

# **Effects of Cathode Corrosion on Through-Plane Water Transport in Proton Exchange Membrane Fuel Cells**

Joseph D. Fairweather,<sup>a,\*,z</sup> Dusan Spernjak,<sup>a,\*</sup> Adam Z. Weber,<sup>b,\*</sup> David Harvey,<sup>c</sup> Silvia Wessel,<sup>c,\*</sup> Daniel S. Hussey,<sup>d,\*</sup> David L. Jacobson,<sup>d</sup> Kateryna Artyushkova,<sup>e,\*</sup> Rangachary Mukundan,<sup>a,\*</sup> and Rodney L. Borup<sup>a,\*</sup>

<sup>a</sup>Los Alamos National Laboratory, Los Alamos, New Mexico 87545, USA <sup>b</sup>Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA <sup>c</sup>Ballard Power Systems, Burnaby, British Columbia V5J5J8, Canada <sup>d</sup>Physical Measurement Laboratory, NIST, Gaithersburg, Maryland 20899, USA <sup>e</sup>University of New Mexico CEET, Albuquerque, New Mexico 87131, USA

The corrosion of carbon in the cathodes of proton-exchange-membrane fuel cells leads to electrode collapse, reduced active catalyst area, and increased surface hydrophilicity. While these effects have been linked to performance degradation over cell lifetime, the role of corrosion in the evolving water balance has not been clear. In this study, neutron imaging was used to evaluate the through-plane water distribution within several cells over the course of accelerated stress testing using potential holds and square-wave cycling. A dramatic decrease in water retention was observed in each cell after the cathode was severely corroded. The increasing hydrophilic effect of carbon surface oxidation (quantified by ex situ X-ray photoelectron spectroscopy) was overwhelmed by the drying effect of increased internal heat generation. To evaluate this mechanism, the various observed electrode changes are included in a multiphase, non-isothermal one-dimensional cell model, and the simulated alterations to cell performance and water content are compared with the idea that collapse and compaction of the catalyst layer is the dominant limitation to cell performance and not the lower amounts of active Pt surface area, and that higher temperature gradients result in drying out of the cell.

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The corrosion of carbonaceous components in proton-exchangemembrane fuel cells (PEMFCs) is a concern for long-term durability. Carbon corrosion can cause performance losses through several mechanisms.<sup>1</sup> As carbon catalyst support is lost, catalyst activity is lost due to particle detachment, agglomeration and/or isolation. The pore space is collapsed, blocking transport pathways for oxygen to the active catalyst sites. Surfaces can be made more hydrophilic by roughening and addition of oxide surface groups,<sup>2,3</sup> thereby increasing the propensity of flooding. While the kinetics of carbon corrosion are usually slow at PEMFC operating temperatures and normal potentials, regional reversals and starvation lead to high local potentials and accelerated oxidation.<sup>4,5</sup> Moreover, carbon corrosion is catalyzed by contact with platinum in the electrodes.<sup>6,7</sup>

Automotive applications of PEMFCs require an estimated 5500 h of operation including 38,500 startup/shutdown cycles.<sup>8</sup> Each of these cycles involves brief high potential excursions that can accelerate corrosion.<sup>4,5</sup> During operational periods, transient power demands and localized water blockage<sup>9</sup> can result in bulk or regional fuel starvation,<sup>10–12</sup> also leading to more corrosive conditions. Altogether, this is a demanding environment for carbonaceous components, and requires a combination of corrosion-resistant materials (typically graphitized carbons)<sup>13</sup> and careful system management strategies<sup>14</sup> to achieve acceptable durability. To evaluate rapidly the suitability of different support materials for a PEMFC cathode, accelerated stress tests (ASTs) have been developed which greatly accelerate corrosion. These ASTs commonly raise the electrode potential to between +1.2 V and +1.5 V vs. a standard hydrogen electrode (SHE), either as a constant hold or part of a repeated cycle.<sup>1,15,16</sup>

Carbon corrosion has a complex relationship with cell water content. Water serves as an oxidant in the corrosion mechanism:<sup>17</sup>

$$C + 2H_2O \rightarrow CO_2 + 4H^+ + 4e^-, \quad E_0 = 0.207 V_{RHE}$$
 [1]

The pace of carbon corrosion thus partially depends on local water activity. The rates of several different corrosion mechanisms have been shown to scale linearly with inlet humidification,<sup>18</sup> though the relationship with humidification is more complex in operating cycles due to internal water generation.<sup>19</sup> Humidification has also been demonstrated to have a significant impact on in situ component degradation.<sup>20</sup> Design changes that increase water retention may thus also increase performance losses caused by corrosive conditions.

The cell water holdup and performance is also expected to change based on the extent of corrosion, since several of the factors that regulate water retention and removal are affected by corrosion:

- 1) Catalyst layer porosity is reduced as the carbon support is lost and the pore structure collapses. Scanning electron microscopy (SEM) imaging of membrane electrode assembly (MEA) cross sections typically shows that the cathode catalyst layer experiences substantial thinning following corrosion.<sup>21</sup> Yu et al. have compared the degradation of several different carbon supports during 1.2 V holds, and reported that a weight loss of only 8% of the carbon support can lead to a 30% reduction in electrode thickness, corresponding to a large drop in porosity.<sup>8</sup> Carter et al. have studied cathode corrosion as a result of localized anode starvation and found a strong correlation between the time dependence of electrode thinning and that of reduced limiting current.<sup>12</sup>
- 2) Reduced efficiency in a corroded cell increases internal heat generation and thermal gradients. While this subject has not been well explored with respect to cell aging, the general role of thermal gradients in the water balance has received attention in recent years. Water flux under intentional temperature gradients has been measured in fuel-cell hardware.<sup>22-25</sup> Phase-change-induced (PCI) flow has been confirmed where water flow towards cooler regions in the gas phase roughly scales with the temperature gradient,<sup>22,25</sup> but only if a vapor gap is present.<sup>23,24</sup> Nonisothermal cell models have been used to predict temperature gradients within operating cells and quantify their contribution to water transport.<sup>26–29</sup> The thermal conductivities of cell components have been experimentally measured to improve the accuracy of such temperature predictions.<sup>30</sup> Temperature gradients formed by internal heat generation have been invoked to explain the neutron imaging results of Hickner et al.<sup>28,31,32</sup> In particular, the larger overpotentials required for higher current densities appeared to contribute to less overall water retention because of larger internal heat generation and accelerated vapor transport out of the cell. This is particularly relevant to the present discussion in that

<sup>\*</sup>Electrochemical Society Active Member.

<sup>&</sup>lt;sup>z</sup>E-mail: jofair@lanl.gov

	Cell 1 "BC Cell"	Cell 2 "BA Cell"	Cell 3 "Ballard Cell"			
MEA	PRIMEA 510 electrodes, GO	ORE-SELECT 710 membrane	Ballard			
Pt loading (anode/cathode)	$0.2/0.4 \text{ mg cm}^{-2}$		$0.1/0.4 \text{ mg cm}^{-2}$			
GDLs (anode/cathode)	SIGRACET 24BC/24BC	SIGRACET 24BC/24BA	BMP			
Flow field	Single-serpen	tine, 11 passes	Parallel, 6 channels			
Active area	2.5	cm <sup>2</sup>	$1.1 \text{ cm}^2$			
AST conditions						
Cathode potential (vs. H <sub>2</sub> anode)	$80 \min \text{ holds } @ +$	1.3 V 320 min total	Square-wave cycling:			
			30 s @ +0.6 V			
			60 s @ +1.4 V			
			750 cycles total			
Gas flows (anode/cathode)	0.1/0.2 sl	$pm H_2/N_2$	1.5/2.5 slpm H <sub>2</sub> /air			
Pressure	No backpressure (109/121	kPa absolute at an/ca inlet)	138 kPa absolute (20 psia) at inlet			
ECSA conditions	+0.1 to 1.0	V at 50 mV/s	+0.1 to 1.0 V at 50 mV/s			
Gas flows (anode/cathode)	0.1/0.2 sl	$pm H_2/N_2$	1.5/2.5 slpm H <sub>2</sub> /N <sub>2</sub>			
Pressure	273 kPa absolute	(39.7 psia) at outlet	273 kPa absolute (39.7 psia) at outlet			
Imaging conditions	0.8 A	$cm^{-2}$	+0.6 V			
Gas flows (anode/cathode)	0.1/0.2 sl	pm H <sub>2</sub> /air	1.5/2.5 slpm H <sub>2</sub> /air			
Pressure	No backpressure (109/121	kPa absolute at an/ca inlet)	138 kPa absolute (20 psia) at inlet			

Table I. Components and testing conditions used for the three cells discussed in this study. Unless otherwise noted, all operations took place at 80°C, 100% inlet RH.

the overpotential required to sustain a given current density will increase as a cell becomes more corroded.

3) Carbon surfaces become more hydrophilic as surface oxide groups are added. A higher oxygen content has long been known to promote wetting of carbon blacks by water.<sup>33</sup> This effect has been studied in the context of phosphoric-acid fuel cell (PAFC) electrodes, and it was observed that corrosive potential holds at PAFC operating temperatures add oxygen content to carbon blacks and lower water contact angles.<sup>34</sup> More recently, it was shown that surface oxide formation at corroding potentials also changes the wetting of carbon supports at more moderate PEMFC conditions.<sup>2</sup> Corrosion likely contributes to contact angle reduction seen on PEMFC electrodes following testing.<sup>31</sup> Aged gas diffusion layers (GDLs) also show an increase in water adhesion forces compared to virgin ones, although the bulk capillarity does not change significantly as long as polytetrafluoroethylene (PTFE) is present.<sup>36</sup> Surface oxide formation may be linked to wetting changes in the GDLs, as X-ray photoelectron spectroscopy has shown an increase in oxygen content of GDL substrates following long-term drive cycle testing.<sup>37</sup>

The different effects of carbon corrosion compete with respect to how they influence the water balance during an AST. More hydrophilic oxidized carbon surfaces should increase liquid water holdup, while larger heat generation should increase water removal. Catalyst-layer collapse could reduce the water removal rate by increasing masstransport resistance, yet decrease the space available for liquid retention. This work seeks to illuminate how the balance of these different mechanisms changes water retention and distribution in an AST-aged cell. Since a design change that increases water retention may also be expected to affect degradation rates during a corrosion AST, the case of an omitted cathode microporous layer (MPL) is also examined. Data is compiled from several sets of experiments under different conditions, presented here together because of the complementary observations made from each series. Cell simulations are used to compare experimental water profiles with those predicted from the known degradation mechanisms discussed above.

# Experimental

Corrosion ASTs and performance testing were carried out in custom cell assemblies designed for high-resolution neutron imaging, so that through-plane water profiles could be quantified during all steps of the corrosion process. Degradation resulting from the ASTs was evaluated by polarization, impedance spectroscopy, electrochemically active surface area (ECSA), and post-mortem characterization of components.

*Cell components.*— Cell end plates were made of aluminum with integrated, gold-coated flow fields. Three different cell configurations were tested:

- Commercial cell components with a single-channel serpentine flow field and a nominal active area of 2.5 cm<sup>2</sup>. Gore PRIMEA series 57 membrane-electrode assemblies (MEAs) were used, each including a GORE-SELECT M710.18 membrane, carbonsupported An510.2 anode (0.2 mg Pt cm<sup>-2</sup>) and Ca510.4 cathode (0.4 mg Pt cm<sup>-2</sup>).\* SGL SIGRACET 24BC GDLs were used for both anode and cathode support.<sup>†</sup> This case will be referred to below as the "BC cell."
- Identical with (1), except the cathode microporous layer was omitted by using a SIGRACET 24BA GDL on the cathode side, hereafter referred to as the "BA cell."
- 3) Ballard Power Systems components with a six-channel parallel flow field and a nominal active area of 1.1 cm<sup>2</sup>. The MEA was made in-house and consisted of DuPont NR211 membrane, anode/cathode catalyst loadings of 0.1/0.4 mg cm<sup>-2</sup>, and Ballard Material Products (BMP) GDLs. This case will be referred to as the "Ballard cell."

Configurations (1) and (2) were chosen to compare the effects of the cathode microporous layer on water distribution and durability. Configuration (3) was designed to emulate the inlet region of a larger Ballard apparatus, where high gas flows effectively create differential conditions (negligible in-plane variation). Components and test conditions for all cells are summarized in Table I.

Accelerated corrosion and performance testing of PRIMEA/ SIGRACET cells.— For the BC and BA cells above, a constant potential AST was used to produce targeted degradation of carbon materials. With  $N_2$  flowing through the cathode side, a potentiostat was used to

<sup>\*</sup>Certain trade names and company products are mentioned in the text or identified in an illustration in order to adequately specify the experimental procedure and equipment used. In no case does such identification imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the products are necessarily the best available for the purpose.

<sup>&</sup>lt;sup>†</sup>PRIMEA and GORE-SELECT are trademarks of W.L. Gore & Associates, Inc. SIGRACET is a trademark of SGL Group, GmbH.

hold the cell cathode at +1.3 V vs. H<sub>2</sub> anode, for steps of 80 min at a time. Cell temperature was 80°C, and both gas streams were humidified to 100% relative humidity (RH), at ambient pressure. The +1.3 V hold was chosen to accelerate corrosion beyond that of the +1.2 V recommended by the 2010 USDrive (formerly FreedomCar) protocol,<sup>15</sup> so that significant performance degradation could be observed within the limited window of the neutron imaging beam-time. In addition, the cathode catalyst layer used does not represent the state of the art in the Gore product line, and the less durable catalyst support was specifically chosen for study so that corrosion effects could be observed quickly.

After each potential hold, the cell was switched to  $H_2/air$  (anode/cathode) operation at 80°C, 100% RH, and the performance was characterized by polarization curves and electrochemical impedance spectroscopy (EIS). Constant gas flows of 0.1 slpm  $H_2$  and 0.2 slpm air were used, as high-stoichiometric flows were required to maintain the operational stability of the small cells. Cyclic voltammetry in  $H_2/N_2$  was also used to quantify electrochemical surface area (ECSA) at select points. To evaluate the relationship between performance degradation and the water distribution, the cell was imaged by neutron transmission during the +1.3 V AST holds and during constant current operation at 0.8 A cm<sup>-2</sup>.

Finally, post-mortem characterization of the cathodes was carried out by X-ray photoelectron spectroscopy (XPS), to quantify changes in surface chemistry. XPS spectra were acquired on a Kratos Axis Ultra DLD X-ray photoelectron spectrometer using a monochromatic Al K $\alpha$  source operating at 150 W with no charge compensation. The base pressure was about 2 × 10<sup>-10</sup> mbar, and operating pressure was around 2 × 10<sup>-9</sup> mbar. Survey and high-resolution spectra were acquired at pass energies of 80 eV and 20 eV respectively. Data analysis and quantification were performed using CasaXPS software. Sensitivity factors provided by the manufacturer were utilized, and a 70% Gaussian/30% Lorentzian line shape was utilized in the curve-fit of O 1s and C 1s spectra.

Accelerated corrosion and performance testing of Ballard cell.— The Ballard cell was tested using an aggressive potential-cycling AST, reflecting the robust catalyst support used in the Ballard MEA and the stressors necessary to observe performance changes within the time window (total 18.75 h of potential cycling). In addition, potential cycling may better reflect the actual degradation imposed by startup/shutdown cycling, as the degradation rate at any given potential during cycling has been shown to be much higher than during static potential holds.<sup>18</sup> However, repeated cycles do not solely target the carbon support, but also accelerate Pt particle degradation through accelerated dissolution.<sup>1</sup> A square-wave potential was applied to the cell, with the cathode held for 30 s at +0.6 V followed by 60 s at +1.4 V relative to anode. The cell temperature was held at  $80^{\circ}$ C. Flows were 1.5 slpm H<sub>2</sub> and 2.5 slpm air for the anode and cathode respectively, and the inlet pressure of both streams was held at 138 kPa absolute (20 psia). These flows and pressures were chosen to emulate the conditions of a larger one-dimensional (1-D) Ballard research cell. Gases were humidified to 100% RH.

Similar to the BC and BA cell procedure, the AST was interrupted periodically for performance characterization and ECSA measurement. Water distribution was quantified by neutron imaging during constant voltage holds of 0.6 V; constant voltage was used in this case because of the greater interest in constant cell potential for the cell application. Keeping the potential constant also has the effect of keeping constant the fraction of heat produced by reaction, which will be discussed later.

*Neutron imaging.*— Neutron imaging was conducted at the thermal neutron imaging facility at the National Institute of Standards and Technology (NIST) Center for Neutron Research, located at the port beam tube 2 (BT2). Each test cell was mounted on a motorized rotation stage so that the through-plane direction of the test sections could be aligned perpendicular to the optical axis of the neutron beam. The resulting cross-sectional transmission image was projected on the



Figure 1. Exploded view and neutron imaging orientation for the BC Cell.

detector, as illustrated in Figure 1. The beam-defining aperture was a 10 mm by 1 mm slit, yielding an L/D ratio of 600 (horizontal) by 6000 (vertical), with a neutron fluence rate of  $6 \times 10^5$  cm<sup>-2</sup> s<sup>-1</sup>. The detector employed for these measurements was a micro-channel plate (MCP) with a cross-strip readout anode, which has a sensitive area of 40 mm in diameter, a 5  $\mu$ m pixel pitch, and a thermal neutron stopping power of about 20%. The intrinsic spatial resolution of the detector (10% modulation transfer function, MTF) is about 13  $\mu$ m, as calculated from the profile of a sharp gadolinium edge.<sup>38</sup> The detector reconstructs each neutron capture event to determine the position; this introduces a dead time (10% at an event rate of 1 MHz) and effectively limits the field of view of the detector. For these measurements, a beam mask limited the field of view to 35 mm by 3 mm, which was sufficient to image the active area of the test cells.

To calculate water content across the cell, a dry transmission image was first acquired for each cell. The cell was then allowed to equilibrate under each operating condition before a wet transmission image was acquired. The water thickness (t) at each location was calculated from the change in neutron intensity between the wet case ( $I_{wet}$ ) and the dry case ( $I_{drv}$ ),

$$I_{wet}/I_{dry} = e^{-\mu t - \beta t^2}$$
<sup>[2]</sup>

where  $\mu$  (0.38483 mm<sup>-1</sup>  $\pm$  0.00025 mm<sup>-1</sup>) and  $\beta$  (–0.00947 mm<sup>-2</sup>  $\pm$  0.00015 mm<sup>-2</sup>) are attenuation coefficients fit to water thickness calibration data reported elsewhere.<sup>38</sup> This calculation differs from a standard Beer-Lambert relationship in that the optical density is assumed to have a quadratic (instead of linear) relationship with water thickness, to account for beam hardening due to the polychromatic beam used at the BT2 imaging facility. In the present work, the neutron imaging data will be presented in two ways: (1) colorized images of water distribution, and (2) through-plane water profiles obtained by averaging water content in vertical columns of these images.

Images were acquired at 2 min intervals, with about a 2 s image download time. The detector is sensitive to gamma rays, and a background measurement was made by blocking the thermal neutron beam with a 1 mm thick Cd sheet which negligibly reduces the gamma ray fluence; this background was subtracted similar to the dark noise in CCD-based detector systems.  $I_{wet}$  and  $I_{dry}$  were thus background corrected, and also normalized for varying neutron source intensity.<sup>39</sup>

#### **One-Dimensional Cell Model**

To understand better the observed experimental results, a multiphase, nonisothermal model was used to simulate select cell conditions (i.e. beginning- and end-of-life performances). The model is based on the work of Weber and coworkers, <sup>26,28,40–42</sup> and is detailed in the Appendix; herein a brief summary is given with a focus on the liquid-saturation-related and fitting terms. The modeling domain

is the 1-D through-plane direction composed of the membrane, catalyst layers, and diffusion media, where the latter uses an effective diffusion-media thickness to account for land/channel effects.43

In terms of governing equations, overall mass and energy balances are used where the latter accounts for both reversible and irreversible heat generation. For the transport equations, one uses concentrated-solution theory in the membrane, Stefan-Maxwell for gas-phase diffusion where the effective binary diffusion coefficients account for the impact of tortuosity, porosity, and saturation using the measured coefficients for the SGL GDLs and expected functionality for the MPLs by<sup>44</sup> r the MPLs by  $D_{i,j}^{\text{eff}} = D_{i,j}^0 f(\varepsilon_0) g(S) = D_{i,j}^0 \varepsilon_0^{3.8} \frac{1}{2} \left\{ 1 + \text{erf} \left[ -\frac{\ln(S) + 1.27}{0.82} \right] \right\}$ [3]

and

$$D_{i,i}^{\text{eff}} = D_{i,i}^0 \varepsilon_0^3 \tag{4}$$

respectively, where  $\varepsilon_0$  is the porosity of the sample, S is the liquid saturation or pore volume filled by liquid, and  $D_{i,j}^0$  is the bulk binary gas diffusion coefficient between species i and j and is a function of temperature and pressure. Butler-Volmer kinetics are used for the hydrogen oxidation reaction and Tafel kinetics are used for the oxygen reduction reaction with exchange current densities and other parameters taken from the literature.<sup>45,46</sup> To model the reaction at the reaction site within the catalyst layer, an agglomerate-model approach is used with a possible external film. Thus, the exchange current for the oxygen reduction reaction (ORR) is

$$\nabla \cdot \mathbf{i}_{1} = 4Fp_{O_{2},ext}^{0.8} \left( \frac{1}{\frac{1}{R_{O_{2},film}} + \frac{1}{k_{s}E}} \right)$$
[5]

where ext denotes the external (gas-phase) condition,  $R_{O_2, film}$  is the oxygen resistance through the film,  $k_s$  is given by the Tafel kinetics, and E is the effectiveness factor of the agglomerate which is a function of the kinetics and aggregate transport resistance in the agglomerate,  $R_{O_{2,agg}}$  (see Appendix). Standard boundary conditions are used as described in the Appendix.

Finally, to compare the water profiles between the data and simulation, for the porous media, the predicted liquid saturation is used and integrated along the beam path, and for the membrane the water content is used in a similar fashion.<sup>28,38</sup> All parameters are taken from the literature and are functions of temperature and local conditions except as noted. The various cell component thicknesses were taken from the neutron and scanning-electron-microscopy images.<sup>21</sup> To simulate the effects of the corrosion AST on aged cells, the cathode ECSA, thickness and porosity were reduced to reflect experimentally observed values, and the values of the film and agglomerate resistances changed as discussed below.

## Results

Performance loss during corrosion ASTs.- Polarization curves after sequential AST steps are shown in Figure 2 for the BC and BA cells. The initial polarization curve in Figure 2a indicates that using the 24BC cathode GDL (with MPL) resulted in a noticeable masstransport limitation around 1.2 A cm<sup>-2</sup>. For comparison, the initial curve in Figure 2b shows that the BA cell (no cathode MPL) had a significantly higher limiting current. This can be explained by an additional mass-transport resistance imposed by the MPL. The limiting current difference is contrary to the beneficial effect typically observed with the addition of an MPL,<sup>47,48</sup> and should be interpreted as distinct to this particular combination of flow field, materials and operating condition. Subsequent polarization curves show that performance loss following 80 minute holds at +1.3 V occurred faster in the BA cell, so that the overall performance of the BC cell was slightly higher by the end of the corrosion AST.

EIS was used to compare the contribution from different performance loss mechanisms<sup>49</sup> for the two cell configurations. Figure 3a Figure 2. Polarization curves for BC and BA cells: H<sub>2</sub>/air, 80°C, 100% RH; (a) using 24BC cathode GDL; (b) using 24BA cathode GDL. Common legend

Current Density (A cm<sup>-2</sup>)

and Figure 3b show impedance spectra at a constant potential of 0.8 V. At this low overpotential (low current density), transport losses are relatively small, and the EIS high-frequency arc is controlled mainly by kinetic resistance (first derivative of overpotential as a function of superficial current density, assuming Tafel kinetics). The spectra are sensitive to changes in catalyst ECSA and utilization from particle swelling and agglomeration, with the caveat that any other effect that lowers current density will also increase arc size. The two cells show only a small initial difference at 0.8 V. Arc growth during the AST in the BA cell case indicates that kinetic resistance grew slightly faster than in the BC cell. That is, the catalyst utilization appeared to drop faster when no cathode MPL was used, suggesting that the electrode corrosion was accelerated in this case.

Figure 3c and Figure 3d compare impedance spectra at 0.8 A cm<sup>-2</sup> for each cell. At this current density, kinetic resistance diminishes and mass-transport resistances become dominant. Resistance decreased for both cells after the first 80 min potential hold. This may be the result of initial carbon corrosion removing some excess material within the cathode, increasing the effective permeability. Resistance quickly grew for both cells in subsequent steps, but the total increase during the test was much greater for the 24BC cell. This indicates that the cathode MPL makes the cell vulnerable to additional masstransport losses during the corrosion AST. One explanation is that mass-transport resistance of the MPL itself is increasing as it corrodes, either through collapse of its pore space or through increased flooding due to decreased hydrophobicity. It has been previously demonstrated that performance losses during startup/shutdown cycling can be partially mitigated by using a more highly graphitized carbon in the MPL.<sup>50</sup>

We have performed similar corrosion AST series with 50 cm<sup>2</sup> cells, aging cells at +1.3 V for up to seven hours using identical components to the BC and BA cells presented here; the full results are reported

shown in (a).

a **BC Cell** 0.9 Initial 0.8 △ After 80 min @ +1.3 V After 160 min @ +1.3 V 0.7 • After 240 min @ +1.3 V \* After 320 min @ +1.3 V Voltage (V 0.6 0.5 0.4 0.3 0 0.2 0.8 1.6 0.4 0.6 1.2 1.4 1 Current Density (A cm<sup>-2</sup>) b **BA Cell** 0.9 0.8 0.7





Figure 3. Impedance spectra for the BC and BA cell configurations held at two operating conditions between corrosion AST steps: (a) BC cathode GDL at 0.8 V; (b) BA cathode GDL at 0.8 A cm<sup>-2</sup>; and (d) BA cathode GDL at 0.8 A cm<sup>-2</sup>. Common legend shown in (a).

elsewhere.<sup>21</sup> Accelerated kinetic losses without an MPL are consistent in the larger cells. X-ray diffraction (XRD) indicated that the rate of catalyst agglomeration was faster without an MPL, providing additional evidence that accelerated support corrosion contributed to lower catalyst utilization in this configuration. Carbon corrosion was quantified by measuring exhaust  $CO_2$  during AST, indicating that a small portion of the evolved  $CO_2$  originated from the MPL in the BC cell. However, mass-transport losses associated with MPL degradation appear to be highly dependent on the local cell conditions.

Figure 4 shows polarization and impedance spectra for the Ballard cell at different stages of the potential cycling AST. While the cell shows a similar loss in performance to that experienced by the BC and BA cells at the end of the AST, the more severe conditions required to degrade the Ballard cell (750 total minutes at +1.4 V vs. 320 total minutes at +1.3 V) reflect the highly graphitized carbon used in the cathode support. During the early steps of the AST, the cell shows a modest improvement (Fig. 4a) relative to initial polarization performance. This is partially due to a lowering of high frequency resistance (HFR) during the first 25 cycles. This may indicate improved proton conductivity due to restructuring of the electrode/membrane interface, a small contribution to ionic conductivity from carbon surface oxides, or simple improved membrane/ionomer hydration. Impedance spectra (Fig. 4b) also show that the total resistance at 0.6 V does not increase in the first 50 potential cycles, illustrating a delay in the onset of corrosion effects. Moreover, a significant potential drop does not appear in the polarization curves (Fig. 4a) until after 250 cycles.

A portion of performance loss during each corrosion AST comes from the loss of active platinum surface area as catalyst support is corroded and platinum particles agglomerate. Figure 5 shows relative ECSA remaining for the BC cell after successive potential holds, and for the Ballard cells after potential cycling. Due to time constraints, ECSA was not recorded for the BA cell, but a separate ECSA comparison is available in recent work for larger cells.<sup>21</sup> Both the BC and Ballard cells show a similar pattern: ECSA rapidly drops at the start of the AST, then the rate of decline slows dramatically. This trend is consistent with the general observation that the corrosion rate is highest for an electrode at the beginning of life, and decays with time.<sup>8</sup> The pattern is in strong contrast to the delayed onset of performance degradation seen in Figures 2–4. For instance, Figure 5a shows that 36% of the active area in the BC cell cathode has been lost after 80 minutes at +1.3 V, while Figure 3a shows negligible change in the total resistance at 0.8 V. It is possible that not all of the catalyst area measured by proton desorption is utilized at this condition, and there is sufficient extra capacity that 36% can be lost without appreciable performance loss.

Using the Tafel slope analysis of Makharia et al.<sup>51</sup> for estimating the purely kinetic voltage change for platinum area loss, a 36% reduction in ECSA should result in a drop of roughly 13 mV. This degree of change may be observable in the kinetic region of the BC cell polarization curve after 80 minutes at +1.3 V (Figure 2a), but the difference is within the uncertainty of the measurement. More dramatically, the Ballard cell lost more than 60% of ECSA after 100 potential cycles (Figure 5b), with no measureable decrease in performance (Figure 4a). Given the relatively small effect of ECSA reduction, the more severe performance losses observed later in each AST may signal the onset of other degradation mechanisms, i.e. electrode collapse.

*Neutron imaging of BC and BA cells.*— To evaluate how changes in cell performance were related to changes in water management, neutron imaging was used to measure water content throughout the corrosion ASTs. Figure 6 shows colorized water-thickness images for the cross section of the BC cell, at a constant 0.8 A cm<sup>-2</sup>, before and after the sequential potential holds. Each pixel in a colorized image



a

Cell potential (V)

b

0.2

BOL
 △ After 25 cycles

After 50 cycles

After 100 cycles
 After 250 cycles



Figure 4. Performance changes for the Ballard cell during potential cycling AST. (a) Polarization curves after sequential cycling:  $75^{\circ}$ C, 100% inlet RH, 1.5/2.5 slpm H<sub>2</sub>/air. (b) Impedance spectra at 0.6 V after sequential cycling:  $80^{\circ}$ C, 100% inlet RH, 1.5/2.5 slpm H<sub>2</sub>/air.

represents the water content integrated in the direction of the beam. The width of the active area along the beam path is 12 mm, so that a calculated water thickness of 1.2 mm corresponds to 10% of the path length occupied by water. Figure 7 compares the corresponding through-plane water profiles for the BC and BA cells. The profiles are averaged over the entire active height of each cell, so that the water thickness represents the mean water content at a given through-plane position. Interfaces between cell components were identified from dry images. The thickness of the cathode GDL in Fig. 7b is less than in Fig. 7a, since the BA cell has only the carbon-fiber substrate (no MPL) on the cathode. The repeatability of the initial water content was checked with rebuilds of both the BC and BA cells, and the repeated profiles (included in Figure 7) showed agreement within 0.2 mm of water thickness at every point across the cell profile. Various contributions to error in water content have recently been explored for high-resolution neutron imaging,<sup>38</sup> including a  $\sim 1\%$  uncertainty from the water thickness calibration (Equation 2) and  $\sim 0.01$  mm uncertainty from Poisson counting statistics under the present imaging conditions. However, all contributions are predicted to be smaller than the difference observed between cell rebuilds, and cell-to-cell variation is therefore taken to be the dominant source of uncertainty. It should also be noted that geometric blurring of the components (for example, waviness of the GDL boundaries induced by the channel/land transitions) reduces the sharpness of the profiles, below the inherent resolution of the neutron detector. This contributes to the uncertainty of true water thickness at any one point in the cell profile, but this uncertainty is reduced when comparing across larger length scales such as the total GDL thickness.



**Figure 5.** Percent of initial ECSA remaining, calculated from proton desorption peak of cyclic voltammograms using conditions in Table I: (a) for BC cell after potential holds at +1.3 V; and (b) for Ballard cell after square-wave cycling between 0.6 and 1.4 V.

In the initial case (before AST series), both cells show a large difference in water content across the MEA, with more water in the cathode GDL due to oxygen-reduction reaction and electro-osmotic flow. Figure 6 further shows that the majority of liquid water is in the GDL adjacent to the cathode lands, and this is also where the largest changes in water content occur during the corrosion AST. Meanwhile, Figure 7 confirms that the cathode-side MPL has a significant impact on the water profile, resulting in much less water next to the MEA when using the 24BC cathode GDL vs. the 24BA. This result qualitatively agrees with a previous imaging comparison of cells with and without a cathode MPL.<sup>47</sup> Note that the MEAs used in the present study are too thin to resolve absolute water thickness within the membrane and electrodes, and the water thicknesses in the middle of each cell profile represent a combination of (much higher) MEA water content and that of adjacent GDL regions. Measurements with thicker membranes and thorough image processing<sup>38,52</sup> have shown that the expected membrane water content for these cell conditions is between that of ionomer equilibrated at 100% RH and that of ionomer equilibrated with liquid water.

Both cells show a dramatic decrease in water content after sequential potential holds. Since all images were taken at the same current density, water production in each cell is identical, and decreased water retention implies increased transport out of the cell. This is most easily explained in terms of internal heat generated by the less efficient reaction within a corroded cell. As the electrical potential drops due to the various losses, more heat is generated at the MEA. This waste heat increases the temperature gradient between the MEA and the flow fields, which promotes evaporation and vapor transport away from the MEA. This topic will be addressed in more detail in the discussion.

The two cells were also imaged for time-resolved water content during the +1.3 V potential holds. Figure 8 shows typical water profiles. The cell with no cathode MPL (24BA GDL) consistently retained more water in the MEA during each corrosion step. The difference was remarkably constant throughout multiple potential holds and across



**Figure 6.** Colorized water-thickness images for the BC cell, calculated from neutron transmission during the course of the carbon corrosion AST. Each image was taken over 20 min while the cell current density was held constant at 0.8 A cm<sup>-2</sup>. 80°C, 100% inlet RH, 0.1 slpm/0.2 slpm H<sub>2</sub>/air.

**Figure 7.** Through-plane water profiles for the BC and BA cell configurations at  $80^{\circ}$ C, 100% RH, with constant current density of 0.8 A cm<sup>-2</sup>: (a) BC cell, and (b) BA cell (no MPL). Profiles averaged over the entire active area from 20 minute neutron transmission images. Common legend shown in (a).



**Figure 8.** Through-plane water profiles for the BC and BA cell configurations at  $80^{\circ}$ C,  $H_2/N_2$  flow, 100% RH, during a corrosion AST potential hold (cathode at +1.3 V vs. anode). Error bars show the standard deviation of water in the cathode across all corrosion holds for each cell configuration.

cell rebuilds. Error bars show the standard deviation of water thickness in the cathode for all holds at +1.3 V for each cell configuration, with an average of 24% more water when using the 24BA GDL. Increased retention in the BA cell may be due to the tendency of water to pool at the GDL substrate surface when no MPL is used;<sup>53</sup> water could build up at the GDL/MEA interface during operation and then be retained throughout the potential hold. Since water is the primary oxidant during the AST, having more water in the cathode catalyst layer implies that corrosion should be faster without the cathode MPL. This provides a mechanism for the accelerated losses observed from impedance spectroscopy of the BA cell at low overpotential (Figure 3b).

*Neutron imaging of Ballard cell.*— Colorized water-thickness images of the Ballard cell are shown in Figure 9, at a constant potential of 0.6 V after increasing numbers of potential cycles. The water con-

tent is again largest adjacent to the cathode lands, but due to the very narrow lands in this flow field, the liquid is confined to much smaller bands compared with the BC and BA cells. Figure 10 gives the corresponding water profiles, calculated for three different areas of interest. The averaged profile for the full active area (Fig. 10a) indicates that the total water content slightly increased at the start of the AST, peaking after 50 potential cycles and declining afterward. The increase and subsequent decline is large if only the center region under each land is averaged (Fig. 10b), and negligible if the center of each channel is averaged (Fib. 10c). That is, all the observable change in water content throughout the AST happens around the lands. Liquid water collects at the lands partially due to the longer transport pathways, and due to the operating temperature gradient between the MEA and cell hardware. The lack of change at the channel centers is partly an indication that these regions start relatively dry at the high stoichiometric flows used for the Ballard cell. Water is effectively removed in the vapor phase, so there is little liquid formation despite the moderate current density at the start of the AST.

Comparing the peak in water content under the lands after 50 cycles (Fig. 10b) to the similar peak in cell performance (Fig. 4a), the water content at a constant 0.6 V correlates with current density and the corresponding water production rate. The much drier land regions by the end of 750 potential cycles represent a much lower current density due to component degradation, and the water retention under the lands approaches that of the channel centers. This is a different case from the BC and BA cells, which were compared at constant current density and the same water production rate, but the Ballard cell demonstrates that water retention trends are similar during a corrosion AST whether the cell is compared at constant current density or at constant potential.

Post-mortem characterization.— After the AST experiments, the BC and BA cells were dismantled and the cathode side of the MEAs were characterized by XPS, to look for changes in the surface composition caused by corrosion. Calculated elemental percentages and carbon group speciation are shown in Table II. Unfortunately, a significant amount of MPL material stuck to the MEA surface in the case of the BC cell cathode, as evidenced by the dramatic reduction in platinum signal. This makes a direct comparison with the corroded



Figure 9. Colorized water-thickness images for the Ballard cell at 0.6 V, after progressively greater numbers of potential cycles.  $80^{\circ}$ C, 100% inlet RH, 1.5/2.5 slpm H<sub>2</sub>/air.

Total element:	C 1s %	O 1s %	F 1s %	Pt 4f %	S 2p %	O/C %				
PRIMEA 510.4 fresh	38.5	5.2	55.2	0.73	0.43	14				
BC cell cathode	47.7	1.5	50.8	0.11	_	3				
BA cell cathode	32.2	5.9	61	0.96	—	18				
Binding energy (eV): Carbon species:	283.3 C≡C %	284.1 Pt-C %	284.8 C <sub>gr</sub> %	285.8 C* %	286.9 C-OH&C-OC %	287.9 C=O&C-F %	288.8 COOH %	289.7 C(O) <sub>3</sub> %	290.7 CF <sub>2</sub> %	292.1 CF <sub>3</sub> %
PRIMEA 510.4 fresh	3.3	24.1	7.5	4.1	1.9	3.7	5.2	9.6	33.7	7.0
BA cell cathode	5.6	14.2	9.3	4.9	3.6	5.4	8.6	18.4	24.5	5.5

Table II. XPS peak speciation of cathode catalyst layers, for total elemental composition and for carbon surface groups. BC and BA cell results are for each cathode at the end of the AST (320 min total at +1.3 V).

BC cell difficult, as carbon and fluoropolymer from the MPL largely mask the MEA signal in that case, but the BA cell results may still be used to examine surface changes that occurred during the AST.

For the BA cell cathode after 320 total minutes at +1.3 V, total carbon fraction decreased and oxygen content slightly increased. Meanwhile, carbon group speciation shows an increase in all oxygencontaining groups, a loss of Pt-C bonding, and a decrease in fluoropolymer surface groups, thereby confirming the extensive changes to the electrode that occur during the AST. While the trends are rea-



**Figure 10.** Through-plane water profiles for the Ballard cell, at 80°C, 100% RH, at constant cell potential of 0.6 V. Exposure time was 20 minutes, with profiles averaged over three regions of interest: (a) full cell active area; (b) average of all land centers; and (c) average of all channel centers. Common legend shown in (a).

sonable for a corroded electrode, the magnitude of increase in total oxygen is much less than what has previously been observed for carbon supports severely corroded ex situ.<sup>2,54</sup> However, the initial elemental composition is rather close to that determined by XPS for Nafion<sup>‡</sup> alone,<sup>55</sup> suggesting that much of the oxygen signal for the fresh PRIMEA electrode comes from the ionomer.

To attempt to isolate the surface composition of the catalyst support carbon from the overall electrode surface (including ionomer), the following calculation was made. Assuming that the peaks at 290.7 eV and 292.1 eV are contributed only by the ionomer, a reference ionomer-only spectrum was used to calculate that 82.5% of all ionomer carbon is included in these two peaks. The estimated carbon in the ionomer was then subtracted from the total C surface atoms. Using a similar procedure for the O 1s high-resolution spectrum, the ionomer oxygen contribution was also subtracted from the total. The ratio of ionomer-free oxygen to ionomer-free carbon could then be estimated. Surprisingly, the ionomer-free O/C ratios were consistent with the total O/C ratios in Table II, remaining at 14% for the fresh MEA and 18% for the corroded BA cell cathode. These ratios will therefore be used as the representative carbon support surface changes for comparison with available literature in the discussion below.

## **Discussion and Modeling**

A number of factors contribute to the degradation and water transport behavior of the corroded cells considered in this study. Here three factors are explored: electrode collapse, heat generation, and wetting changes. Throughout, the fuel-cell model is used to support the discussion.

*Electrode collapse.—* To understand the impact of the potential hold on the performance, 1-D cell simulations of the BA and BC cells were performed. As mentioned above, most of the model parameters were taken from the experimental data/conditions or literature. To fit the initial BA and BC curves, the porosity of the GDL and MPL (for BC) was set to values of 0.77 and 0.32, respectively, and these values were held constant for all simulations. It was found that to fit the initial BA curve, a film resistance had to be added to decrease the limiting current, while the initial BC curve did not require this adjustment. This film resistance is probably due to accumulation of liquid water inside the catalyst layer or perhaps at the catalyst-layer\GDL interface.

To fit the curves after the cumulative 320 min potential hold, different cathode-catalyst-layer properties were changed. The measured change in ECSA was used to calculate the change in the specific interfacial area *a* (see equation A6). That calculation also required a change in cathode thickness. This value was estimated from a complementary potential-hold AST recently performed with identical materials in 50 cm<sup>2</sup> cells.<sup>21</sup> After seven hours at +1.3 V, 80°C, 100% RH, a 50 cm<sup>2</sup> PRIMEA 510.4 cathode using BC cell components decreased in thickness from 11.5  $\mu$ m to 3.5  $\mu$ m. The other parameters used to fit the data were the porosity of the cathode, the internal agglomerate mass-transport resistance, and the external film resistance (see equation 5). The values used to fit the parameters are given in Table III. As

Parameter	BC Initial	BC +320 min	BA Initial	BA +320 min
Porosity, ɛ []	0.6	0.03	0.6	0.03
Film resistance, $R_{O_2, film}$ [cm <sup>2</sup> s bar <sup>0.8</sup> mol <sup>-1</sup> ]	0	$1.3 \times 10^{-6}$	$3 \times 10^{-7}$	$2 \times 10^{-6}$
Specific reaction area, $a_{1,2}$ [cm <sup>-1</sup> ]	$1.5 \times 10^{5}$	$2.2 \times 10^{5}$	$1.5 \times 10^{5}$	$2.2 \times 10^{5}$
Cathode thickness, <i>l</i> [µm]	11.5	3.5	11.5	3.5
Aggregate resistance, $R_{\Omega_2}$ and $[\text{cm}^2 \text{ s bar}^{0.8} \text{ mol}^{-1}]$	1	$1 \times 10^{6}$	1	$1 \times 10^{6}$

Table III. Fit (italics) or taken from experiment or literature modeling parameter values for the cathode catalyst layer for initial and 320 minutes at 1.3 V) cells.

a point of reference, a film resistance of  $1 \times 10^{-7}$  cm<sup>2</sup> s bar<sup>0.8</sup> mol<sup>-1</sup> is equivalent to an ionomer film thickness of 16 nm of bulk Nafion and an agglomerate resistance of 1 cm<sup>2</sup> s bar<sup>0.8</sup> mol<sup>-1</sup> is equivalent to 100 nm agglomerates, although it is expected that for both cases the internal and external thin-film morphology of Nafion demonstrate higher transport resistances than the bulk membrane.<sup>56–59</sup>

To estimate the porosity change, the complementary experimental results are again used where after seven hours at +1.3 V, 80°C, 100% RH, the 50 cm<sup>2</sup> PRIMEA 510 cathode using BC cell components was found to have lost 5.8 mg of carbon as CO<sub>2</sub>.<sup>21</sup> This value can be used to estimate the final porosity by calculating the final solids volume from the initial electrode properties and the mass of carbon oxidized to CO<sub>2</sub>, m<sub>corr</sub>,

$$\epsilon = 1 - \left(V_{Total}^0(1-\epsilon^0) - m_{corr} \big/ \rho_C \right) \big/ V_{Total} \eqno(6)$$

where  $V_{Total}^0$  is the initial electrode volume and  $\rho_C$  is the representative carbon black density (~2.1 g cm<sup>-3</sup>). Normalizing by the cell geometric area, A, yields

$$\varepsilon = 1 - (l^0 (1 - \varepsilon^0) - m_{\text{corr}} / (\mathbf{A} \cdot \rho_{\text{C}})) / l$$
[7]

where  $l^0$  and l are the initial and final electrode thicknesses, respectively. Thus, assuming an initial porosity of 0.6, the final porosity is effectively zero. This analysis assumes that the oxidized carbon was the only change in the solids content of the electrode during the AST; any solid particles swept from the cathode layer as it degraded, or any compression of the polymer components, would result in a larger actual porosity. Even allowing for this uncertainty, the electrode at the end of the AST has been compressed such that the pore volume is a small fraction of its original value in a new electrode. The calculated porosity change is lower than that used for the modeling (see Table III) as lower values prevented the calculation from converging, although at such values one would expect the underlying physical changes as discussed below. Also, lower porosities are mathematically equivalent to higher agglomerate mass-transfer resistances due to the discrete nature of transport pathways at low porosities, which also partially explains the high agglomerate resistance values needed to fit the post-AST experimental data.

To understand the limiting issues caused by the AST, the simulation results from the initial to the final parameters set (see Table III) are plotted stepwise for the BC cell in Figure 11; it should be noted that the BA cell demonstrated similar agreement and contributions to the loss in performance for each parameter change. The first thing that is apparent is that the change in thickness (under constant porosity) and ECSA does not have a large impact on the performance, in agreement with the above experimental discussion. One reason is that the thinner electrode (with the same bulk properties) allows for good penetration of oxygen and proton transport within the cathode ionomer, and thus is not limiting. In addition, the specific interfacial area remains relatively high (see Table III). As the porosity is decreased, more severe mass-transport limitations occur, which are further exacerbated by increasing the mass-transfer resistance within the agglomerate. As noted above, these have similar effects of decreasing the oxygen penetration to the reaction sites while also enhancing some ionic resistance since the current-density distribution shifts toward the GDL (although this is a minor effect). As these parameters increase, what is physically occurring is that the cathode is collapsing and compacting. Thus, the cathode becomes more like a flooded electrode rather than a porous one. To fit the limiting current and shape of the final curve, an external film resistance is required. This resistance can be thought of as liquid buildup around the active sites or even increased ionomer coverage or a similar external mass-transfer limitation. In this light, the larger film thickness required to fit the BA cell could correspond to a more significant change in hydrophilicity of that sample or higher amount of electrode compaction and thus higher amounts of oxygen resistance getting to the active site. This may reflect the highly non-uniform electrode damage (concentrated at fiber contact points) previously observed by X-ray tomography for a corroded BA-style cell cathode.<sup>21</sup> Finally, as mentioned, the porosity and resistances have somewhat similar effects and thus there is an envelope of values that can fit the data and while the trends should remain the same; the specific values given in Table III should be understood in that context.

Despite the lower overall water content in the corroded cells at both constant current density (Figure 7) and at constant potential (Figure 10), it would take only a small amount of liquid to flood much of the pore space of the collapsed cathode and hence cause the increased film resistance discussed above. This observation helps reconcile the trends found in this study with previous assertions that corroded cells are more sensitive to flooding.<sup>12</sup> The cathode saturation in the tested cells may be high enough to contribute to the increased mass-transport resistance at the end of the AST (Figs. 3c and 3d) despite the lower total cell water retention. Such small volumes in the thin electrode will be very difficult to quantify using established methods of neutron imaging. However, efforts are currently underway to increase spatial resolution and to examine electrode water content directly.<sup>60</sup> An alternative method to examine whether corroded cells are more sensitive to water buildup is the careful study of performance as a function of inlet humidity,<sup>37</sup> as it has been suggested that electrode collapse should lead to greatly reduced performance at high RH.<sup>12</sup> Such techniques will also be useful for examining pore wetting in the earlier steps of the corrosion AST, where pore collapse is not yet as severe.



Figure 11. Experimental data (see Figure 2) and corresponding model fits for the initial and 320 min 1.3 V AST polarization curves for the BC cell. Model breakdown curves by parameter are also shown.



**Figure 12.** Simulated (a) absolute water content, (b) smoothed water content and (c) temperature distributions for the BC cell for initial cell at 0.67 V, 0.8 A cm<sup>-2</sup> and after 320 min at +1.3 V simulated both at 0.67 V and at 0.8 A cm<sup>-2</sup>. Common legend shown in (b).

Heat generation.— To further explore the link between cell performance degradation and water transport, the water-thickness profiles from the BC Cell model are shown in Figure 12a. Initial operation at 0.8 A cm<sup>-2</sup> and 0.67 V is compared to operation after corrosion, both at constant current density and at constant voltage. Comparison of the figure to the measured water profiles (Figure 7a) exhibit similar qualitative trends, especially after considering that the thinness of the membrane and related blurring affect the experimental data. Smoothed water profiles are shown in Figure 12b for easier comparison with experimental data; a Voigt distribution has been applied to the model profiles to simulate the blurring effects of real observation.<sup>38</sup> One sees that the trends are the same in that there is a valley near the MPL interface and upon close examination PCI flow results in a small increase of water content near the flowfield boundaries. It should be noted that the water buildup under the lands is not accounted for rigorously in the model since it is only 1-D, which is probably one of the main reasons that there is not strong quantitative agreement, as well as perhaps having slightly different residual saturations and capillary pressure - saturation relationships than those used in the model. However, the trend of decreasing water content at constant current density after corrosion is replicated by the model. In addition, a simulation at constant potential demonstrates that there is less liquid in the cathode side, consistent with the Ballard cell data since after



**Figure 13.** Experimental heat generation and total water content for the three cell configurations under imaging conditions throughout the corrosion ASTs. (a) BC and BA cell data at constant current density after successive potential holds; (b) Ballard cell data at constant potential after successive potential cycles.

corrosion the current density is much lower for a given potential. A simultaneous prediction for more water in the anode GDL following corrosion (due to the vanishing temperature gradient) is not borne out in the experimental data, but highlights the delicate combination of capillary transport and PCI flow in the model.

The cause of the lower water content at constant current density seems to stem from the higher heat generation and temperature gradients (Figure 12c). At 80°C, the change of a couple of degrees results in significantly more water being moved in the vapor rather than in the liquid phase due to PCI flow,<sup>22,23,28</sup> which also flattens the temperature gradients as well, since heat is also transported. In contrast, the temperature gradients largely disappear for the corroded cell at constant potential, due to the severely limited reaction rate.

The concept of the higher temperatures causing the lower water contents can also be analyzed by examining the total heat generated. The total heat generated within the cell can be calculated by<sup>61</sup>

$$Q = i \left( U_H - V \right) \tag{8}$$

where V is the (observed) cell potential and  $U_H$  is the enthalpy potential for the fuel-cell reaction,

$$U_H = \frac{\Delta H}{2F} = U_H^{\theta} - T \frac{\partial U_H^{\theta}}{\partial T}$$
[9]

where  $U_{\rm H}^{0}$  is the standard enthalpy potential (assuming liquid water as a product), 1.481 V at 25°C. Figure 13 compares the heat generation and total water content (including MEA and GDLs) for the three cells imaged between steps of their respective corrosion ASTs. The difference between a constant current density versus a constant potential condition is well illustrated by this data, in agreement with the simulation results in Figure 12. At constant current density, the BC and BA cells experience increased internal heat generation throughout the AST (Figure 13a). This led to larger thermal gradients within the cell, accelerating water mass transport and lowering the total water content despite the constant water generation rate. In contrast, the

Ballard cell was held at constant potential during image acquisition between AST cycles, resulting in lower heat and water generation as increasing resistances lowered the current density (Figure 13b). The total water content still dropped in the corroded cell, due to the slower water generation rate at lower current density. The initial increase in heat generation and water content is a result of the improvement in current density and overall performance after the first 50 cycles, likely related to enhanced hydration of the electrolyte, as indicated by the lower HFR (Figure 4b).

Wetting changes due to oxide formation.- XPS analysis (Table II) indicates that the oxygen content of the BA cell cathode surfaces increases from 5.2% to 5.9% total atomic fraction over the course of the AST, while the O/C ratio increases from 14% to 18%. An empirical relationship between water wicking and bulk oxygen and hydrogen contents has been fit by Studebaker and Snow for various carbon blacks,<sup>33</sup> but no similar relationship has been proposed for surface composition as measured by XPS. The available data for PEMFC electrodes is anecdotal. For a carbon-black electrode made with Vulcan XC-72/PTFE, a 120 h hold at +1.2 V in 1 M H<sub>2</sub>SO<sub>4</sub> resulted in a surface contact angle decrease from 147° to 111°, an increase in surface oxygen from 4.8% to 9.3%, and an O/C ratio increase from 7% to 13%.<sup>2</sup> For a Vulcan XC-72R/Nafion electrode, a more accelerated 24 hours of cycling between +0.6 V and +1.4 V resulted in a contact angle decrease from 156° to 102°, an increase of surface oxygen from 4% to 20%, and an O/C ratio increase from 7% to 44%.54

It has been found that surface composition from XPS alone cannot predict contact angle for different support materials, but it can serve as a qualitative indicator of surface degradation.<sup>54</sup> However, it is clear that the magnitude of oxygen increase in the corroded BA cell cathode is lower than that observed in the available literature. This is likely due to the corrosion-vulnerable carbon support and very short AST used in this study, which resulted in severe structural degradation before a more significant buildup of surface oxides could form. We can therefore put an upper bound on the magnitude of contact-angle change that resulted from such surface oxide changes; the external contact angle drop during the BA & BC cell AST should be much less than 36°.

If the small increase in wetting of the cathode carbon support plays a role in mass-transport resistance of the corroded cells, it is apparently a subtle one. This is consistent with the findings of Das et al. where ex situ accelerated aged carbons did not demonstrate significant contact angle or capillary changes as long as they were treated with PTFE.<sup>36</sup> Neutron imaging reveals little evidence of increased water content in any cell as the ASTs progress. The total liquid water retention at constant current density or constant potential is definitely less in a severely corroded cell, as explained above. Also, as noted, changing the wettability per se was not required to fit the experimental polarization curves, although one could link the increase in film resistance to higher flooding amounts. Early in the corrosion ASTs, the water content increases slightly in both the BC cell (Figure 13a) and Ballard cell (Figure 13b). Surface wetting changes may contribute to this increase, before the effects of electrode collapse become dominant later in the AST. However, any such effect cannot be separated from concurrent performance and heat transport changes. The impact of wetting changes in this early stage may be larger using lower gas stoichiometries than are required for these small imaging cells, and should be explored further with larger cell designs.

# Conclusions

Degradation mechanisms in a PEM fuel cell during carbon corrosion accelerated stress tests were examined by a variety of experimental methods as well as by 1-D simulation. Electrochemical performance during corrosion AST series showed a mixture of masstransport and kinetic losses. Omitting the microporous layer of the cathode GDL accelerated total performance loss, but slowed the masstransport resistance increase, suggesting that the MPL itself may have

degraded during the AST. Neutron imaging at constant current (constant water production rate) displayed a dramatic decrease in water retention following corrosion, demonstrating that mass-transport losses were not a result of increased water retention and should instead be attributed to pore structure collapse and compaction of the cathode catalyst layer. Mathematical modeling was consistent with this analysis where the catalyst layer becomes more of a flooded rather than porous electrode. The overall decrease in water holdup at constant current can be explained by greater heat generation in a less efficient cell and associated water transport along the larger temperature gradients. The observed decrease in water retention at constant voltage can be attributed to the decrease in current (water production) in aged cells. Comparing the cases with and without the cathode MPL, water profiles showed a higher water content in the MEA when no microporous layer was present on the cathode (both during fuel cell operation and during AST potential holds), confirming that faster corrosion of the catalyst layer should be expected in this case. Examination of a corroded cathode by XPS showed changes to surface functionality due to increased oxygen content, but no effects of carbon surface oxidation on water retention could be distinguished from the simultaneous heat and current effects. Work is still on-going to understand certain results such as the contribution of GDL/MPL degradation to performance decay<sup>62</sup> and the exact nature of the film resistance in the model after corrosion. Finally, future studies of water transport and cell aging will take advantage of strategies to quantify the water content in the electrode itself.60

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## Appendix

The 1-D model was derived from the work of Weber and coworkers.<sup>26,28,40–42</sup> For transport in the membrane, a concentrated-solution-theory approach is utilized where the governing equations for water and current density are

$$\mathbf{i}_2 = -\kappa \nabla \Phi_2 - \frac{\kappa \xi}{F} \nabla \mu_{\mathbf{w}}$$
 [A1]

and

$$\mathbf{N}_{\mathrm{w}} = -\frac{\kappa\xi}{F} \nabla \Phi_2 - \left(\alpha + \frac{\kappa\xi^2}{F^2}\right) \nabla \mu_{\mathrm{w}}$$
 [A2]

respectively, where  $N_w$  is the flux of water,  $\xi$  is the electroosmotic coefficient, F is Faraday's constant,  $i_2$  is the ionic current density,  $\kappa$  is the ionic conductivity,  $\Phi_2$  is the ionic potential,  $\alpha$  is the water transport coefficient, and  $\mu_{\text{w}}$  is the water chemical potential which can be obtained from the water activity and pressure. These equations are used both within the membrane and in the catalyst layers (with the requisite volume fraction).

As noted, for transport in the gas phase of the porous media, Stefan-Maxwell equations are used,

$$\nabla x_i = \sum_{j \neq i} \frac{y_i \mathbf{N}_j - y_j \mathbf{N}_i}{c_T D_{i,j}^{\text{eff}}}$$
[A3]

where  $y_i$  and  $N_i$  are the mole fraction and molar flux of species *i*, respectively,  $D_{i,i}^{\text{eff}}$  is the effective binary diffusion coefficient between species *i* and *j* and is given by equations 3 and 4 for GDLs and MPLs, respectively, and  $c_T$  is the total molar concentration of gaseous species as derived from the ideal-gas law. For the pressure drop in the gas phase, Darcy's law is used

$$\mathbf{v}_k = -\frac{k_k}{\mu_k} \nabla p_k \tag{A4}$$

where  $\mathbf{v}_k$ ,  $\mu_k$ ,  $k_k$ , and  $p_k$  are the mass-averaged velocity, viscosity, effective permeability, and pressure of phase k, respectively. Darcy's law is also used for transport in the liquid phase. Using Darcy's law necessitates a two-phase model to predict the effective permeabilities, and this is done using the contact-angle-distribution (CAD) approach of Weber.<sup>41</sup> The same CAD model is also used for calculating the liquid saturation, S, within the fuel-cell porous media, which is based on measured capillary-pressure curves for the SGL materials.<sup>36,41,63</sup>

The above transport equations require mass balances, which, for the steady-state simulations, are provided in the form

$$\nabla \cdot \mathbf{N}_{i,k} = -\sum_{h} a_{1,k} s_{i,k,h} \frac{i_{h,1-k}}{n_h F} + \sum_{g} s_{i,k,g} a_{g,k} R_{g,k}$$
[A5]

where the terms on the right side account for changes in the total amount of species *i* held in phase *k* within a differential control volume. The first term of the right corresponds to electron-transfer reactions, where  $s_{i,k,h}$  is the stoichiometric coefficient of species *i* residing in phase *k* and participating in electron-transfer reaction *h*,  $n_h$  is the number of electrons transferred in reaction *h*, and  $a_{1,k}$  is the specific interfacial reaction area, and can be determined by

$$a_{1,k} = \frac{m_{\rm Pt}A_{\rm Pt}}{l}$$
 [A6]

where *l* is the thickness of the catalyst layer and  $m_{Pt}$  and  $A_{pt}$  are the catalyst loading and surface area. The second term on the right of equation A5 is for interfacial reactions such as evaporation/condensation where  $R_g$  is the corresponding interfacial reaction rate.

As noted, Butler-Volmer kinetics are used for the hydrogen oxidation reaction and Tafel kinetics are used for the oxygen reduction reaction, with equation 5 showing the exchange current for the oxygen reduction reaction,

$$\nabla \cdot \mathbf{i}_1 = 4F p_{O_2,ext}^{0.8} \left( \frac{1}{\frac{1}{R_{O_2,film}} + \frac{1}{k_s E}} \right)$$

where  $k_s$  is given by

$$k_s = \frac{a_{1,2}i_{0_{\text{ORR}}}}{4Fc_{0_2}^{\text{ref}}} \exp\left(-\frac{\alpha_c F}{RT}(\eta_{\text{ORR},1-2})\right)$$
[A7]

where  $i_0$  is the exchange current density,  $\alpha_c$  is the charge transfer coefficient, and  $\eta$  is the reaction overpotential. The effectiveness factor, *E*, is given by

$$E = \frac{1}{\phi^2} \left(\phi \coth(\phi) - 1\right)$$
 [A8]

where  $\phi$  is the dimensionless Thiele modulus

$$\phi = r_{agg} \sqrt{\frac{k_s}{\psi_{O_2,agg}}} = \sqrt{k_s R_{O_2,agg}}$$
[A9]

where  $R_{O_2,agg}$  is the effective transport resistance of oxygen into the agglomerate and is used as a fitting parameter since the size and transport properties of agglomerates are unknown. It should be noted that although equation A8 is not rigorously valid for nonunity powers of oxygen partial pressure (equation 5), as shown in Yoon and Weber,<sup>40</sup> the error is minimal when equation A8 is used as long as the correct concentration dependence is used in the Thiele modulus (equation A9).

For transport of thermal energy, an energy balance is used<sup>26</sup>

$$\sum_{k} \rho_{k} \hat{C}_{p_{k}} \mathbf{v}_{k} \cdot \nabla T + \nabla \cdot \left(k_{T}^{\text{eff}} \nabla T\right) = \sum_{k} \frac{\mathbf{i}_{k} \cdot \mathbf{i}_{k}}{\kappa_{k}^{\text{eff}}} + \sum_{h} i_{h} \left(\eta_{h} + \Pi_{h}\right) - \sum_{g} \Delta H_{g} R_{g}$$
[A10]

where  $\Pi$  is the Peltier coefficient,  $\hat{C}_{\rho}$  is the heat capacity,  $H_g$  is the enthalpy of reaction (e.g., evaporation/condensation),  $k_T$  is the thermal conductivity, and  $\rho$  is the density. Finally, for electron transport in the solid, Ohm's law is used.

In terms of boundary conditions, the cell operating conditions are used as inputs along with an arbitrary zero potential at the anode and the cell potential or current density at the cathode. To ensure mass continuity, the species and temperature boundary conditions are of the Dankwertz-Wehner-Wilhelm type, which essentially involve coupled mass and energy balances at the gas channel to account for the flows in and out of the cell and 1-D model. For the cathode gas channel, these expressions are of the form

$$\begin{split} \mathbf{O}_{2} : \mathbf{y}_{O_{2}} &= 1 - \mathbf{y}_{H_{2}O} - \mathbf{y}_{N_{2}}; \quad \mathbf{N}_{O_{2}} &= \frac{0.21\lambda_{\mathrm{air}}I}{4F} + \mathbf{N}_{O_{2}}\big|_{\mathrm{GDL}} \\ \mathbf{N}_{2} : \mathbf{y}_{N_{2}} &= 0.79(1 - \mathbf{y}_{H_{2}O}); \quad \mathbf{N}_{N_{2}} &= \frac{0.79\lambda_{\mathrm{air}}I}{4F} \\ \mathbf{H}_{2}\mathbf{O}_{(G)} : \begin{cases} \mathbf{y}_{H_{2}O} &= \frac{p_{H_{2}O}}{p_{G}}; \quad \mathbf{N}_{H_{2}O,G} = (\mathbf{N}_{O_{2}} + \mathbf{N}_{N_{2}}) \frac{\mathbf{y}_{H_{2}O}}{1 - \mathbf{y}_{H_{2}O}} & \text{for } p_{L} \geq p_{G} \\ \mathbf{N}_{H_{2}O,G} &= \mathbf{N}_{H_{2}O,G}\big|_{\mathrm{GDL}} + \mathbf{N}_{H_{2}O,L}\big|_{\mathrm{GDL}} + \mathbf{y}_{H_{2}O}^{\mathrm{in}} \frac{\lambda_{\mathrm{air}}I}{4F} - \mathbf{N}_{\mathrm{H_{2}O}}^{\mathrm{cond}}; \\ \mathbf{y}_{H_{2}O} &= \frac{\mathbf{N}_{H_{2}O,G}}{\mathbf{N}_{O_{2}} + \mathbf{N}_{N_{2}} + \mathbf{N}_{H_{2}O,G}} & \text{for } p_{L} < p_{G} \end{split}$$

$$\mathbf{H}_{2}\mathbf{O}_{(\mathrm{L})}: \begin{cases} p_{\mathrm{L}} = p_{\mathrm{G}}; \quad \mathbf{N}_{\mathrm{H}_{2}\mathrm{O},\mathrm{L}} = \mathbf{N}_{\mathrm{H}_{2}\mathrm{O},\mathrm{L}} \big|_{\mathrm{cGDL}} + \mathbf{N}_{\mathrm{H}_{2}\mathrm{O}}^{\mathrm{cond}} & \text{for } p_{\mathrm{L}} \ge p_{\mathrm{G}} \\ \mathbf{N}_{\mathrm{H}_{2}\mathrm{O},\mathrm{L}} \big|_{\mathrm{GDL}} = 0; \quad \mathbf{N}_{\mathrm{H}_{2}\mathrm{O},\mathrm{L}} = \mathbf{N}_{\mathrm{H}_{2}\mathrm{O}}^{\mathrm{cond}} \middle| & \text{for } p_{\mathrm{L}} < p_{\mathrm{G}} \end{cases}$$

Heat flux : 
$$Q = -k^{\text{eff}} \Delta T |_{\text{GDL}} + \mathbf{N}_{\text{H}_2\text{O}}^{\text{cond}} \Delta H_{\text{vap}} + H_{\text{G}}^{\text{in}} \left( \frac{\lambda_{\text{ear}}}{4F} \frac{1}{1 - y_{\text{H}_2\text{O}}^{\text{in}}} \right)$$
  
- $H_{\text{G}} \left( \mathbf{N}_{\text{O}_2} + \mathbf{N}_{\text{N}_2} + \mathbf{N}_{\text{H}_2\text{O},\text{G}} \right) + H_{\text{G}} |_{\text{GDL}} \left( \mathbf{N}_{\text{H}_2\text{O},\text{G}} |_{\text{GDL}} + \mathbf{N}_{\text{O}_2} |_{\text{GDL}} \right)$   
- $H_{\text{L}} \left( \mathbf{N}_{\text{H}_2\text{O},\text{L}} - \mathbf{N}_{\text{H}_2\text{O},\text{L}} |_{\text{GDL}} \right) - h \left( T - T_{cool} \right)$ 

[A11]

where  $\lambda_{air}$  is the air stoichiometry, I is the total current density,  $N_i|_{cGDL}$  denotes the flux of species *i* coming from the 1-D simulation, y<sub>i</sub> is the gas-phase mole fraction of species *i*,  $\mathbf{N}_{H_2O}^{cond}$  is the mass of water that condenses in the gas channel,  $H_k$  is the molar enthalpy of phase k, which can be calculated from its composition and handbook values,  $^{64,65}$  the superscript "in" correspond to the inlet to the cell, h is the heat-transfer coefficient from the GDL interface to the cell hardware, and  $T_{cool}$  is the long-range hardware temperature which is assumed to remain at the inlet temperature (80°C, confirmed constant at thermocouple wells in the experimental case). Since it is a 1-D simulation, all concentrations were linearly averaged between their inlet and outlet values, although this is not shown in the above equations for brevity. The set of boundary conditions for the anode gas channel are essentially the same as equation A11, except that the directions of the fluxes from the anode GDL will have the opposite sign as those from the cathode, and, since pure hydrogen is used, there is no equation for the inert (i.e., no N2-type equations). The above boundary conditions are separated depending on whether the liquid pressure is above the gas pressure in order to ensure a smooth transition between cases of liquid movement out of the cell and those of subsaturation where there is no liquid movement out and where the relative humidity of the vapor could be below 100%.

Finally, the model was solved using the Intel Visual Fortran compiler.

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