquid electrolyte can be assigned completely to these three degradation mechanisms (calculated loss: ~74%; experimental loss: ~72%), the ionomer/catalyst interface loss mechanism seems essential to explain the total ECSA loss using solid electrolyte (calculated loss: ~35%;
experimental loss: ~42%). Hence, the remaining fraction of ECSA loss not accommodated in the three other mechanisms has been attributed to the ionomer/catalyst interface loss.

Table 2: Quantification of degradation mechanisms (AST for 7000 stress cycles as described in 2.2) excluding ionomer/catalyst interaction loss

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>$D_f$ (nm)*</th>
<th>ESA,* $m^2/g_{Pt}$</th>
<th>DLC (F/g)</th>
<th>$R_i/R_f$</th>
<th>$l_{Total}$</th>
<th>$l_{No_i}$</th>
<th>$l_d$</th>
<th>$l_{e^-}$</th>
<th>$l_{H^+}$</th>
<th>$I_a$</th>
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</thead>
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<tr>
<td>Liquid</td>
<td>9.2</td>
<td>7.3</td>
<td>205</td>
<td>0.41</td>
<td>0.72</td>
<td>0.74</td>
<td>0.13</td>
<td>0.23</td>
<td>-</td>
<td>0.36</td>
</tr>
<tr>
<td>Solid</td>
<td>1.8 &amp; 9.8</td>
<td>3.3 &amp; 6.5</td>
<td>217</td>
<td>0.82</td>
<td>0.42</td>
<td>0.35</td>
<td>0.03</td>
<td>0.19</td>
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</tbody>
</table>

$l_{Total}$: Total ESA loss measured experimentally; $l_{No_i}$: Total ESA loss calculated without considering the contribution from ionomer corrosion; $l_d$: ESA loss due to particle growth; $D_f$: Post-AST particle size ($D_{f1}$: Smaller particles (74%); $D_{f2}$: Larger particles (26%)); $^*$Particle size of pristine catalyst: TEM: 2.3 nm, XRD: 3.7 nm

* Different lower integration limits are applied to the two setups as described in 2.2.

4.3 Degradation mechanism comparison for liquid and solid electrolytes

As can be seen in Table 2 and Fig. 6, the nature of catalyst ECSA loss during AST differs considerably for the two AST setups. Higher total degradation in case of liquid electrolyte (72% as compared to that of 42% using solid electrolyte) with ~50% fractional contribution from particle growth suggests higher rate of Pt-dissolution and transport for redeposition in liquid electrolyte as compared to that in the polymer electrolyte. Similar reasoning may be applied to the relatively lower Pt-dissolution and particle growth losses for solid electrolyte as compared to that for liquid electrolyte.

The dissimilar Ostwald ripening/migration behavior of Pt in liquid and polymer electrolytes and the different H⁺ conduction pathways provide significant difference in the observed particle growth for the standard and the half-MEA setups, with the reduction in physical surface area values being ~50% and ~30%, respectively. Apart from this, the observed lower growth of particle size for the
half-MEA setup may partially be attributed to the comparatively higher fraction of isolated particles due to the H⁺ connectivity loss.

Figure 6: Quantification of degradation mechanisms for AST using liquid and solid electrolytes.

Further, loss attributed to the e⁻ connectivity loss (based on final DLC loss) contributes similar fractions to the total ECSA loss for both of the liquid and solid electrolytes. However, significant difference between the DLC variations with stress cycles for liquid and solid electrolytes (Fig. 2d) suggests dissimilar DLC loss mechanisms. A comparison between the initial voltammograms (Fig. 7a) for the two cells reveals the specific DLC measured in solid electrolyte to be similar to the corresponding value obtained in liquid electrolyte. This suggests the origin of DLC being the catalyst layer only and not the GDL as the later cannot contribute to DLC of half-MEA due to lack
of \( \text{H}^+ \) connectivity (no presence of ionomer phase in GDL). The GDL, however does not contribute in case of liquid electrolyte due to lack of \( \text{H}^+ \) access owing to its hydrophobic nature. In addition, variations of the DLC with GDL contributions with the ECSA for the two setups (Fig. 7b) exhibit similar trends for ECSA losses. On the other hand, the corresponding variations for variations for the DLC without GDL contributions show different trend at higher potential cycles. Hence, the initial sharp loss of DLC below 2000 stress cycles may be attributed to the catalyst support corrosion while the DLC increase for stress cycling beyond 2000 cycles may be due to increased contribution from the microporous and mesoporous layers of the GDL in contact with the liquid electrolyte (increased wettability with AST), as shown in figure 2 (d). On the other hand, monotonic decrease of DLC during AST using half-MEA may be assigned fully to the catalyst support corrosion with negligible contributions from rest of the GDL. Slight difference between the ECSA vs. DLC variations for the liquid and solid electrolytes for the ECSA loss below 40% may also be attributed to increased contribution from GDL, owing mainly to its increased wettability with potential cycling in liquid electrolyte.

![Figure 7](image-url)

Figure 7: (a) Initial cyclic voltammograms and (b) ECSA vs. DLC (with and without GDL contributions) plots for standard (liquid electrolyte) and half-MEA (solid electrolyte) setups.
The fact that the e- connectivity loss from carbon corrosion takes place through electrochemical oxidation of carbon (eq. 2)\textsuperscript{19-20}, both H\textsuperscript{+} and e\textsuperscript{-} connectivity values are essential for a forward reaction.

\begin{equation}
C + 2H_2O \leftrightarrow CO_2 + 4H^+ + 4e^- \quad (E = 0.207 \text{ V vs. RHE})
\end{equation}

Hence, similar to the lower dissolution/transport rate of Pt/ions in solid electrolyte, the carbon corrosion rate may be affected by the mass transport limitations for water through PEM and CO\textsubscript{2} through the porous GDL as compared to those for liquid electrolytes. Moreover, the high acidity from perfluorinated sulfonic acid ionomer also prevents the forward reaction. For half-MEA, assignment of DLC loss to the e- connectivity loss is valid under the assumption that the change in DLC contribution from the catalyst particles due to their H\textsuperscript{+} connectivity loss does not affect the overall DLC having major contribution from high surface area carbon support.

As stated in the introduction section, ECSA loss due to ionomer/catalyst interface loss cannot be detected using the standard setup based on liquid electrolyte or any other currently available configurations or technique. Estimations made from the AST using half-MEA setup based on solid electrolyte suggest \~19\% contribution to ECSA loss due to loss of H\textsuperscript{+} connectivity through ionomer/catalyst interface loss. ECSA loss contribution due to Pt particle isolation in the electrode by loss of electron and proton connectivity shows 32\% through liquid and 64\% through solid electrolyte.

In summary, the study highlights following points

- AST estimated with liquid electrolyte is limited to the catalyst material itself; it does not reflect electrode property.
- AST estimated with solid electrolyte through the half-MEA configuration provides realistic stress conditions for specific electrode development
• Platinum catalyst isolation in the electrode and heterogeneous degradation are important and realistic degradation patterns

• As indicated in this study, carbon corrosion during air-air start-up/shutdown, is the major bottle neck of the current low-temperature-PEMFC technology and therefore, replacement of amorphous carbon with more robust catalyst support is urgently needed.

• Studies investigating the parameters affecting the ionomer/catalyst interaction are of high interest towards development of catalyst layers with high Pt utilization throughout the catalyst life.

5. Conclusions

Attempt has been made to quantify the ECSA loss mechanisms during AST of a PEMFC catalyst layer. In addition to the standard three-electrode setup based on liquid electrolyte, a half-MEA based three-electrode setup using solid electrolyte has been demonstrated to study the durability of such electrodes and to quantify the ECSA loss due to loss of H\textsuperscript{+} connectivity of the catalyst particles. The half-MEA setup, being more close to the real PEMFC, provides more realistic degradation mechanisms during AST. ECSA loss contributions due to the particle growth of Pt is found to be 50% and 30% during AST using standard and half-MEA setups, respectively. Again, in the half-MEA setup based on solid electrolyte, restricted migration of Pt-ions through PEM leads to the reduced Pt-dissolution loss as compared to that in the liquid electrolyte of the standard setup. Moreover, corrosion of catalyst support and hence loss of e\textsuperscript{-} connectivity is found to be the most severe degradation mechanism with ~45% contribution to total ECSA loss in half-MEA. Similarly, the loss of H\textsuperscript{+} connectivity due to ionomer/catalyst interface loss was found to be significant (19% of ECSA loss). This 64% activity loss due to catalyst isolation by either e\textsuperscript{-} or H\textsuperscript{+} connectivity loss signifies great importance of catalyst support and catalyst/ionomer interface optimization. Identification and quantification of the degradation mechanisms are essential to all aspects of
PEMFC development ranging from material selection, catalyst layer design, electrode structure, flow field optimization and water management.

Supporting Information

Estimation of electrochemically active surface area (ECSA) and double layer capacitance (DLC), correction of X-ray diffraction (XRD) pattern (Pt (111) peak) for GDL and PEM contributions, quantification of degradation mechanisms (mathematical background)

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References


Table of Contents Graphic on

Homogeneous degradation (liquid electrolyte)

Heterogeneous degradation (solid electrolyte)