

Effect of Microporous Layer Cracks on Catalyst Durability of Polymer Electrolyte Fuel Cells for Heavy-Duty Applications

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Abstract

Polymer electrolyte fuel cells (PEFCs) have demonstrated great potential in heavy-duty vehicles (HDVs) due to their unique scalability and smaller additional weight penalty for longer driving range. To enable the deployment of HDVs, increased durability of platinum (Pt), which is the catalyst used in PEFCs, and understanding of degradation mechanism are the top priorities. In this study different configurations of cracks were introduced into the microporous layer (MPL) of the membrane electrode assemblies (MEAs) and accelerated stress tests (ASTs) simulating HDV lifetime were performed. Electrochemical characterization of the MEAs with and without MPL cracks all demonstrated similar durability trends. Cracks in the MPLs do not significantly improve the performance of the cell. However, identical location μ -X-ray fluorescence spectroscopy (μ -XRF) performed on the MEAs showed significant in-plane movement of Pt over the course of AST, especially for the MEAs with vertical cracks in the MPLs. This is indicative that cracks in the MPLs can have negative impact on the PEFCs' durability because of water flooding. The modeling study showed water distribution and oxygen transport through the MPL with cracks.

Introduction

Need for flexible utilization of renewable energy sources is increasing. Use of low-cost green hydrogen with high efficiency is being pursued by governments and industries worldwide. PEFCs have demonstrated great potential in heavy-duty vehicles (HDVs) due to their high energy density. HDVs are critical to reduce energy consumption and emissions of the transportation sector. HDVs combined with medium-duty vehicles, produced 26% of the total carbon dioxide emissions in 2020, and consumed 25% of the total annual vehicle fuel use in the United States^{1,2}. In addition, the annual freight truck miles travelled is projected to increase by 54% by 2050²; there is an urging need for emission-free HDVs.

Fuel cells for light-duty vehicles (LDVs) have been under development for over two decades and demonstrated great potential. However, PEFCs for HDVs have different drive cycle and operating condition and require longer lifetimes than LDVs. One of the major degradation issues in PEFCs is oxygen reduction reaction (ORR) electrocatalyst loss. The ORR catalyst is typically made of platinum (Pt) or Pt alloys. Increased durability of Pt and understanding of degradation mechanism are the top priorities to enable HDVs deployment³. To improve performance and reduce the cost of PEFCs, highly dispersed Pt nanoparticles on carbon support are being used as electrocatalyst because small particle size can increase the electrochemical surface area (ECSA) and, therefore, the electrocatalyst utilization, while reducing the Pt loading and cost at the same time. However, these nanoparticles can be subjected to degradation during HDV lifetime⁴.

Currently, the MPL is known to improve the performance of PEFCs at high current densities due to better water management, and due to better contact with the catalyst layer that facilitates electron transport⁵. With the absence of the hydrophobic MPL, the pores of the gas diffusion layer (GDL) at the interface with the catalyst layers will be filled with water, which can block oxygen access to the cathode catalyst layer^{6,7}. Cracks in the MPL are believed to be advantageous as they can act as large highways for transport and facilitate removal of liquid water from the catalyst layer⁸⁻¹¹. Sabharwal et al. using operando x-ray computed tomography (CT) demonstrated water being transported toward the GDL via the MPL cracks under freeze start condition¹². Liquid water is seen to spread over pores of MPL without cracks, blocking reactant transport pathways to the electrode boundary^{13,14}. On the other hand, for MPL with cracks, water fills the large pores in it, and the meso- and micro-pores remain water-free, which can provide easy access for reactant to reach the electrode. However, too many cracks can result in poor contact between the MPL and the catalyst layer, increasing electric contact resistance and can also pool water and block oxygen transport¹⁵⁻¹⁸. Cracks can also lead to a higher probability of Pt leaving the cathode catalyst layer through effluent water¹⁹. Although these cracks can have both advantages and disadvantages toward the performance of the cell, the effect of MPL cracks on durability of PEMFCs for heavy-duty applications is still an unknown.

In this study, electrocatalyst accelerated stress tests (ASTs) were performed on MEAs with commercially available catalyst coated membranes (CCMs) designed with the potential for the HDV application. Freudenberg H23C6 GDLs having different density and configuration of MPL cracks were used to understand the effect of MPL cracks on durability. In-situ electrochemical characterization and extensive physical characterization was performed to understand the subtle differences in electrocatalyst degradation correlated to the use of crack-free and cracked MPLs. In particular, μ -XRF map of identical locations before and after the AST were employed to study in-plane movement of Pt over the course of AST. Electrochemical characterization for MEAs with and without cracks in the MPLs all demonstrated similar trends in the cells' durability, revealing that cracks in the MPLs do not significantly improve the performance of the cell at the beginning and also at the end of life. However, the μ -XRF identical location maps showed significant in-plane movement of Pt over the course of the AST, especially for the MEAs with vertical cracks in the MPLs. Modeling study was conducted to show that cracks are being filled with liquid water reducing oxygen diffusivity in the MPLs. The presence of liquid water in MPL can also adversely affect Pt durability. This study signifies that under standard operating conditions, MPL design is already optimal and introduction of cracks depending on configuration can only hurt the cell's durability.

Methods

MEA Preparation and Testing Hardware

MEAs with 5 cm² active area were prepared with commercial CCMs and Freudenberg H23C6 GDL. The cathode Pt loading was 500 µg.cm⁻² and anode Pt loading was 50 µg.cm⁻². The average membrane thickness was ~ 8 µm. Cracks were introduced in the MPL of the cathode Freudenberg H23C6 GDL to prepare the MEAs with vertical and diagonal cracks.

Fuel cell quick connect fixture (qCf) coupled with a cell fixture (cF) from balticFuelCells GmbH (Schwerin, Germany) was used. Flow field with two turn 5 cm² x 7 serpentine channel was utilized. The cell compression in this setup is pneumatically controlled, so a pneumatic compression pressure of ~ 0.9 bar was applied to achieve manufacturer-recommended 1-1.1 MPa pressure on the GDL, which resulted in 20-22% of GDL compression.

Polarization curves and mass activity measurements were performed using 850e fuel cell test system from Scribner Associates (Southern Pines, NC). Cyclic voltammograms (CVs), linear sweep voltammograms (LSVs), electrochemical impedance spectroscopies (EISs), and the HDV AST were performed using Interface 5000 potentiostat from Gamry Instruments (Warminster, PA).

Modification of MPL

Vertical and diagonal cracks of 1 mm and 2 mm apart, respectively, were milled into the MPL of Freudenberg H23C6 GDL using the tip of tungsten micro needle, which has a width of around 15 µm and results in cracks of ~ 40 µm width. When assembling the cells, the vertical cracks in the MPL were positioned to be perpendicular to the flow field (**Figure 1a**), and the diagonal cracks were positioned to be 45° to the flow field (**Figure 1b**). The fabrication was done by hand under an optical microscope (x 20) with a pitch of 1 mm, and µ-XCT was performed to confirm the morphology (**Figure 1c-d**).

AST and Electrochemical Characterization

The ASTs were performed at 80°C cell temperature in 100% RH under atmospheric pressure. Both hydrogen/nitrogen (anode/cathode) environment and hydrogen/air (anode/cathode) environment AST were conducted on three types of MEAs with different MPL (no crack, vertical cracks, and diagonal cracks). The HDV AST comprised of 0.6 V lower potential limit and 0.9 V of upper potential limit with a dwell time of 3 seconds at each potential. Gas flow rates of 0.2 slpm and 0.2 slpm were used for anode and cathode, respectively, for both environment AST. During the AST, each MEA was characterized after 0, 10000, 30000, 60000 and 90000 AST cycles.

CV, LSV, and EIS were all collected in hydrogen/ nitrogen (anode/cathode) environment at 80°C in 100% RH under atmospheric conditions with gas flow rates of 1 slpm/1 slpm. CVs were collected with a potential scan from 0.1 V to 1.2 V at a scan rate of 100 mV·s⁻¹. LSVs were collected from 0.05 V to 0.8 V at sweep rate of 1 mV·s⁻¹. EIS was collected at 0.2 V from 20 kHz to 0.1 Hz with 6 points/decade. Voltage break-in was performed at 80°C in 100% RH under atmospheric pressure by cycling the voltage between 0.8 V, 0.6 V and 0.3 V (with a dwell time of 30 seconds at each potential) for 200 cycles in a hydrogen/air (anode/cathode) environment. Voltage recovery consisted of voltage hold at 0.2 V for 1 hour at 40°C in 150% RH under 150 kPa absolute pressure in a hydrogen/air (anode/cathode) environment. Polarization curves in hydrogen/air (anode/cathode) and hydrogen/oxygen (anode/cathode) environments were collected at 80°C in 100% RH under 150 kPa absolute pressure with gas flow rates of 1 slpm and 2.5 slpm at anode and cathode, respectively. 4-minute holds from high current density (2 A.cm⁻²) to low

current density (0 A.cm^{-2}) were performed for air cathode environment. For oxygen cathode environment, 3-minute holds from 0.75 V to open circuit potential with increments of 25 mV were performed. The data collected during the last minute of the holds was averaged and used to plot polarization curves (air) and Tafel plots (oxygen).

Identical Location μ -X-ray Fluorescence

To ensure identical locations were mapped before and after the AST, a 25- μm PTFE template was prepared, and, using the cathode flow field as a reference, holes were cut out in the template near the inlet and outlet regions of the flow field. The diameter of the hole was the same as the diagonal of a 2048 μm by 2048 μm area.

Ex situ μ -XRF measurements were performed using the XGT-9000 Horiba XRF microscope. A focus distance of 1 mm and a 10 μm capillary with 1024 pixels in both the x and y directions were used to map an area of 2048 μm by 2048 μm . The x-ray energy was 50 keV, and the reflected x-ray signal to the detector included Pt contribution from both the anode and the cathode as the x-ray penetrated through the entire MEA. Therefore, the total average Pt loading is the sum of anode and cathode loadings, and it was quantified using a calibration curve generated from 10 μm capillary maps of samples with known Pt loading. 2D colormaps were generated in MATLAB using the quantified total average Pt loading and raw fluorescence images from the microscope.

μ -X-ray Computed Tomography

μ -X-ray CT was conducted at Beamline 8.3.2 at Advanced Light Source (ALS) synchrotron at Lawrence Berkeley National Laboratory (LBNL), Berkeley, CA. Photon source energy of 26 keV was selected with 1025 number of projections collected per scan, with exposure time of 300 ms. The scintillator used was 0.5 mm LuAG, the optic system consisted of 5x lenses and sCMOS (PCO.Edge) camera. The resulting field of view (FOV) was $3.3 \times 3.3 \text{ mm}^2$ and the image resolution was 1.3 μm . The image processing was done with open-source software ImageJ.

Synchrotron μ -X-ray Diffraction

The synchrotron micro-XRD mapping was conducted at Beamline 12.3.2 at Advanced Light Source, Lawrence Berkeley National Laboratory. The CCM samples were mounted on a high-resolution x–y scan stage and tilted 20° relative to the incident X-ray beam (10 keV monochromatic focused to a size of $2 \times 5 \text{ }\mu\text{m}^2$). Two-dimensional X-ray diffraction images were recorded in reflection mode using Pilatus 1M area detector mounted at 60° to the incoming X-ray, approximately 150 mm from the probe spot. The exposure time at each position was 8s. Calibrations for distance, center position and tilt of the detector were performed based on an Al_2O_3 polycrystal reference taken at the same geometry. Mapping of each $2 \text{ mm} \times 2 \text{ mm}$ area MEA sample, a two-dimensional scan of 20×20 points was performed with a step size of 1 mm. The X-ray diffraction data were processed using XMAS²⁰.

Scanning Electron Microscopy

A small (approximately 3 mm x 4 mm) sample was extracted from each MEA. The MPL on both the anode and cathode sides was carefully removed from the sample with tweezers. A new razorblade was used to cut one of the two longer sides of each extracted sample once the MPL was removed. The sample was mounted on a vertical stub holder and a FEI Tescan S8252G environmental SEM was used to image the cross-sectioned samples in Analysis mode using both the primary SEM detector and a dedicated

backscattering detector (BSE N° 2). Images were acquired with a scan speed of 5 or 6 using 5 kV accelerating voltage with a 300 pA current and a working distance in the range of 10 – 15 mm. Images were rotated using the image rotation feature to allow the cathode side of the MEA to face up.

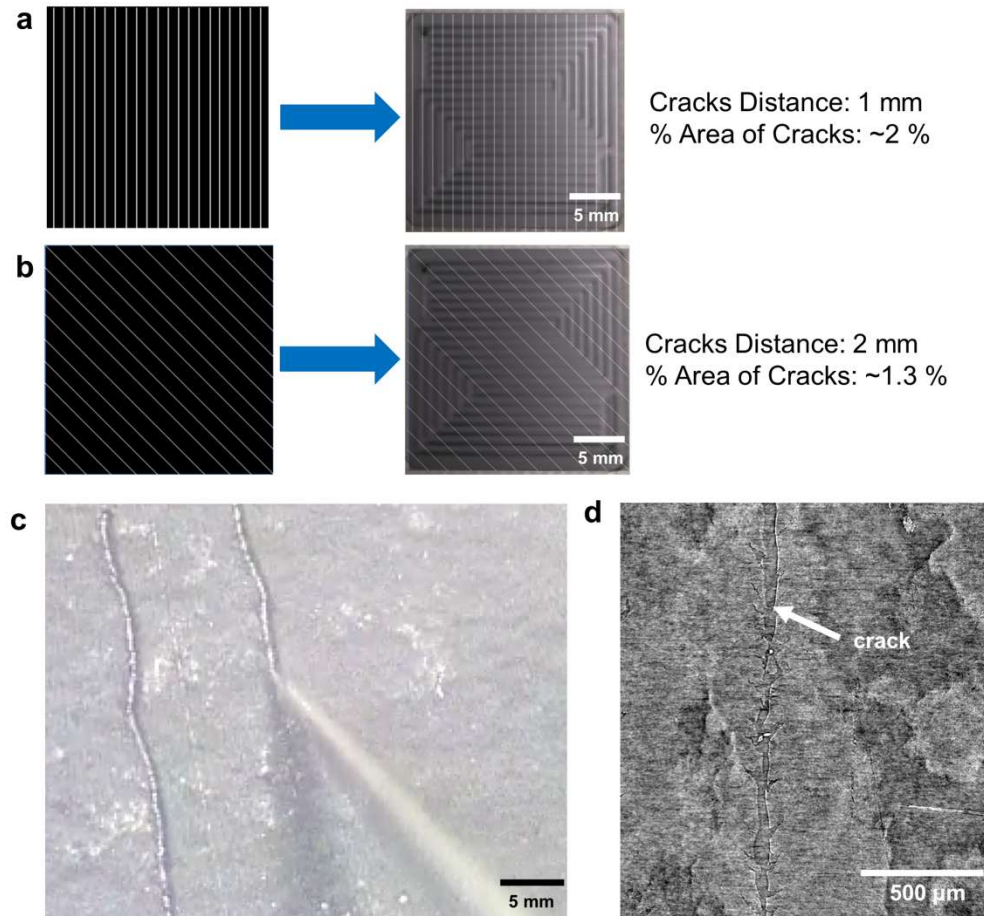


Figure 1. Schematic of MPL with (a) vertical and (b) diagonal cracks. **c**, Optical image of MPL cracks made with a tungsten micro needle. **d**, In-plane image from μ -X-ray CT of Freudenberg H23C6 GDL with cracks fabricated in the MPL.

Computational Simulations

A large computational campaign, spanning 300 simulations, was performed to examine the effect of crack volume fraction on average liquid water saturation and mass transport resistance in an MPL+GDL assembly. The size of each representative sample in the material plane was fixed to $1.5 \times 1.5 \text{ mm}^2$, with a thickness of $250 \text{ }\mu\text{m}$ ($200 \text{ }\mu\text{m}$ for the GDL and $50 \text{ }\mu\text{m}$ for the MPL, including an interpenetration region with mixed properties of $40 \text{ }\mu\text{m}$). The microscopic properties (local dry effective diffusivity and entry capillary pressure) of the porous media were extracted from POREnet and were then imported into the Computational Fluid Dynamics model of ANSYS® FLUENT for numerical simulation. Water transport was modeled using a standard invasion-percolation (IP) algorithm without trapping, starting from a random distribution

prescribed at the bottom surface of the MPL. Local liquid water saturation was set equal to 1 in macroscopic pores with a pore radius higher than one micron (i.e., GDL and cracks), while it was set equal to 0.4 in microscopic pores with a pore radius lower than one micron (i.e., fine porous regions of the MPL). Gas diffusion through the partially-saturated MPL+GDL was modeled considering a local normalized effective diffusivity, $D^{\text{eff}}(D^{\text{bulk}})^{-1}$, equal to^{21,22}

$$\frac{D^{\text{eff}}}{D^{\text{bulk}}} = f(\varepsilon)(1 - s)^3 \quad (1)$$

where $f(\varepsilon)$ is the normalized dry effective diffusivity extracted from POREnet ($f(\varepsilon) = 1$ in cracks) and s is the local saturation obtained from IP.

Average saturation, s^{avg} , and mass transport resistance, $R_{\text{mpl+gdl}}$, were determined by volume averaging the local saturation distribution, s , and through-plane flux, j_{tp} , respectively, as given by

$$s^{\text{avg}} = \frac{\sum \varepsilon s V_{\text{cell}}}{\sum \varepsilon V_{\text{cell}}} \quad (2.1)$$

$$R_{\text{mpl+gdl}} = \frac{\Delta C}{j_{tp}^{\text{avg}}}; j_{tp}^{\text{avg}} = \frac{\sum j_{tp} V_{\text{cell}}}{\sum V_{\text{cell}}} \quad (2.2)$$

where ε is the local porosity, ΔC is the prescribed concentration difference across the sample, and V_{cell} is the volume of a grid cell.

Results and Discussion

First, MPLs were characterized to ensure that the cracks go through only MPL layer but GDL remains intact. μ -X-ray CT was used to confirm the morphology of the MEAs at the end of life (EOL). The in-plane image (**Figure 1d**) showed the crack in the MPL has a width of around 20 μm . The through-plane grayscale images in **Figure S1b-c** showed the presence of cracks in the modified MPL of the cathode GDL, while no cracks were observed in the baseline MPL (**Figure S1a**), as Freudenberg GDLs generally have crack-free MPLs¹³. It can be noticed that the cracks penetrated through the entire thickness of the MPL but GDL was not damaged. The MEA with vertical cracks has a crack density of 1 crack per 1 mm; however, at the EOL formation of additional cracks within the MPL can be observed, which has been previously demonstrated by Lapique et al²³. This might be due to in plane stress that the MPL with cracks does not hold as well as solid baseline MPL.

Polarization curves with high frequency resistance (HFR) at 0 and 90,000 N_2 AST cycles stages for MEAs with different density and configuration of cracks are shown in **Figure 2a-b**. All the MEAs show increase in kinetic and mass transport cell overpotentials over the course of the heavy-duty AST. All the HFRs at beginning of life (BOL) were around $60 \text{ m}\Omega \cdot \text{cm}^2$, and a slight decrease in HFR is observed at end of life (EOL), which can be attributed to additional cell conditioning. For MEAs subjected to N_2 AST, MEAs with cracks degraded more than MEAs without cracks. At geometric current densities of $800 \text{ mA} \cdot \text{cm}^{-2}$, the increase in overpotential were $\sim 25 \text{ mV}$, $\sim 33 \text{ mV}$, and $\sim 49 \text{ mV}$ (**Figure 2c**) for N_2 environment, No Cracks, Vertical Cracks, and Diagonal Cracks, respectively. Shown in **Figure 2d**, at geometric current densities of $1500 \text{ A} \cdot \text{cm}^{-2}$ the increase in overpotential were $\sim 33 \text{ mV}$, $\sim 36 \text{ mV}$, and $\sim 62 \text{ mV}$ for N_2 environment, No Cracks, Vertical Cracks, and Diagonal Cracks, respectively. None of these

MEAs achieved the DOE target of $\leq 30 \text{ mV}^{24}$ of voltage loss at $800 \text{ mA} \cdot \text{cm}^{-2}$. In N_2 environment, Diagonal Cracks degraded the most, and, unlike No Cracks and Vertical Cracks, which had monotonic decrease in voltage over the course of AST, Diagonal Cracks had a sharp decrease at the last stage of the AST between 60,000 and 90,000 AST cycles. This suggests that MPLs with diagonal cracks may result in higher Pt degradation and perhaps different degradation mechanism. Since the change in slope in the polarization curve is evident for N_2 environment, Diagonal Cracks MEA and its HFR was about the same as the other MEAs, we believe the degradation was dominated by increase of the oxygen transport resistance in the cathode catalyst layer.

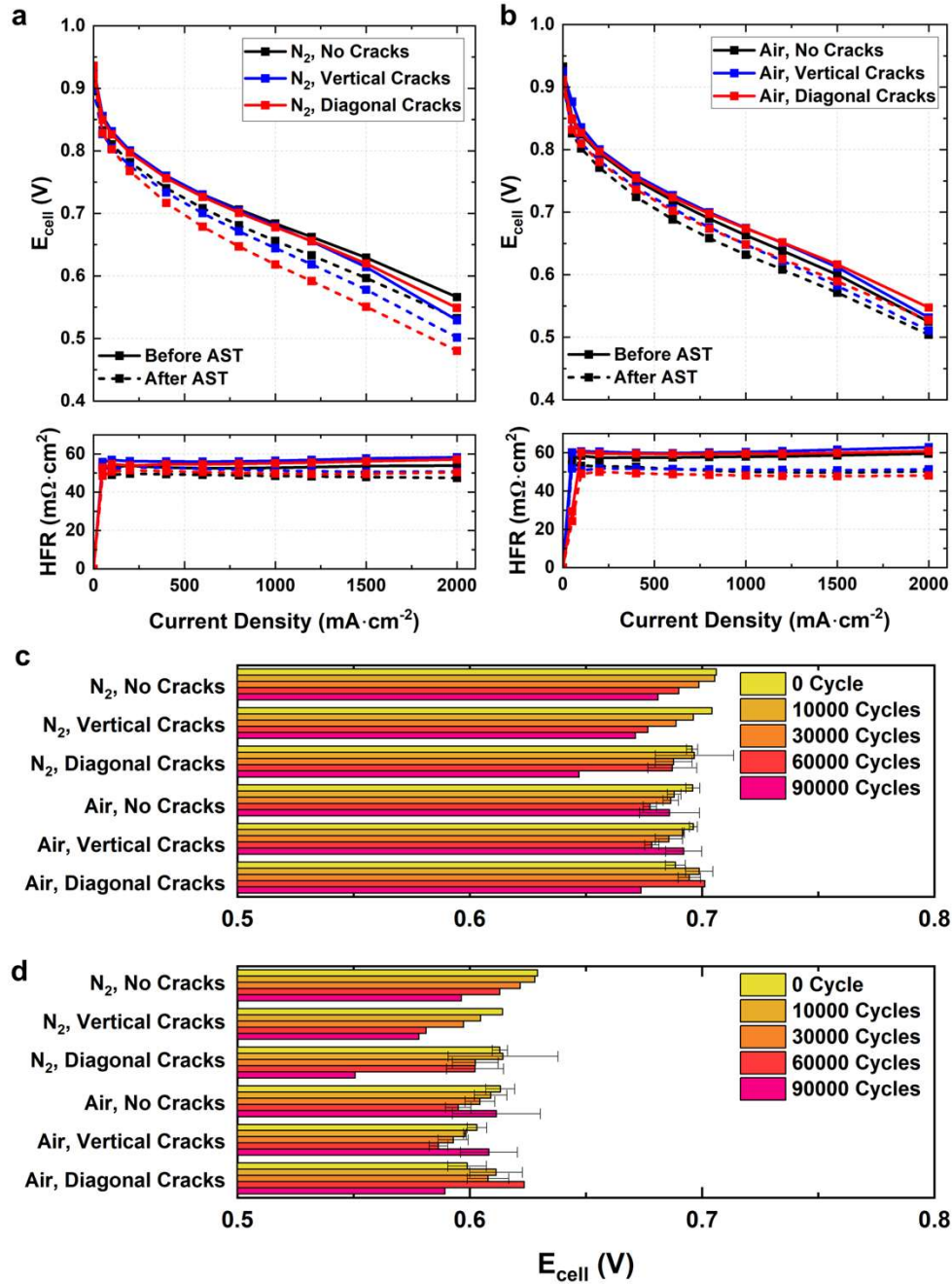


Figure 2. a-b, Polarization curves with HFR collected at 80°C in 100% RH under 150 kPa of absolute backpressure in H_2 -air environment for (a) nitrogen and (b) air cathode environment AST. c-d,

Comparison of E_{cell} at (c) 800 mA cm^{-2} and (d) 1500 mA cm^{-2} . The error bars indicate more than one cell built for the specific AST condition, where average is shown and standard deviation is the width of the error bars.

Compared to MEAs subjected to N_2 AST, MEAs under Air AST degraded less as the iR-corrected potentials under air condition are slightly lower than those under N_2 , resulting in a milder AST condition (**Figure 2b**). At 800 mA cm^{-2} as shown in **Figure 2c**, all MEAs subjected to Air AST reached DOE target of $\leq 30 \text{ mV}$ in performance loss, with voltage loss of $\sim 10 \text{ mV}$, $\sim 4 \text{ mV}$, and $\sim 15 \text{ mV}$ (**Figure 2c**) for No Cracks, Vertical Cracks, and Diagonal Cracks, respectively. Also, the performance of MEAs with cracks were slightly better under Air AST because more water is generated in air environment and cracks can improve water transport in the cell^{10,25}. It can be noticed that for the Air, Diagonal Cracks MEA there is a slight increase in voltage at 10,000 AST cycle, which demonstrated that MEA under this condition may require addition cell conditioning to reach better BOL performance.

The Tafel plots of the iR-corrected voltage against the logarithm of the current density are shown in **Figure 3a-b**. The Tafel slopes, which demonstrate how efficiently an electrode can produce current in response to change in applied potential, were close to the theoretical oxygen reduction reaction value of 70 mV dec^{-1} and did not change much through the course of the AST except for the case of Air, No Cracks (**Figure S2a**), where slope was reduced from 76.7 to 70.2 mV dec^{-1} . In addition, the mass activity was calculated at 0.9 V, where for air environment, No Cracks MEA had the largest reduction of $\sim 63\%$, while the other MEAs only had decrease of $\sim 42\%$ to $\sim 50\%$ (**Figure 3c**). Thus, the degradation for the Air, No Cracks MEA was dominated by kinetic loss, as there was not evident increase in HFR.

For MEAs with different MPL crack configurations, the normalized ECSAs during nitrogen and air environment ASTs were plotted as a function of the number of AST cycles in **Figure 3d**. The ECSA was calculated by integrating the hydrogen underpotential deposition region of CVs collected in hydrogen/nitrogen (anode/cathode) environment, and normalized against the ECSA at BOL. The loss in the ECSA agreed well with the observed increase in cell overpotentials. More severely degraded MEAs (MEAs with larger decrease in normalized ECSA) had greater performance losses. The loss in ECSA and degradation can be attributed to Pt dissolution and electrochemical Ostwald ripening, a process which dissolved Pt ions can redeposit on larger Pt atoms can cause significant particle size growth. The largest performance loss can be observed in the high current density region, where increasing oxygen mass transport overpotentials directly correlates with the decrease in the normalized ECSA. In contrast to the mass transport penalties, ORR kinetic overpotentials should have a minor contribution to the overall performance losses due to the logarithmic nature of the Tafel kinetics, where a 90% roughness factor (rf)-loss is required for an overpotential increase by $\sim 70 \text{ mV}$.

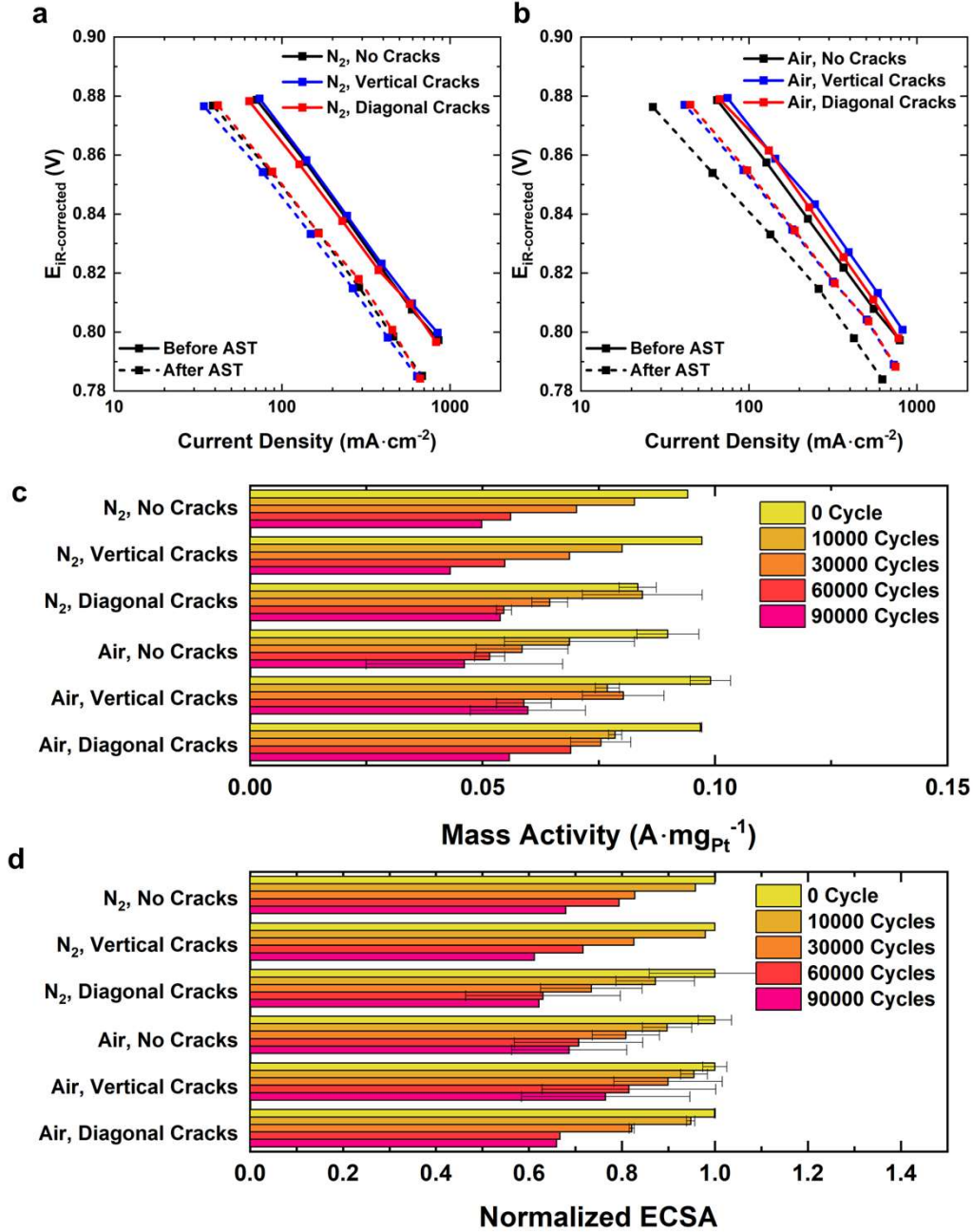


Figure 3. **a-b**, Tafel plots collected at 80°C in 100% RH under 150 kPa of absolute backpressure in H_2 - O_2 environment for **(a)** H_2 -Nitrogen and **(b)** H_2 -Air cathode environment AST. **c**, Mass activity at 0.9 V calculated from Tafel plots. **d**, Normalized ECSA to the ECSA of the BOL calculated from CVs collected at 80°C in 100% RH under 100 kPa of absolute backpressure in H_2 - N_2 environment. The error bars indicate more than one cell built for the specific AST condition, where average is shown and standard deviation is the width of the error bars.

The cell potentials measured at various geometric current densities under hydrogen/air (anode/cathode) environment were plotted as a function of r_f for MEAs with different MPL crack configurations (**Figure**

4). Rfs were extracted from CVs at 0 to 90,000 AST cycles, as AST progressed the rf decreased, therefore one can also think of this plot as cell voltages at different stages of AST (**Table S1**). Overall, the measured voltage vs. rf for all the MEAs fall into the same pattern, especially at low current density region: with decrease in rf the voltage decreases too. If the voltage plots are overlapping for the type of MPL used it means that the same degradation mechanism was present in all cases²⁶. At 0.4 A cm^{-2} this was mostly the case, expect the ones with diagonal cracks, whereas at high current densities at 2 A cm^{-2} we observed a significant spread in voltages for different MPLs. Since oxygen transport overpotential is a function of the cathode rf and local oxygen mass transport resistance only depends on the value of cathode rf²⁶, the cell voltage at high current density was affected the most by the oxygen mass transport resistance. The plots at 2.0 mA cm^{-2} had larger slopes than those at 0.4 mA cm^{-2} , which means that the cell voltage at high current densities will be more strongly affected when the cathode rf decreases. Most of the MEAs fall into the same pattern of decreasing rf value resulting in decreasing cell voltage, with the exception of N_2 , Diagonal Cracks and Air, Diagonal Cracks, which suggest that MPL with diagonal cracks would result in different degradation mechanism. Here, it is difficult to pinpoint what type of change of degradation mechanism this would be, as cracks mostly affect heat and water management. We hypothesize that Pt will still dissolve but its redeposition through Ostwald ripening is dependent on local water content, which can be impacted by crack distribution in the MPL.

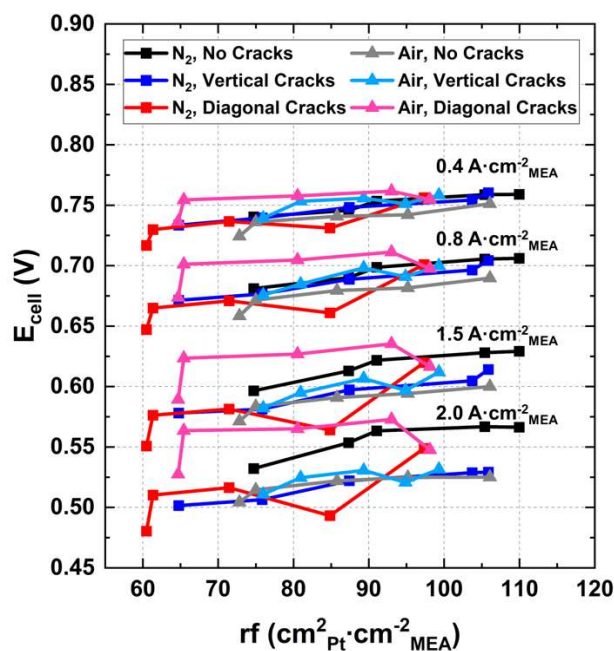


Figure 4. Measured cell voltages for various geometric current densities (0.4 , 0.8 , 1.5 , and 2.0 A cm^{-2}) as a function of cathode rf over the course of the ASTs. The measurements were performed at 80°C in 100% RH under 150 kPa of absolute backpressure in H_2 -air environment.

Ex situ μ -XRF mapping of identical locations of the inlet and outlet regions were performed before and after the AST. **Figure S3a** shows the 2D μ -XRF maps of the inlet regions of MEAs subjected to nitrogen environment AST and their corresponding loading histograms. Regions marked with dashed lines were used to demonstrate identical locations. Local loading hotspots caused by agglomeration of the carbon

support²⁷ were observed in the μ -XRF maps before AST, and increase in the intensity of these hotspots can be noticed in the maps taken after the AST. As previously reported²⁸, the evolution of Pt distribution during AST depends on the initial local Pt loading. The small distance between the Pt nanoparticles and decrease in the local surface energy are the main factors that drive the formation of these hotspots. The development of cracks in the catalyst layer can also be observed in the maps of inlet regions after AST, especially for the N₂ environment, Vertical Cracks and Diagonal Cracks MEAs, suggesting that under inert AST environment cracks in the MPL can facilitate development of cracks in the catalyst layer. The formation of the hotspots and cracks was caused by Pt dissolution and redeposition of the Pt on nearby larger nanoparticles through electrochemical Ostwald ripening²⁹. No band feature within the membrane was observed in any of the MEAs (**Figure S4**). The loading histograms (**Figure S3b**) demonstrated unimodal distribution of Pt loading, and the distribution remained unimodal after the AST.

Inlet vs. Outlet Regions

For the MEAs subjected to air environment AST, 2D μ -XRF maps of their inlet regions are shown in **Figure 5a-c**. Similar to those subjected to nitrogen environment AST, Air, No Cracks, Air, Vertical Cracks, and Air, Diagonal Cracks all had unimodal distribution of Pt loading in their corresponding loading histograms of the inlet regions (**Figure S5a-c**). In addition, the MEA with vertical cracks had a measurable decrease in the total average Pt loading as shown in its corresponding histogram (**Figure S5b**). The total Pt loadings were measured to be 458.8 $\mu\text{g}\cdot\text{cm}^{-2}$ and 417.4 $\mu\text{g}\cdot\text{cm}^{-2}$ before and after AST, respectively, for this inlet region. This phenomenon can be attributed to the development of cracks in its catalyst layer because Pt dissolution can be affected by the local environment³⁰ and cracks formation. Pt moving in-plane away from the cathode catalyst layer cracks was also observed, which could be thermodynamically driven due to the difference between local surface energies of the regions. Since air environment AST would produce a greater amount water, high liquid water flux can flow through the cathode catalyst layer cracks and further decrease the local concentration of Pt ions. Cracks can also aid the through-plane movement of Pt ions either towards the membrane (via ionomer phase) or out of the cathode catalyst layer (via effluent water). The MEA with diagonal cracks had a slight increase in the total average Pt loading as shown in its corresponding histogram (**Figure S5c**), which can be contributed to movement of Pt ions caused by Pt dissolution and Ostwald ripening. However, because the Pt loading histograms represent the inlet region of the MEA mapped with XRF, which was 1 mm², while the entire active area was 5 cm². These histograms cannot be representative of the overall behavior and the change was minimal.

The 2D identical location μ -XRF maps of the outlet regions of MEAs subjected to nitrogen and air environment AST and their corresponding loading histograms were shown in **Figure S6-S7**. Unimodal distribution of Pt loading before and after the AST can be observed in all of the histograms. However, unlike the inlet regions, the outlet regions had a minimal change in total average Pt loading and no clear development of cracks in the catalyst layer.

Figure S8 shows 2 cm by 2 cm synchrotron μ -X-ray diffraction (μ -XRD) maps of CCM after AST. All the maps have similar distribution of particle sizes and showed the largest increase in Pt particle sizes near the corners, where the serpentine channels in the flow field bend. The areas of where the bends area

tend to have the highest pressure drop and condensation of water, which can increase in Pt nanoparticle size through Pt dissolution and electrochemical Ostwald ripening.

The percentage of the area containing cracks in the catalyst layer before and after AST were obtained from the identical location μ -XRF transmission images (**Figure S2b**). These cracks were present in the catalyst layer at BOL and became more prominent after AST as the increase in the percentage of the area containing cracks in the catalyst layer were observed for all MEAs' inlet and outlet regions. When compared to those of the outlet regions, the percentage of catalyst layer cracks in inlet regions increased significantly after AST, especially the N₂, Vertical Cracks MEA, which had a 5-fold increase from 2% to 10.3%. And the inlet of the Air, Diagonal Cracks MEA had the largest percentage of cracks of 19.66% at EOL.

Cracks in the cathode catalyst layer can also be seen in the in-plane x-ray CT images (**Figure S1d-f**) obtained after AST. The difference between the inlet and outlet regions regarding the change of Pt loading distribution and the development of cracks suggested that the inlet and the outlet regions went through different degree and mechanism of degradation. Thus, Pt degradation is heterogeneous in the active area over the course of heavy-duty AST.

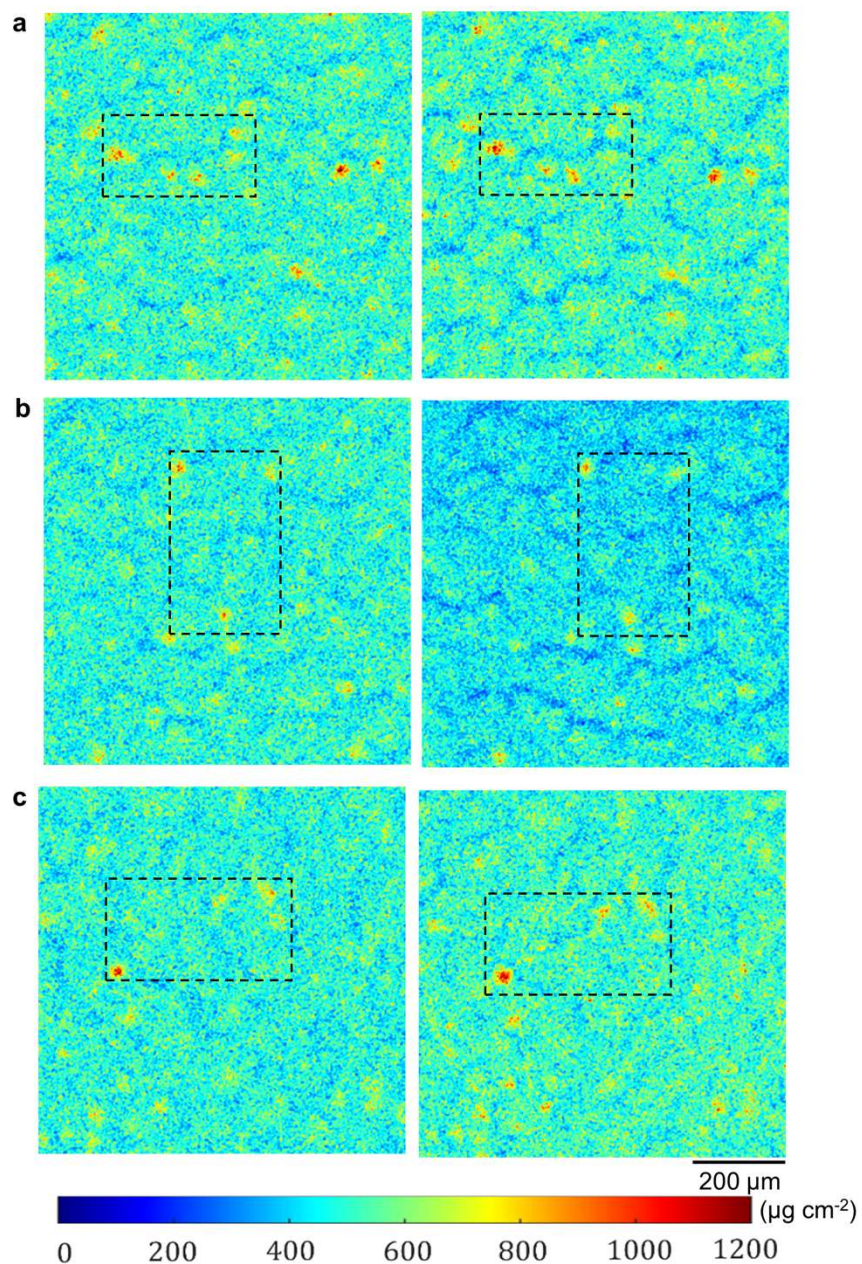


Figure 5. a-c In-plane Pt loading maps of inlet with regions marked to establish identical location before and after the AST for (a) Air, No Cracks, (b) Air, Vertical Cracks, and (c) Air, Diagonal Cracks.

Computational Simulation

Computational simulations were conducted to understand the effect of MPL cracks on gas diffusion through the MPLs. As shown in **Figure S9**, the random distribution of cracks leads to large stochastic variations at a given crack volume fraction. On average, average water saturation and mass transport resistance increase with crack volume fraction due to facilitated capillary transport in cracks (low entry capillary pressure),

which hinders gas diffusion across the MPL+GDL assembly. The mean variation of average saturation and mass transport resistance can be correlated with crack volume fraction by exponential functions

$$s^{\text{avg}} = 0.04\exp(35.4\varepsilon_{\text{crack}}) \quad (3.1)$$

$$R_{\text{mpl+gdl}} = 0.63\exp(6.9\varepsilon_{\text{crack}}) \quad (3.2)$$

The simulations show that oxygen transport will be inhibited with the presence of cracks in the MPL because they will be filled with water and water will introduce higher oxygen transport resistance. Although not shown in the simulations, the experimental data indicates that cracks can also potentially serve as pathways for dissolved Pt removal from the catalyst layer. As Pt dissolves during AST, water can serve as highway for Pt removal from the catalyst layer and larger amount of water can result in more Pt ions removal through the cracks.

Conclusions

Here we have reported the effects of MPL cracks on durability of Pt within the catalyst layer. MPL cracks can help remove liquid water from the catalyst layer, which can alleviate flooding if it is present. However, MPL cracks can also lead to larger Pt loss, as more Pt can be removed with effluent water. This study aimed to systematically investigate how MPL cracks impact Pt dissolution within the commercially made catalyst layer. Two catalyst AST cycles designed for HDVs were conducted: one in N_2 and one in air environments. The ASTs were conducted for 90,000 cycles, with electrochemical characterization being performed at the BOL, 10,000, 30,000, 60,000 and 90,000 cycles, which also identified as EOL. When MEAs with different configurations of MPL cracks were subjected to heavy-duty electrocatalyst ASTs, the presence and configuration of these cracks did not have a significant effect on the performance of the MEAs. N_2 diagonal cracks showed the largest polarization loss at the EOL, and also showed off-trend behavior compared to other MEAs, when V_{cell} was plotted against the rf. This signifies that N_2 diagonal cracks had different degradation mechanism compared to the other MEAs. Furthermore, identical location μ -XRF maps showed significant in-plane movement of Pt over the course of the AST for the MEAs with vertical cracks in the MPLs, suggesting the cracks can affect the degradation mechanism of the MEAs. The modeling study indicates that cracks in the MPL that are water-filled can inhibit oxygen transport.

Data availability

The data that supports the plots within this paper and other findings of this study are available from the corresponding author upon reasonable request.

Author contributions

C.C. K.K. and A.Z. were chiefly responsible for most of the experiments. L.C. and N.T. performed combined XRD experiments at the synchrotron. M.C. and S.P. performed microscopy experiments. P.A., L.C, J.B., C.J. and I.Z. helped with data interpretation and did conception of the study. C.C. produced the first manuscript draft and all the authors edited it. L.C., C.J., P.A. and I.Z. obtained funding support and oversaw the study.

Competing Interests

The authors declare no competing interests.

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