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Carbon Corrosion in PEM Fuel Cells and the Development of Accelerated Stress Tests

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Carbon corrosion is an important degradation mechanism that can impair PEMFC performance through the destruction of catalyst connectivity, collapse of the electrode pore structure, loss of hydrophobic character, and an increase of the catalyst particle size. In this study, carbon corrosion was quantified in situ by measurement of carbon dioxide in the fuel cell exhaust gases through non-dispersive infrared spectroscopy during simulated drive cycle operations consisting of potential cycling with varying upper and lower potential limits. These studies were conducted for three different types of carbon supports. A reduction in the catalyst layer thickness was observed during a simulated drive cycle operation with a concomitant decrease in catalyst layer porosity, which led to performance losses due to increased mass transport limitations. The observed thickness reduction was primarily due to compaction of the catalyst layer, with the actual mass of carbon oxidation (loss) contributing only a small fraction (< 20%). The dynamics of carbon corrosion are presented along with a model that simulates the transient and dynamic corrosion rates observed in our experiments. Accelerated carbon corrosion stress tests are presented and their effects are compared to those observed for the drive cycle test.

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Proton exchange membrane fuel cells (PEMFCs) show great promise to increase fuel efficiency and decrease emissions for transportation applications. However, operational conditions (such as impurities in either the fuel or oxidant stream), cell environment, temperature (including sub-freezing exposure), pressure, current, voltage, etc.; or transient vs. continuous operation (including start-up and shut-down), represent some of the factors that can affect the useful life of PEMFCs.¹⁻³ To be competitive with present-day technologies, automotive PEMFCs must have durability comparable to current internal combustion engines. The fuel cell light duty automotive durability target (DOE) is set at 5,000 hrs for 2020, with an ultimate target of 8,000 hrs, equivalent to 150,000 miles of driving, with less than 10% loss in performance.⁴ The durability target must be met under operating and ambient conditions representative of automotive driving: dynamic load cycles, start-stop operation, road vibrations and shocks, and extreme weather ranging from hot and dry to sub-freezing.^{5,6}

Carbon-based materials are commonly used in PEMFC components including catalyst supports, granular microporous layers (MPLs), and the fibrous gas diffusion layers (GDLs). On the cathode side of a fuel cell, these carbon-based components are exposed to oxidizing conditions. The cathode electrocatalyst and catalyst layer are susceptible to degradation in this environment, causing performance degradation due to both losses in kinetics of the oxygen reduction reaction (ORR) and losses in oxygen mass transport. One of the major degradation mechanisms involving the electrocatalyst is corrosion (oxidation) of the carbon black used as the catalyst support during potential excursions generated by start-up/shutdown (SU/SD) cycling,⁷ where water is the primary oxidant in electrochemical carbon corrosion with CO₂ the ultimate product.⁸



$$E_0 = 0.207V_{RHE}$$

Oxidation of the carbon black support in the cathode can lead to performance loss due to loss of active catalyst surface area,⁹ decreased electrical connectivity of the catalyst support structure within the electrode,¹⁰ and an alteration of pore morphology and pore surface characteristics.¹¹ Although the kinetics of carbon oxidation are slow at typical PEMFC operating temperatures and potentials, the reaction is catalyzed by Pt and occurs more rapidly in the presence of water. Thus, carbon corrosion is a major concern for long-term durability of PEM fuel cells. Carbon corrosion can also be active during operation if there are localized regions that are temporarily starved of hydrogen, e.g., flooding of the anode catalyst. Reiser et al.⁷ are generally credited as being first to propose and explain the reverse current mechanism. Numerous follow-on publications^{10,12,13} expanded on this initial research to measure the actual current distributions, anode and cathode potential profiles, and local CO₂ emission rates. A large number of PEMFC studies combined external potential control with cell exhaust analysis to directly measure complete carbon oxidation (CO₂ production) under a range of operating conditions.¹⁴⁻¹⁹ Representative of this body of literature are the works by Shen et al.,²⁰ who used a reference electrode to measure the interfacial potentials, and Brightman and Hinds,²¹ who developed an innovative reference electrode array to characterize the transient profiles of cathode potentials. Kreitmeyer et al.²² constructed a cell with linear parallel channels and multiple gas extraction ports in the cathode flow field to characterize carbon corrosion by measuring the local CO₂ concentrations using a mass spectrometer. Ishigami et al.²³ used an oxygen-sensitive dye, porphyrin, to characterize the differences in carbon corrosion during SU/SD conditions by measuring the O₂ partial pressure in the anode of a cell with single-serpentine flow field. While carbon support corrosion is exacerbated during SU/SD and hydrogen starvation excursions, carbon is also thermodynamically unstable at room temperature and normal cathode potentials, with carbon corrosion being ubiquitous (albeit at lower rates) over the full potential range under which the cathode operates.²⁴⁻²⁶

Materials and engineering mitigation strategies are being investigated to extend the durability of carbon catalyst supports, especially during SU/SD;²⁷ primarily due to the high associated cost of the platinum catalysts supported on the carbon. The high corrosion rates of high surface area carbons, which have a high defect density and

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Table I. Pt electrocatalyst and carbon supports used in the cathode catalyst layer in MEAs.

Catalyst	Carbon support	Pt Wt%	Pt loading (mg/cm ²)	Pt surface area* (m ² /g _{Pt})	Catalyst (Pt/C) surface area* (m ² /g _{Pt})
TEC10E20E	High surface area (HSAC) 800 m ² /g	18.5	0.2	152.9	546.3
TEC10V20E	Vulcan (V) ≈ 250 m ² /g	19.6	0.2	137.6	167.9
TEC10EA20E	Graphitized (LSAC) ≈ 150 m ² /g	19.8	0.2	106.8	113.4
TEC10V40E	Vulcan (V)	39.3	0.2	97.8	121.6
TEC10EA40E	Graphitized (LSAC)	38.7	0.2	71.1	109.6

*Surface areas provided by supplier using CO adsorption on catalyst powders.

meso-graphitic structure, have led to exploring the use of highly graphitized carbons that exhibit significantly lower carbon corrosion characteristics. However, graphitized carbon particle surfaces are inherently hydrophobic and do not promote optimal platinum dispersions, resulting in lower platinum utilization that has hindered their widespread use.^{28,29} Additional mitigation strategies for carbon corrosion induced by start-up/shut-down processes include systems strategies such as voltage limitation as the key to maintaining the carbon support within the safe operating envelope during start-up and shutdowns, mitigating local and gross fuel starvation,³⁰ optimizing the opening size of the cathode outlet,³¹ using a stack shunt by optimizing the opening size of the cathode outlet,³² as well as mitigation of carbon corrosion in microporous layers through employing graphitized carbon material.³³

Several Accelerated Stress Tests (ASTs) for PEMFC components (e.g. electrocatalyst, catalyst support, membrane) have been developed by the U.S. Department of Energy (DOE), the U.S. DRIVE Fuel Cell Tech Team (FCTT), and the Japan Automobile Research Institute (JARI).³⁴ These ASTs help evaluate materials durability in short time periods and have been used extensively in this study. Primarily, two types of carbon corrosion ASTs that been recommended by the U.S. DRIVE FCTT; 1.2 V cathode potential hold (2007, see Table AI in Appendix)³⁴ and cycling from 1–1.5 V at 500 mV/sec (2013, see Table AII in Appendix)³⁵, have been used in this study.

The results presented here evaluate the oxidation behavior of three different types of carbon black supports under potential transients simulating a transportation drive cycle in a PEMFC environment. The carbon corrosion was quantified by monitoring the evolution of CO and CO₂ at the cathode cell outlet coupled with extensive post-mortem microscopy characterization of the cathode catalyst layer (CCL) structure. We distinguished the potential regimes relevant for carbon corrosion using non-dispersive infrared spectroscopy (NDIR). To complete the study, steady-state and transient mechanistic models were developed, using the rate constants extracted from the NDIR experiments, to simulate carbon corrosion under drive cycle conditions. Finally, the two different U.S. DRIVE recommended carbon corrosion ASTs were applied to membrane electrode assemblies (MEAs) incorporating the various carbon supports in the CCLs while monitoring the exhaust with NDIR for a quantitative comparison of their respective effects on the resulting catalyst layer structure.

Experimental

Custom MEAs using different cathode catalysts were fabricated by Ion Power (New Castle, DE). Each MEA incorporated a DuPont Nafion XL membrane, Nafion ionomer, SGL Sigracet GDLs (24BC,

25BC, 29BC), and carbon-supported Pt catalysts (Pt/C) from Tanaka Kikinzoku Kogyo K.K. (Kanagawa, Japan). Three different Pt/C cathode catalysts were evaluated in this study: Pt supported on high surface area carbon (HSAC or E-carbon), medium surface area carbon (Vulcan or V-carbon), or a highly graphitized carbon (LSAC or EA-carbon), the characteristics of which are summarized in Table I.

MEAs were tested in 50 cm² cell hardware with either quadruple (fuel cell drive cycle testing) or single serpentine (ASTs) flow fields, and conditions were controlled by a fuel cell test stand (Fuel Cell Technologies, Inc., Albuquerque, NM). Carbon corrosion testing was performed using the high relative humidity (RH) portion of the U.S. DRIVE FCTT drive cycle durability protocol (of Ref. 4). We refer to this as the wet drive cycle, which consists of current cycling from 0.02 A/cm² to 1.2 A/cm² for 30 s each at a cell temperature of 80°C with anode and cathode dew points at 83°C (see Table II). To evaluate the effect of operating potential on carbon corrosion, the wet drive cycle was modified to operate with potential control, with the upper and lower potential limits varied independently; e.g., upper potential limit varied from 0.95 to 0.60 V in increments of 0.05 V and lower potential limit varied from 0.40 V to 0.80 V in increments of 0.05 V, with potential hold times ranging from 0.5 min. to 5 min. CO₂ was measured at the cathode exhaust using an NDIR from California Analytical Instruments, Inc. The CO₂ present in air was removed by a lime bed to below detection levels prior to introduction into the fuel cell. Before analysis, the water was removed from the cathode exhaust gases using a condenser and an in-house Nafion membrane dryer.

Two types of carbon corrosion ASTs were conducted; the 2007 U.S. DRIVE FCTT employing a 1.2 V cathode potential hold³⁴ and the 2013 U.S. DRIVE FCTT,³⁵ which involved cycling from 1–1.5 V. The same NDIR method was applied during all ASTs, as described above.

Extensive in situ evaluations were acquired periodically during the wet drive cycle aging in air/oxygen/HelOx (HelOx = 21%-O₂/79%-Helium), including cyclic voltammetry, AC impedance, and polarization curves. Ex situ characterization included scanning electron microscopy (SEM), mercury intrusion porosimetry (MIP), and scanning transmission electron microscopy (STEM), were performed on MEAs at beginning of life (BOL) and at end of life (EOL). Electrochemical surface area (ECSA) and mass activity (MA) were measured using recommended protocols from the U.S. DRIVE FCTT.³⁴

Results and Discussion

Carbon corrosion during wet drive cycle testing.—Performance degradation was observed during the wet drive cycle durability

Table II. Wet Drive Cycle protocol.

Test Point #	Current Density [A/cm ²]	Anode Inlet H ₂ % inlet/dry	Anode H ₂ Stoich [-]	Anode Dew point Temp [°C]	Anode Inlet Temp [°C]	Anode Pressure outlet [kPa _{abs}]	Cathode Inlet O ₂ % inlet/dry	Cathode Inlet N ₂ % inlet/dry	Cathode O ₂ Stoich [-]	Cathode Dew point Temp [°C]	Cathode Inlet Temp [°C]	Cathode Pressure Outlet [kPa _{abs}]	Cell/ Stack control Temp [°C]	Test pt. Run Time [min]
Wet w/load cycling														
POT1	0.02	100%	96	83°	85°	101.3	21%	79%	108	83°	85°	101.3	80	0.5
POT2	1.2	100%	1.6	83°	85°	101.3	21%	79%	1.8	83°	85°	101.3	80	0.5

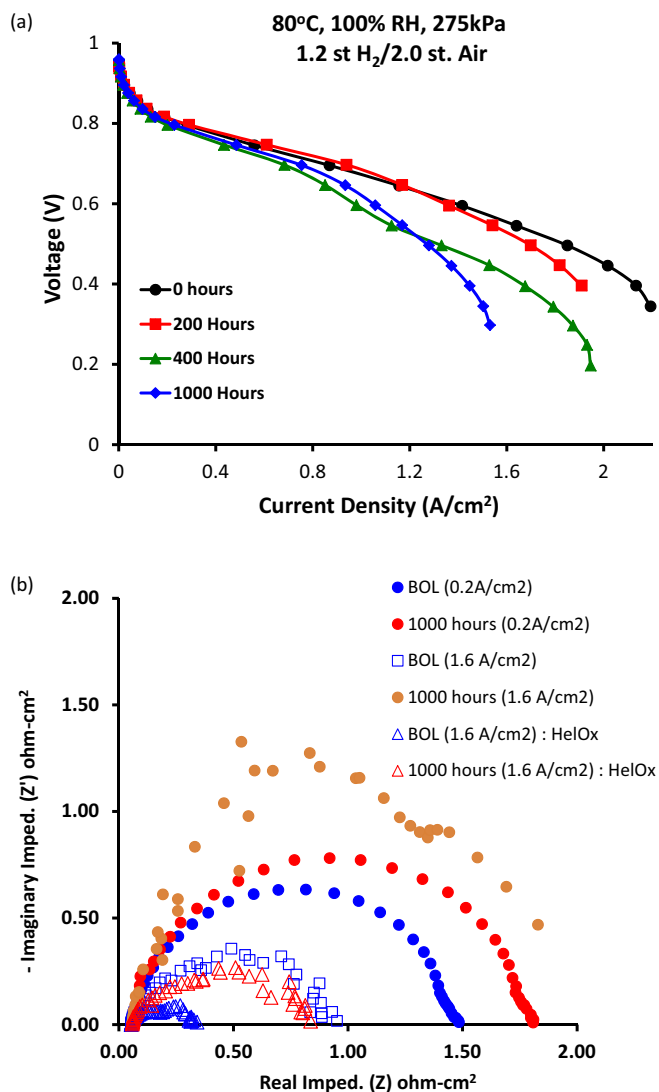


Figure 1. a) Polarization curves for MEAs with Pt/V cathode over 1000 hours of wet drive cycle test, b) Impedance at BOL and after 1000 hrs of wet drive cycle testing.

protocol conducted on V-carbon supported Pt CCL (TEC10V40E with Pt loading of $0.15 \text{ mg}_{\text{Pt}}/\text{cm}^2$) over 1000 hrs. The polarization curve results from Figure 1 show a small loss in the kinetic region ($< 0.2 \text{ A}/\text{cm}^2$) but a large decay in performance in the mass transport region ($> 0.8 \text{ A}/\text{cm}^2$). The voltage loss at $0.2 \text{ A}/\text{cm}^2$ is $\sim 25 \text{ mV}$ while the loss at $1 \text{ A}/\text{cm}^2$ is $\sim 80 \text{ mV}$ over the course of the 1000 hr test. Approximately 40% of the ECSA and 30% of the MA was lost over 1000 hrs of wet drive cycle operation. The small reduction in the kinetic performance is due to the lower ECSA and MA, but the large performance reduction at the higher current densities suggest that carbon corrosion is leading to additional mass transport losses by modifying the structure of the catalyst and CCL.

The impedance for the cell at BOL and EOL were measured in both H_2/air and H_2/HelOx . HelOx is used because the oxygen diffusion coefficient in helium is 4x that in nitrogen, thus it is easy to identify oxygen transport limitations by comparison. The impedance (Figure 1b) data at low current density shows an increase in kinetic resistance with cycling, with no difference observed between the resistance measured in air and HelOx (not shown). However, the data at high current density shows a significant difference between air and HelOx (60–65% decrease in resistance under HelOx compared to air) with a noticeable degradation (50–55% increase in resistance)

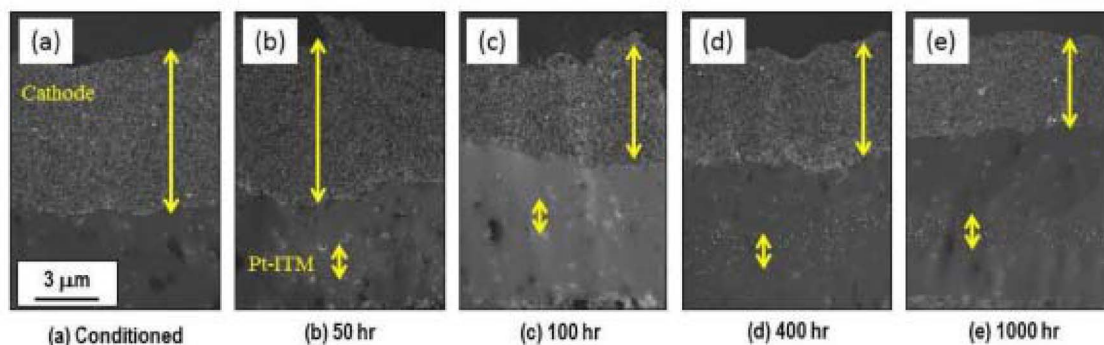
occurring during 1000 hrs of the wet drive cycle test. These results further confirm the increased mass transport losses observed in the polarization curves. Imaging of the MEA cross-sections at BOL and EOL revealed a reduction in the CCL thickness due to compaction that resulted from a loss of void volume or loss of carbon through oxidation, as illustrated by the series of high-angle annular dark field (HAADF)-STEM cross-section images shown in Figures 21a–21e). A sharp decrease in the CCL thickness was observed within the first 100 hr of operation (Figure 21c) 30% reduction). After 1000 hrs, a $\sim 50\%$ decrease in thickness was observed (Figure 21e). Binary images created from TEM images of the same series of CCLs (Figures 211a–211e) where black represents the carbon structure and white represents the porosity) revealed that the CCL porosity decreased from 44% (fresh – BOL, Figure 211a) to 22% (1000 hr – EOL, Figures 211e) over the 1000 hr wet drive cycle test. Mercury intrusion porosimetry (MIP) measurements verified the loss of porosity during the wet drive cycle test, which demonstrated that the changes in the CCL porosity occurred under normal fuel cell operating conditions.

NDIR measurements of the CO_2 in the exhaust gas for the modified drive cycle test were acquired, with the upper and lower cell potential limits varied for MEAs prepared using the three different types of carbon in the CCL. A series of carbon oxidation spikes during potential cycling were observed (Figures 3a–3b for Pt/V in CCL) when varying the upper cell potential from 0.95 V to 0.60 V (0.95, 0.90, 0.85, 0.80, 0.75, 0.70, 0.65, 0.6 V all stepped to 0.40 V) with a constant lower cell potential of 0.40 V. Sharp spikes in the amount of CO_2 evolved due to carbon oxidation were observed during a step increase in the cell potential, where the magnitude of the spikes decreased as the upper cell potential was reduced from 0.95 V to 0.60 V. The carbon corrosion rate at the upper cell potential (0.95 V) decreased with the holding time at potential, indicating the formation of passivating oxides; this is indicated by the lower CO_2 evolution during a 5 min. hold (Figure 3b). The passivating layer was subsequently reduced at the lower potential. Note that a non-zero corrosion rate was observed at all potentials, including cell potential (0.4 V), with the spikes in carbon oxidation observed during the steps in potential.

When the lower potential limits were varied (0.40, 0.45, 0.50, 0.55, 0.60 V) and the upper potential was held constant (0.95 V), the magnitude of the carbon oxidation spikes decreased as the lower cell potential was raised from 0.4 V to 0.6 V. This reduction in the rate of carbon corrosion as the gap between upper and lower potential is reduced suggests that the corrosion rate strongly depends on the amplitude of the square wave potential cycle, and not on the actual potential limits. Both Pt/HSAC and Pt/LSAC showed qualitatively similar trends as those found for Pt/V; e.g., for potentials 0.9 V and lower, the magnitude of the carbon oxidation spikes upon a step change in potential was higher for Pt/HSAC than for Pt/V, although the trends were similar. The carbon corrosion rate for graphitized carbon (Pt/LSAC) showed that for potential cycles to 0.8 V and higher (with fixed 0.4 V lower potential), the corrosion rates are lower for Pt/LSAC than for the two other carbons (Pt/HSAC and Pt/V). For potential cycles below 0.8 V, the magnitude of the carbon oxidation spikes for Pt/LSAC upon a step change in potential was similar to Pt/V. Similar trends were observed for tests where the lower potential limit was varied and the upper potential limit was kept constant. Thus, when the magnitude of the potential cycle was maximum, Pt/LSAC showed the lowest amount of corrosion, whereas the Pt/V and Pt/HSAC exhibited similar corrosion rates. When the magnitude of the potential cycle was minimal, the difference between the types or carbon in the corrosion rate was minimal. These results are summarized in Figures 4, where each data point was generated by integrating five consecutive CO_2 peaks measured at the various voltage levels for each of the types of carbon tested.

When the CCL thickness loss was calculated from the measured carbon oxidation (Figures 3 and 4), e.g., CO_2 evolution, and compared to the actual CCL thicknesses measured from the HAADF-STEM images (Figure 21), it was apparent that most of the CCL thickness loss was not directly due to carbon oxidation/corrosion. This was also supported by the fact that high-resolution TEM imaging showed

I.



II.

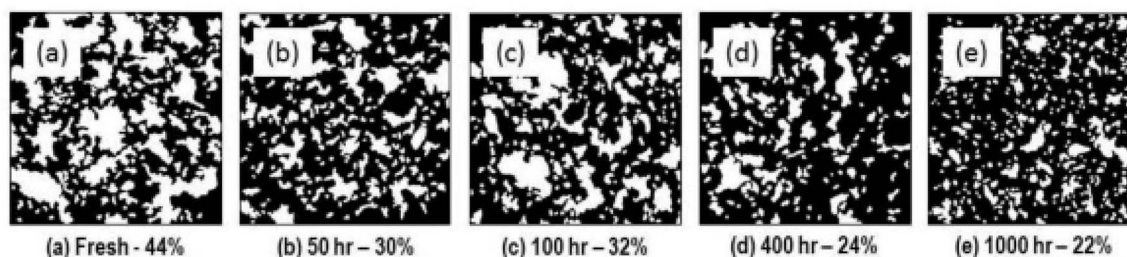


Figure 2. I. Series of cross-section HAADF-STEM images of the Pt/V CCLs (thickness shown by yellow arrows) and II. Binary TEM images (black represents carbon structure and white represents porosity) of the CCLs: (a) after conditioning (BOL), (b) after 50 hrs (c) after 100 hrs (d) after 400 hrs and (e) after 1000 hrs of testing using the wet drive cycle protocol.

little change in the atomic structure of the carbon after testing; e.g., a majority of the Vulcan carbon black particles retained the original meso-graphitic structure. Since a $\sim 50\%$ reduction in the CCL thickness was observed, and the CO_2 evolution measured for the Pt/V indicated a loss of only $\sim 10\%$ of the original amount of carbon, it is clear that simple carbon oxidation did not contribute much to the measured CCL thickness reduction. This was especially evident at the early stage (100 hrs) of the wet drive cycle test, where less than 5% of the thickness reduction could be accounted for by carbon oxidation. These analyses indicated that while carbon corrosion does occur, the reduction in cathode CCL was due to causes other than a simple reduction in the amount of carbon present due to corrosion. It should be noted that these results are probably independent of the catalyst used and more indicative of the catalyst layer manufacturing method.

Modeling of carbon corrosion in PEMFCs during drive cycles.—

To understand the mechanism of carbon corrosion, the carbon corrosion was measured with potentiodynamic experiments for all three types of carbon under the following conditions: 80°C , 100% RH, H_2/N_2 , 5 mV/s scan. To illustrate typical observed oxidation patterns, the potentiodynamic corrosion rates for the three different carbon supports used in the CCLs are shown in Figure 5. Several features for the Pt/HSAC are labeled: we used the peak labeling convention of Maass et al.¹⁹ to describe such plots.

One important feature to note in Figure 5 is the observation of CO_2 peaks in both the anodic (peak IV) and cathodic (peak III) scans. While peak IV is associated with the electrochemical oxidation of carbon by water, peak III corresponds to the oxidation of carbon via spillover oxygen from the reduction of Pt oxides below 0.9 V. CO_2 released

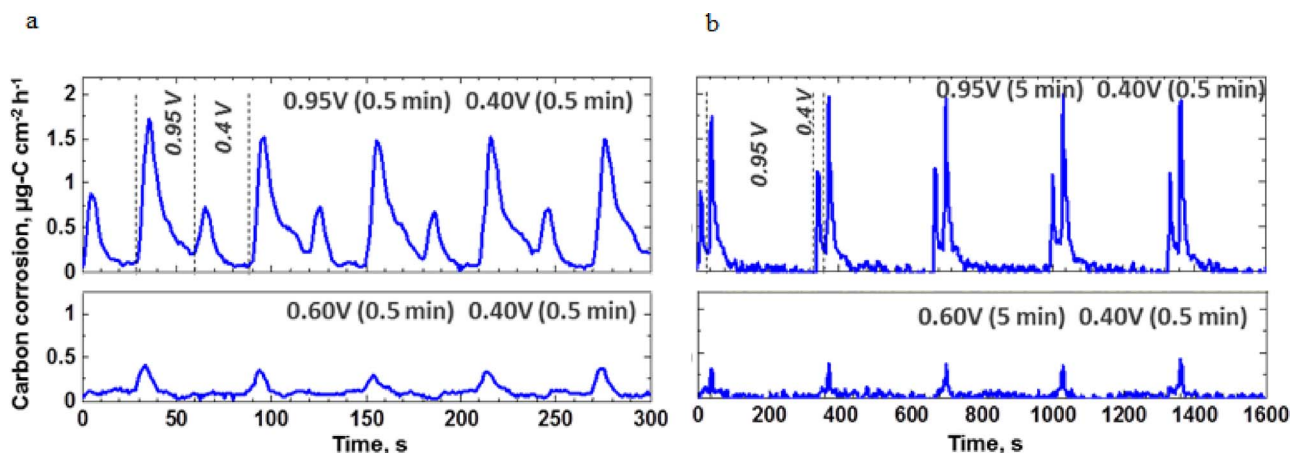


Figure 3. Carbon dioxide emissions from the fuel cell cathode with Pt/V during potential cycling operation varying the upper potential limit (0.95 V and 0.60 V (0.90, 0.85, 0.80, 0.75, 0.70, 0.65 V – not shown)) and constant lower potential of 0.4 V. Figure 3a has 0.5 min. hold times at both upper and lower potential, while Figure 3b has 5 min. hold times at the upper potential limit, and 0.5 min. hold at the lower potential limit. Similar trends for the three types of carbon types were observed, with the trend in corrosion following HSAC > V > LSAC.

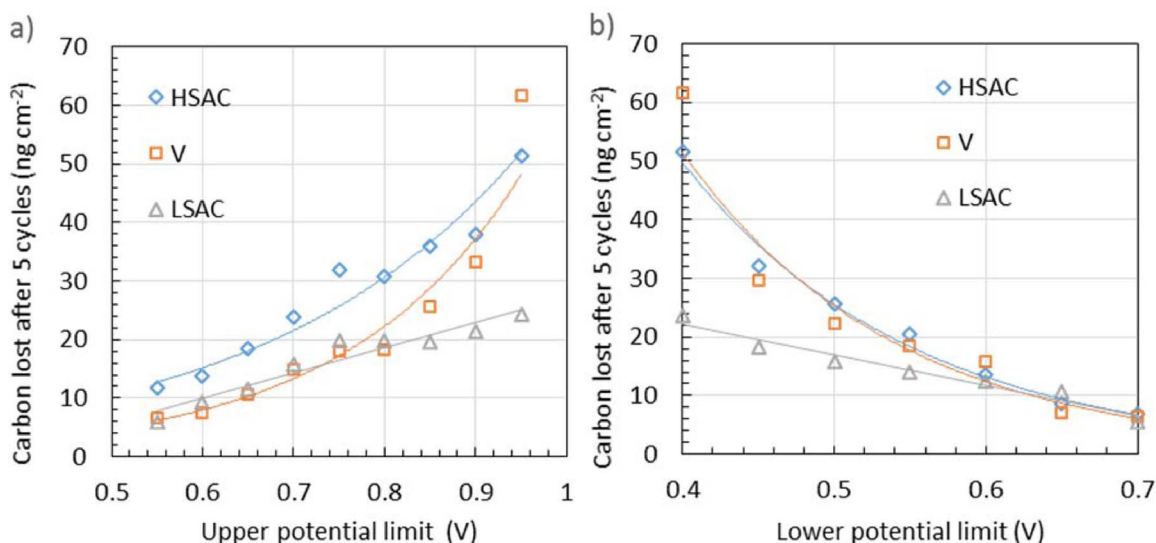


Figure 4. Carbon corrosion during 5 cycles as function of a) high cell potential and carbon type: low cell potential: 0.4 V (0.5 min.); high cell potential: 0.55–0.95 V (5 min.); b) low cell potential and carbon type: low cell potential: 0.40–0.7 V (0.5 min.); high cell potential: 0.95 V (5 min.).

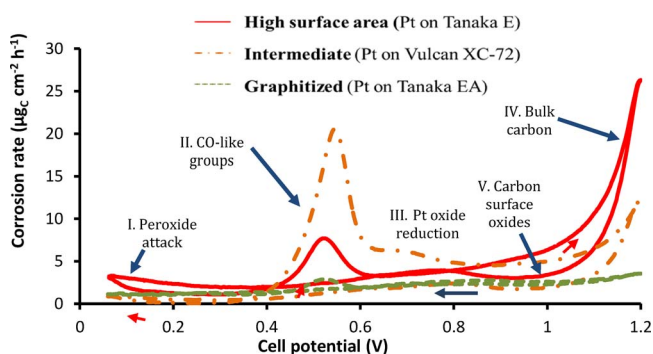


Figure 5. CO₂ evolution from three different types of carbon used in the CCLs (HSAC, V, and LSAC) during potentiodynamic sweeps under N₂. The various corrosion steps are labeled according to the model proposed by Maass et al.¹⁹

at high potentials is generally faster in the presence of Pt,^{25,36,37} and this is thought to be due to the catalyzing role of Pt and/or Pt surface oxides on carbon corrosion. Peak V, which appears as a shoulder to peak IV, corresponds to the oxidation of carbon surface oxides. These three peaks were considered explicitly in the model developed for the

dynamic oxidation of carbon. Peaks I and II, corresponding to the chemical oxidation of carbon by hydrogen peroxide and the oxidation of CO species associated with Pt, respectively, were not considered in the model since their effect on carbon corrosion under fuel cell conditions is negligible.

Figure 5 shows the durability advantage of using a graphitized carbon support (LSAC) vs. Vulcan and HSAC, where the corrosion rates over all potential ranges are reduced, most crucially in the exponential region (peak IV). The penalties for using a graphitized support arise from the increased material's cost (from the additional high temperature treatments required) and a lower initial performance due to the lower Pt ECSA inherent on LSAC.

Figure 6 illustrates the corresponding changes in the cyclic voltammograms for the three different types of carbon used showing various levels of carbon corrosion due to high potential cycling. The quinone redox peak at ~0.6 V can be associated with changes in the carbon surface structures during the carbon corrosion test (exposure to 1.4 V and voltage cycling). The loss of Pt ECSA as a result of carbon corrosion is evidenced by the decrease in hydrogen adsorption/desorption peaks (shown by the arrow at 0.15 V). As expected, the most visible change was observed for Pt/HSAC, where the quinone redox peak dramatically increased (arrow at ~0.55 V) as the structure of the HSAC changed; little Pt active surface area can be measured after a loss of 54% of the carbon. The primary change in the Pt/V and Pt/LSAC

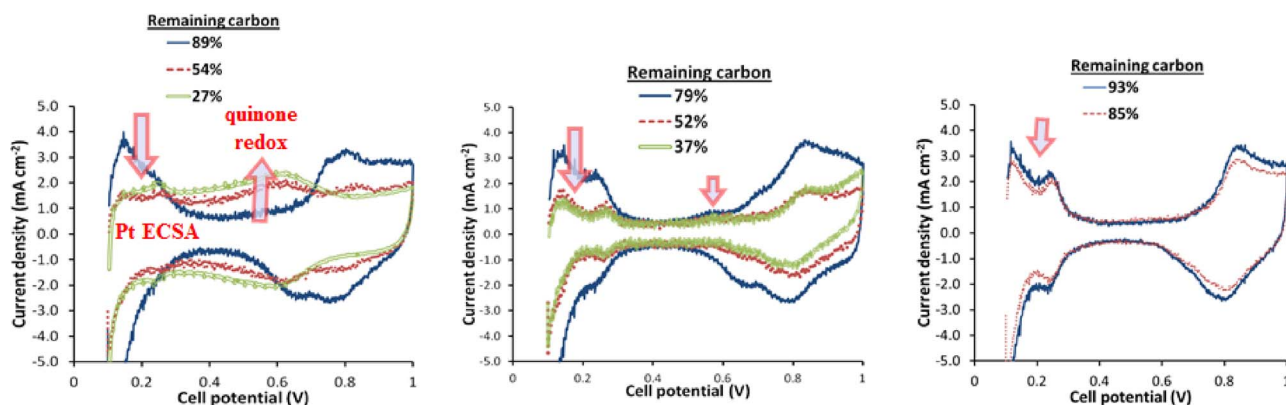


Figure 6. Cyclic voltammograms of MEAs prepared using three different types of carbon in the CCL as a function of carbon corrosion. Quinone redox peak changes in Pt/HSAC MEA as carbon oxidizes.

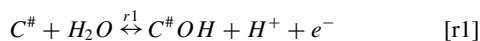
MEAs was due to a loss of Pt ECSA; the Pt/V showed a large loss of ECSA as the carbon was oxidized, whereas minimal Pt ECSA loss was observed for Pt/LSAC since the carbon was more stable (minimal carbon oxidation).

Dynamic model for corrosion of carbon at potentials below 0.95 V.—Measured carbon corrosion rates during square-wave cycles demonstrate extreme sensitivity to electrode history with peaks (i.e., multiple reaction steps during corrosion) that strongly depend on the amplitude of applied potentials. NDIR CO₂ emissions indicate that the steady-state corrosion rate is highest at 0.5–0.6 V intermediate potential, suggesting that surface oxides formed at higher potentials are protective. While the mechanism of electrochemical carbon oxidation remains poorly understood in the literature, the general steps involve a) formation of carbon oxide groups that are prone to irreversible oxidation, and b) electrochemical oxidation of these groups with oxygenated species formed on Pt nanoparticles.^{14,19,38,39}

We have formulated a simple carbon corrosion model to quantitatively capture the essential features of the CO₂ emission data. While the model is illustrated below for HSAC-type support carbon, it has been applied to V and LSAC carbon types with different choice of parameters.

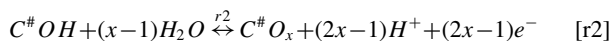
Carbon surface reactions.—Following previous work in the literature,^{40–42} CO₂ evolution involves the formation of unstable carbon surface oxides that are subsequently oxidized in the presence of oxygenated species on Pt. The carbon surface oxide groups may include species such as phenols, ethers, ketones, and carboxylic acids, but are lumped into two groups as follows.

- a) We consider that the carbon support initially contains certain amount of disorder domains and structural surface defect sites, denoted as C[#]. At high enough potentials, E > 0.3 V, these sites are hydrolyzed forming unstable carbon surface oxides (C[#]OH).



$$r_1 = k_{1,f}\theta_v e^{\left(\frac{-\omega_1}{RT}\theta_u\right)} e^{\left(\frac{\beta_{1,a}F}{RT}\eta_1\right)} - k_{1,b}\theta_u e^{\left(\frac{\omega_1}{RT}\theta_u\right)} e^{\left(\frac{-\beta_{1,c}F}{RT}\eta_1\right)} \quad [2]$$

- b) The measured steady-state corrosion rates show a peak at 0.6 V and decrease at higher potentials, suggesting the formation of passive surface oxides on carbon. We assume that the unstable carbon oxides are displaced by the passive carbon oxides (C[#]O_x) that form at higher potentials, E > 0.6 V.

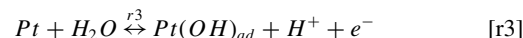


$$r_2 = k_{2,f}\theta_u e^{\left(\frac{-\omega_2}{RT}\theta_p\right)} e^{\left(\frac{\beta_{2,a}F}{RT}\eta_2\right)} - k_{2,b}\theta_p e^{\left(\frac{\omega_2}{RT}\theta_p\right)} e^{\left(\frac{-\beta_{2,c}F}{RT}\eta_2\right)} \quad [3]$$

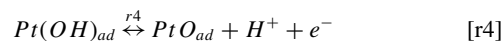
Here, θ_v denotes the fraction of defect carbon sites, θ_u and θ_p are the fractions of unstable and passive carbon surface oxides, ω is a surface interaction parameter specific to the adsorbed species, β is the product of charge transfer coefficient and number of electrons for the respective reaction, and η denotes the over-potential.

Platinum oxide formation.—Literature studies using X-ray photoelectron spectroscopy combined with electrochemical cell experiments have identified different types of adsorbed species as a function of electrochemical potential.^{43–45} At potentials below 0.6 V, H₂O_(ad) appears to be the dominant surface species. Above 0.6 V, hydroxyl groups, OH_(ad), begin to appear from the oxidation of H₂O_(ad). At even higher potentials OH_(ad) oxidizes to O_(ad), which becomes the dominant surface species at potentials above 0.9 V. On the basis of this literature data, we represented the fractional coverage of OH and O

by the reactions r3 and r4 below.



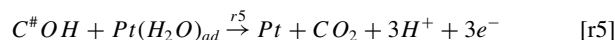
$$r_3 = k_{3,f}\theta_{Pt} e^{\left(\frac{-\omega_3}{RT}\theta_{OH}\right)} e^{\left(\frac{\beta_{3,a}F}{RT}\eta_3\right)} - k_{3,b}\theta_{OH} e^{\left(\frac{\omega_3}{RT}\theta_{OH}\right)} e^{\left(\frac{-\beta_{3,c}F}{RT}\eta_3\right)} \quad [4]$$



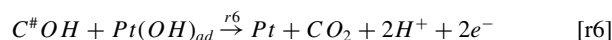
$$r_4 = k_{4,f}\theta_{OH} e^{\left(\frac{\beta_{4,a}F}{RT}\eta_4\right)} - k_{4,b}\theta_{O} e^{\left(\frac{\omega_4}{RT}\theta_O\right)} e^{\left(\frac{-\beta_{4,c}F}{RT}\eta_4\right)} \quad [5]$$

Here, θ_{Pt} denotes the fraction of free platinum site, and θ_{OH} , and θ_O is the fraction of hydroxyl and oxide species on platinum. The remaining symbols have their usual meaning as defined previously. The potential dependence of the oxide formation was determined by fitting the OH_(ad) and O_(ad) coverage from experimental data in the literature.⁴⁵

Carbon corrosion.—Oxidation of unstable carbon species by adsorbed water or hydroxyl groups on Pt are considered as the main CO₂ formation reactions.



$$r_5 = k_5\theta_u e^{\left(\frac{\omega_5}{RT}\theta_u\right)} e^{\left(\frac{\beta_{5,a}F}{RT}\eta_5\right)} \quad [6]$$



$$r_6 = k_6\theta_u\theta_{OH} e^{\left(\frac{\omega_6}{RT}\theta_{OH}\right)} e^{\left(\frac{\beta_{6,a}F}{RT}\eta_6\right)} \quad [7]$$

Adsorption of water on Pt is highly potential dependent and exhibits different states: strongly adsorbed at low potentials and weakly adsorbed at higher potentials.^{43–45} Since an explicit reaction for adsorbed water, Pt(H₂O)_{ad}, was not included in the model, the reactivity of the unstable carbon surface species with water on Pt is coverage dependent through the interaction with unstable carbon oxides. Carbon corrosion rates were tuned using data for both steady-state and transient potential cycles.

All carbon corrosion data were measured in hydrogen/air with 0.4 V as the lowest cell potential. The iR-drop in the electrolyte phase cannot be neglected as the current density can exceed 1.2 A/cm². The over-potential of the cathode electrode, η , was estimated from polarization curves measured at cell potentials between 0.95–0.4 V and corrected via the following expression.

$$\eta = E + iR - E_0 \quad [8]$$

Here i is the current density, R is the combined membrane and contact resistance as measured by impedance spectroscopy, and E_0 is the equilibrium potential for the respective reaction.

Site balances.—Having defined the reaction rates, the following are the site balance equations for carbon and Pt in terms of $N_{C^{\#}}$ and N_{Pt} , the number of carbon defect sites and Pt sites. All model parameters are given in Table III for HSAC-type carbon.

Carbon sites.—

$$N_{C^{\#}} \frac{d\theta_u}{dt} = r_1 - r_2 - r_5 - r_6 \quad [9]$$

$$N_{C^{\#}} \frac{d\theta_p}{dt} = r_2 \quad [10]$$

Table III. Model parameters for HSAC-type carbon corrosion.

Parameter	Symbol	Value	Unit
Equilibrium potential, r_1	E_{01}	0.5	V
Equilibrium potential, r_2	E_{02}	0.55	V
Equilibrium potential, r_3	E_{03}	0.72	V
Equilibrium potential, r_4	E_{04}	0.85	V
Equilibrium potential, r_5	E_{05}	0.6	V
Equilibrium potential, r_6	E_{06}	0.7	V
Reaction rate, r_1	$k_{1,f}/k_{1,b}$	2.8×10^{-7}	$\text{mol cm}^{-2} \text{s}^{-1}$
Reaction rate, r_2	$k_{2,f}/k_{2,b}$	$5.2 \times 10^{-6}/1.05 \times 10^{-5}$	$\text{mol cm}^{-2} \text{s}^{-1}$
Reaction rate, r_3	$k_{3,f}/k_{3,b}$	$2.59 \times 10^{-9}/8.4 \times 10^{-10}$	$\text{mol cm}^{-2} \text{s}^{-1}$
Reaction rate, r_4	$k_{4,f}/k_{4,b}$	$2.59 \times 10^{-9}/8.4 \times 10^{-10}$	$\text{mol cm}^{-2} \text{s}^{-1}$
Reaction rate, r_5	k_5	2.3×10^{-11}	$\text{mol cm}^{-2} \text{s}^{-1}$
Reaction rate, r_6	k_6	3.5×10^{-11}	$\text{mol cm}^{-2} \text{s}^{-1}$
Platinum sites	N_{Pt}	5.96×10^{-7}	mol cm^{-2}
Carbon defect sites	$N_{\text{C}}^{\#}$	3×10^{-5}	mol cm^{-2}
Water vapor pressure at 80°C	P_w	0.468	atm
Area specific resistance	R	72.4	$\text{m}\Omega \text{cm}^{-2}$
Tafel coefficient, r_1	$\beta_{1,a}/\beta_{1,c}$	0.5/0.5	
Tafel coefficient, r_2	$\beta_{2,a}/\beta_{2,c}$	0.05/0.95	
Tafel coefficient, r_3	$\beta_{3,a}/\beta_{3,c}$	0.6/0.5	
Tafel coefficient, r_4	$\beta_{4,a}/\beta_{4,c}$	0.5/0.5	
Tafel coefficient, r_5	$\beta_{5,a}/\beta_{5,c}$	0.17	
Tafel coefficient, r_6	$\beta_{5,a}/\beta_{5,c}$	0.05	
Interaction parameter, r_1	ω_1	-0.68	$\text{kJ mol}^{-1} \text{K}^{-1}$
Interaction parameter, r_2	ω_2	-2.93	$\text{kJ mol}^{-1} \text{K}^{-1}$
Interaction parameter, r_3	ω_3/ω_{3c}	-36.5/1.7	$\text{kJ mol}^{-1} \text{K}^{-1}$
Interaction parameter, r_4	ω_4	14.6	$\text{kJ mol}^{-1} \text{K}^{-1}$
Interaction parameter, r_4	ω_5	-4.7	$\text{kJ mol}^{-1} \text{K}^{-1}$
Interaction parameter, r_4	ω_6	-1.46	$\text{kJ mol}^{-1} \text{K}^{-1}$

$$\theta_v = 1 - \theta_u - \theta_p \quad [11]$$

Pt sites.—

$$N_{\text{Pt}} \frac{d\theta_{OH}}{dt} = r_3 - r_4 - r_5 - r_6 \quad [12]$$

$$N_{\text{Pt}} \frac{d\theta_O}{dt} = r_4 \quad [13]$$

$$\theta_{\text{Pt}} = 1 - \theta_{OH} - \theta_O \quad [14]$$

Model comparison with HSAC potential cycling data.—Steady-state corrosion rates were determined from NDIR data for CO₂ emission with 5 min hold at potentials and used to establish the potential dependence of the active and passive carbon oxide species. Figure 7 shows the extracted steady-state corrosion rates of HSAC carbon and the model results for a) corrosion rates, b) carbon oxide surface coverages, and c) hydroxyl coverage on Pt compared with literature data.⁴⁵ The peak in carbon corrosion rate at ~0.6 V nearly coincides with the modeled coverage of the active carbon oxides species that peaks at ~0.55 V; at higher potentials, C[#]OH converts to C[#]O_x and the coverage of the active carbon oxides decreases. In our model, the steady-state corrosion rate is primarily due to active carbon oxides reacting with water on Pt rather than with the hydroxyl groups, since Pt(OH) only forms at potentials above 0.6 V.

As seen in Figure 8, the transient corrosion rates can be much higher under cyclic potentials. The model features are corroborated by data, showing visible spikes in the corrosion rate as the cell potential is stepped up to 0.95–0.68 V or is stepped down to 0.5 V. The magnitude of spikes decreases as the high cell potential is reduced from 0.95 V to 0.68 V. The corrosion rate also decreases in time as the cell is held at high cell potential.

Figure 9a shows the transient corrosion rates and the corresponding surface coverages of the active carbon species and hydroxyl groups on Pt for the runs in which the potential varies from 0.95 V to 0.5 V. The spike in carbon corrosion after a step increase in potential is mainly associated with the direct oxidation of C[#]OH to CO₂ through

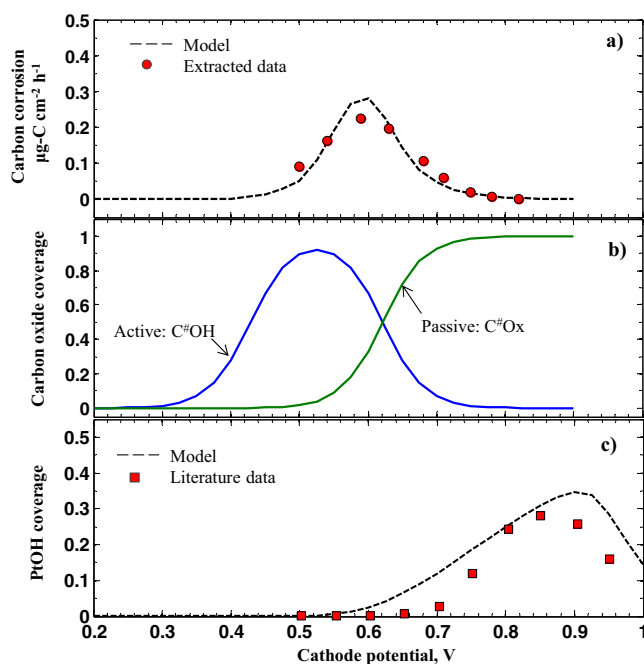


Figure 7. Steady-state corrosion model for 5-min potential holds, where a) the carbon corrosion rate is shown to peak at 0.6 V; b) the active and passive carbon oxide coverages depend on the potential; c) PtOH coverage peaks around 0.9 V based on the model and literature data.⁴⁰

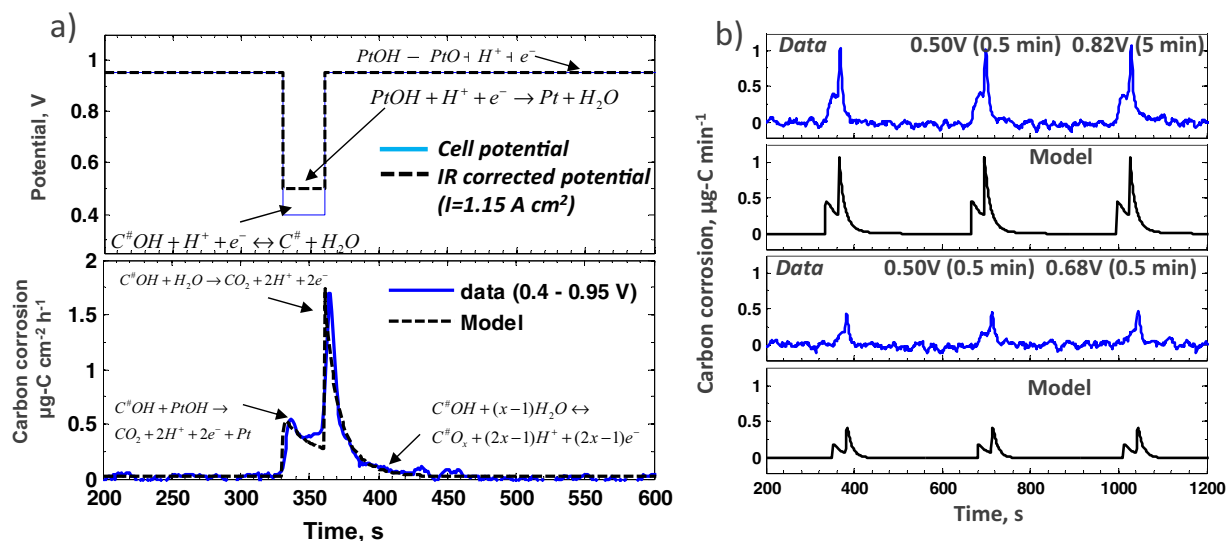


Figure 8. a) Detailed description of transient response of carbon corrosion over time when the iR corrected potential is changed from 0.95 V to 0.5 V and back (IR corrected voltages); and b) potential is changed from 0.82 V and 0.68 V to 0.5 V and back.

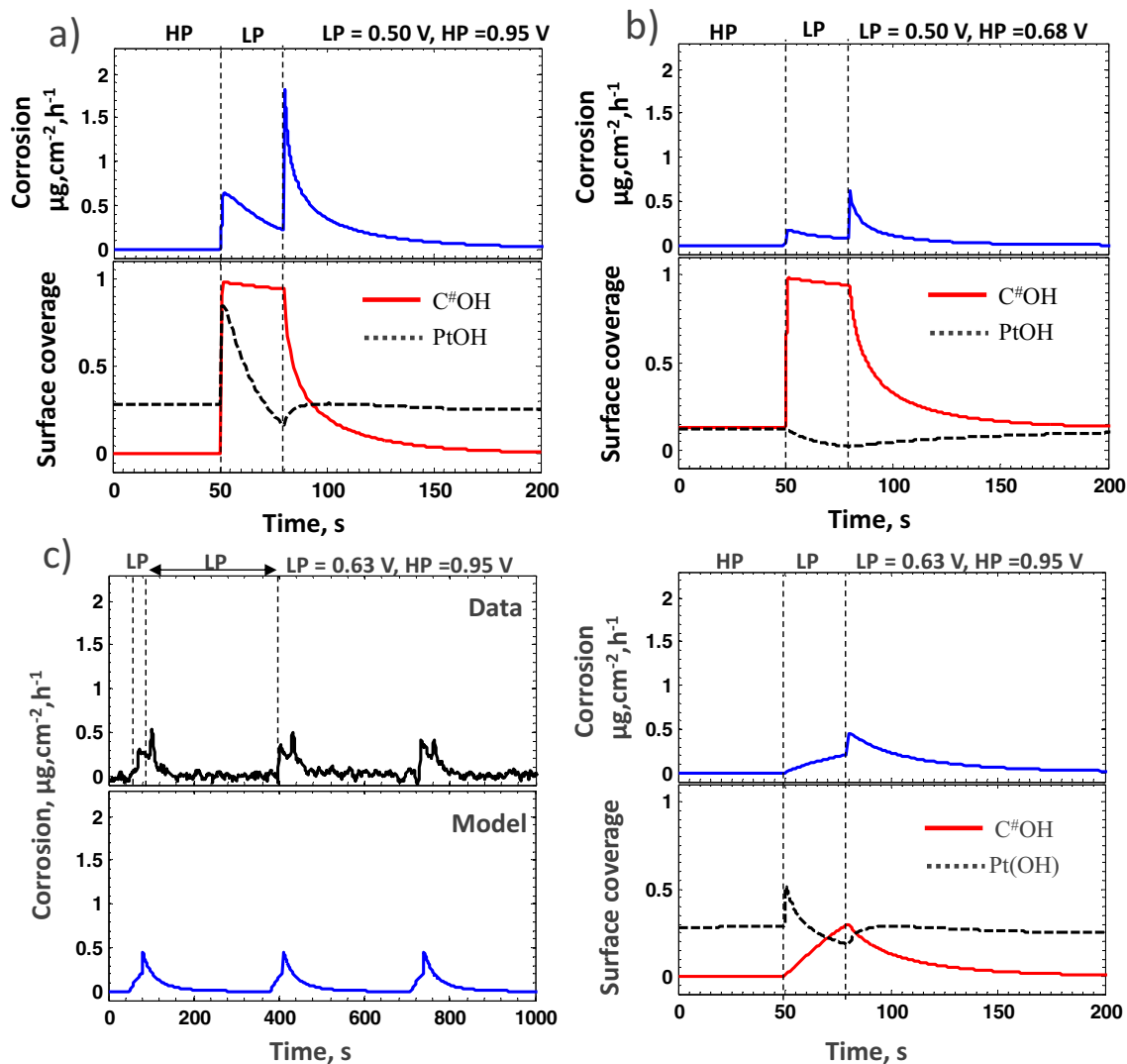


Figure 9. Transient corrosion during a square wave potential cycle and the corresponding surface coverage of unstable carbon species and hydroxyl groups on Pt. a) Low potential = 0.5 V, high potential = 0.95 V. b) Low potential = 0.5 V, high potential = 0.68 V. c) Low potential = 0.63 V, high potential = 0.95 V (Pt/HSAC).

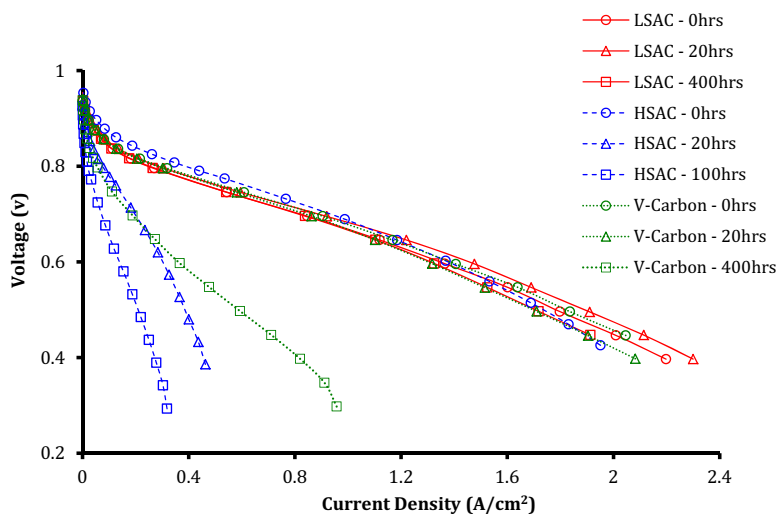


Figure 10. Polarization curves of Pt/C catalysts using three different types of carbon supports (HSAC or E-carbon, Vulcan or V-carbon, LSAC or EA-carbon) before (0 hr - BOL) and after (EOL) carbon corrosion AST (1.2 V potential hold).

its reaction with H_2O . Holding the cell at a high potential leads to the displacement of $\text{C}^\# \text{OH}$ by $\text{C}^\# \text{O}_x$, and the corrosion rate decreases as $\text{C}^\# \text{O}_x$ passivates the carbon surface. Also, at high cell potentials, Pt sites begin to convert to PtOH, and at still higher potentials, PtOH converts to PtO. A step decrease in potential results in the sites occupied by passive $\text{C}^\# \text{O}_x$ being vacated. The vacated sites are available to be occupied by active $\text{C}^\# \text{OH}$ which reacts with the OH-like species that accumulates on Pt surface to produce a spike in carbon corrosion. With time, PtOH gradually reduces to Pt, and the carbon corrosion rate decreases to a lower, non-zero value.

Figure 9b shows the transient data for the runs in which the potential varies from 0.68 V to 0.5 V. The changes in coverage of the active carbon oxides are similar to those in Fig. 9a. The final states of the carbon oxide species do not change when the high potential varies from 0.68 V to 0.95 V. However, since PtOH barely starts to form on the surface of Pt at a potential of 0.68 V, the magnitude of spikes following a step increase or decrease in potential is predominately due to the active carbon oxides reacting with adsorbed water on Pt. As the upper potential increases, the magnitude of the corrosion spikes increases due to a larger contribution of $\text{C}^\# \text{OH}$ reacting with PtOH.

Fixing the higher potential at 0.95 V while raising the lower potential results in the active carbon oxides being displaced by the passive carbon oxides. Figure 9c shows the corresponding transient data when the potential varies from 0.63 V to 0.95 V. In contrast to the case when the lower potential is fixed at 0.5 V, the initial coverage of active carbon species as the lower potential increases is significantly reduced. This lowers the magnitude of the corrosion spikes upon a step increase in the potential to 0.95 V.

In summary, the highest corrosion rates are observed if the potential is cycled between OCV and a low potential where the surface coverage of active surface oxides is maximized. Cycling at cell potentials above 0.6 V reduces the carbon corrosion rate primarily due to the formation of passive carbon oxide species.

While this model can be utilized to quantify corrosion rates under drive cycle operation, corrosion under SU/SD conditions, where potentials exceed 1.2 V, are also of interest. In the next section, we compare the corrosion rates of the three carbon supports at high potentials using carbon corrosion ASTs (protocols used are described in Experimental section).

U.S. DRIVE carbon corrosion ast (2010): 1.2 V hold.—To rapidly evaluate the three carbon supports incorporated in MEA CCLs, we employed the AST with a potential hold of the cathode at 1.2 V.³⁴ The performance of the three different MEAs based on Pt/HSAC, Pt/V, and Pt/LSAC are summarized in Figure 10. The CCLs in the MEAs had

nominal cathode Pt loadings of 0.15 mg-Pt/cm² (Pt/HSAC), 0.17 mg-Pt/cm² (Pt/V), and 0.25 mg-Pt/cm² (Pt/LSAC). Figure 10 also illustrates the performance of these three MEAs after various time periods during the 1.2 V hold AST.

The initial (BOL) performance of all three MEAs on a per Pt basis varied as HSAC > V > LSAC in the CCL, and their degradation rates were distinctly different. After only 20 hrs of the AST, the Pt/HSAC showed significant loss in performance, the Pt/V exhibited a slight loss in performance, and the Pt/LSAC showed a slight improvement in performance. The Pt/LSAC-based MEA showed little performance degradation after 400 hrs of the 1.2 V hold carbon corrosion AST, with a total loss of less than 40 mV at 1.5 A/cm². The Pt/V-based MEA showed little degradation after 20 hrs at 1.2 V, but performance degraded severely after 400 hrs, which was still not as severe as the performance loss of Pt/HSAC after just 20 hrs. The U.S. DOE target of 30 mV loss at 1.5 A/cm² was exceeded after 4 hrs, 32.5 hrs, and 240 hrs for the Pt/HSAC, Pt/V, and Pt/LSAC, respectively.

The ECSA and MA obtained before and after the 1.2 V hold AST are summarized in Figure 11. The performance characteristics of the three different types of carbons tested were significantly different, with the Pt/HSAC having the highest initial ECSA (74 m²/gm-Pt) and

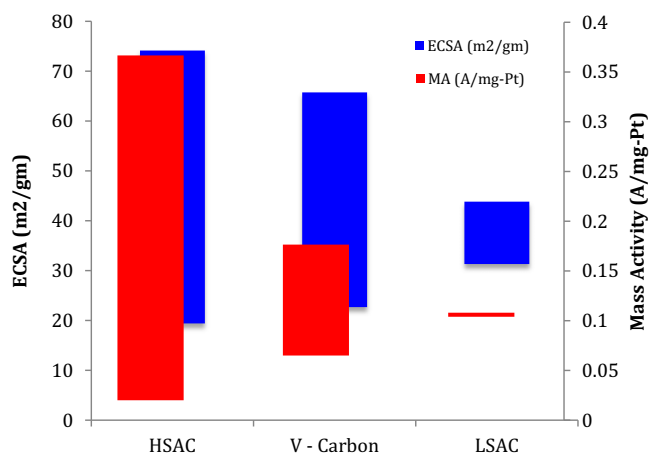


Figure 11. Performance characteristics (ECSA and MA) of the three different catalysts (Pt/HSAC, Pt/V, Pt/LSAC) obtained before (BOL) and after the high potential hold (1.2 V) AST.

Table IV. CCL thicknesses and Pt particle sizes for three different types of carbon support used in MEA cathodes before and after 1.2 V potential hold AST.

	BOL thickness (μm)	EOL thickness (μm)	BOL particle size (nm)	EOL particle size (nm)*
HSAC	25	7	2.94	3.68
V-type	10	4	3.04	8.47
LSAC	14	12	3.87	6.28

*after 100 hrs for HSAC, but 400 hrs for V-type and LSAC.

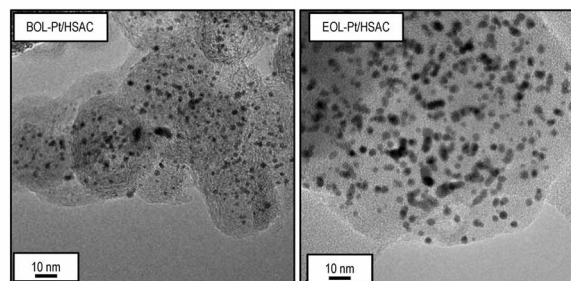
MA (0.37 A/mg-Pt) and the Pt/LSAC having the lowest initial ECSA (44 $\text{m}^2/\text{gm-Pt}$) and MA (0.1 A/mg-Pt). However, the degradation rates of these three carbons were directly linked to, and ultimately depended on, the degree of graphitization within the initial carbon black particles, with the LSAC (highest graphitic content) showing the most resistance to corrosion and the HSAC (lowest graphitic content) showing the lowest oxidation resistance. As a result, after the 400 hr hold at 1.2 V (only 100 hrs for the Pt/HSAC), the Pt/LSAC exhibited the best performance characteristics (final ECSA = 31 $\text{m}^2/\text{gm-Pt}$ and MA = 0.1 A/mg-Pt) and the Pt/HSAC exhibited the worst performance (final ECSA = 19 $\text{m}^2/\text{gm-Pt}$ and MA = 0.02 A/mg-Pt). In summary, the Pt/HSAC showed the expected high initial performance and MA; however, due to the lack of graphitic structure, HSAC also demonstrated the most degradation.

The impedance comparison (not shown) of the Pt/HSAC and Pt/LSAC CCLs confirmed that after the 1.2 V hold AST, the Pt/HSAC showed increased transport resistance even at low current densities (0.02 A/cm²); the increase in transport resistance at high current densities (1.0 A/cm²) was extremely high, after only a 20 hr hold at 1.2 V. There was no increase in mass transport of the Pt/LSAC CCL, even after the 400 hr hold at 1.2 V.

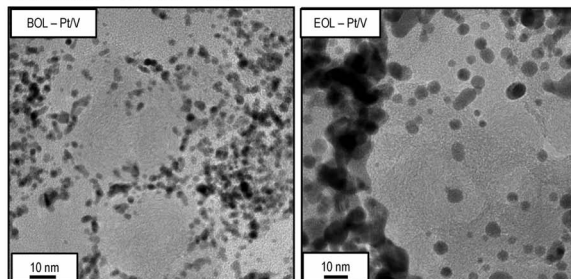
The Pt particle sizes and CCL thicknesses of the three different MEAs (Pt/HSAC, Pt/V, Pt/LSAC) before and after the high potential hold AST are summarized in Table IV. The Pt/HSAC and Pt/V underwent significant corrosion and lost $\geq 60\%$ of their electrode thickness (for 100 and 400 hr holds at 1.2 V, respectively), in contrast to the Pt/LSAC CCL, which exhibited little corrosion (less than 15% thickness loss).

HAADF-STEM images of the CCLs, before and after the high potential hold AST are shown in Figure 12. The Pt/LSAC CCL retained its structure during the 400 hr hold at 1.2 V, while the Pt/HSAC and Pt/V electrodes exhibited not only thickness changes, but also significant densification and loss of porosity, due in part to localized carbon amorphization and sintering. It is interesting to note that the Pt/LSAC-based CCL showed significant Pt particle growth due to Pt particle coalescence and sintering, which was due to the poor initial Pt particle dispersion and extensive agglomeration of the Pt particles

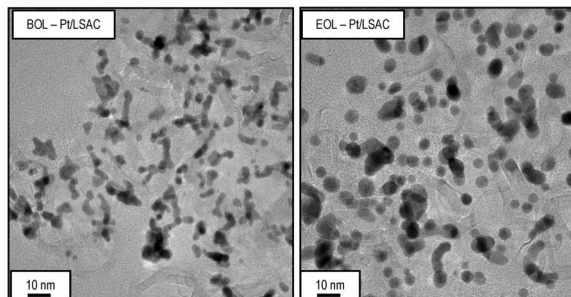
a) Pt/HSAC: 1.2 V hold – 100 hrs



b) Pt/V Carbon: 1.2 V hold – 400 hrs

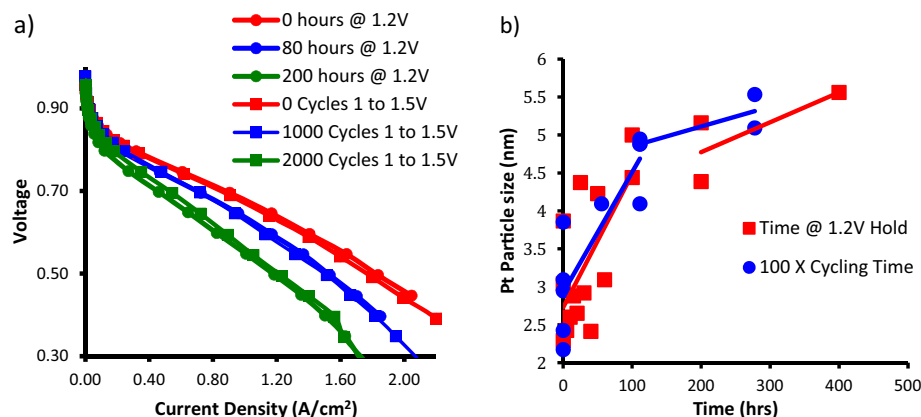


c) Pt/LSAC: 1.2 V hold – 400 hrs

**Figure 12.** Pt particle agglomeration due to carbon corrosion in a) Pt/HSAC, b) Pt/V, and c) Pt/LSAC.

on LSAC (little Ostwald ripening is expected under constant potential conditions).²⁹

U.S. DRIVE carbon corrosion AST (2013): 1.0 to 1.5 V cycling AST.—While carbon corrosion at a constant potential can be lowered due to passivation, maximum corrosion occurs during potentiodynamic conditions. The U.S. DRIVE FCTT replaced the 1.2 V hold AST with a 1.0–1.5 V cycling AST. This section compares these two ASTs for the three types of carbon incorporated in the CCL. A comparison of the 1.2 V hold AST and the 1.0–1.5 V cycling AST is shown in Figure 13a for an MEA with the Pt/V CCL. After 80 hrs at 1.2 V,

**Figure 13.** a) Polarization curves showing similar degradation in the 1.0–1.5 V cycling and 1.2 V hold ASTs (results shown are for Pt/V-carbon); b) Pt particle size growth after new 1.0–1.5 V cycling (blue) and 1.2 V hold (red) ASTs.

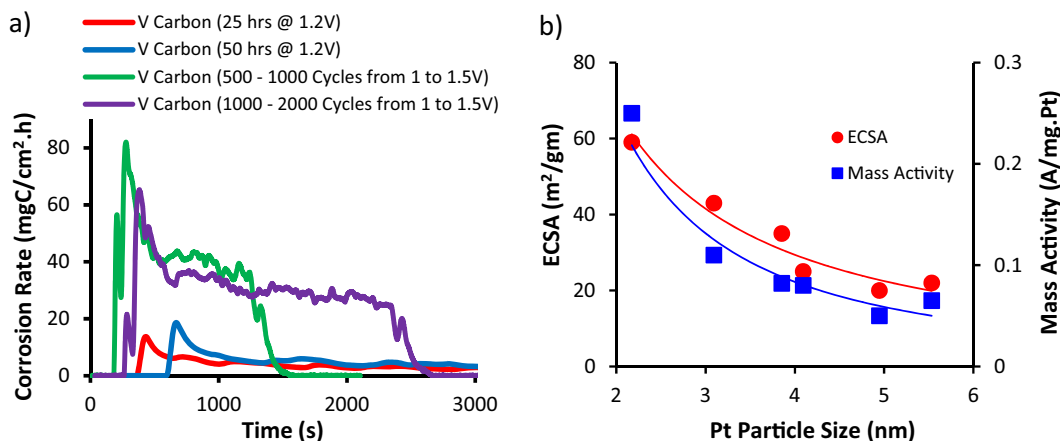


Figure 14. a. NDIR data for Pt/V over time during 1.0–1.5 V cycling and 1.2 V hold ASTs; b) ECSA and MA for Pt/V over time during new 1.0–1.5 V cycling AST; similar trend observed for Pt/HSAC (E-carbon) and Pt/LSAC (EA-carbon).

the MEA exhibited a similar level of catalyst support degradation as observed after 1000 cycles from 1.0–1.5 V. Similarly, 200 hrs at 1.2 V corresponded to the same level of degradation achieved after 2000 cycles from 1.0–1.5 V. The cycling AST exhibited an $\approx 150\times$ faster decay in fuel cell performance over the constant potential hold AST, which was also the case for the other types of carbon (Pt/HSAC and Pt/LSAC, not shown).

Figure 13b shows a comparison of the Pt particle size growth experienced during both ASTs (the 1.0–1.5 V cycling and the 1.2 V hold), where a faster decay rate was initially observed that tapered with more cycles as more carbon oxidized; the Pt particle size stabilized at ~ 5 nm. The 2013 AST (1.0–1.5 V) was faster by 100x while retaining the same degradation mechanism, as suggested by a similar trend in the Pt particle growth, and should also correspond to a worst-case scenario of unmitigated start/stops.

A comparison of the amount of oxidized carbon measured by NDIR during both ASTs is shown in Figure 14a; there was approximately an order of magnitude greater carbon corrosion rate during the 2013 AST (1.0–1.5 V cycles) compared with the 2007 AST (1.2 V hold). This increased carbon corrosion rate correlated to a decrease in the CCL thickness and increase in the CCL compaction (loss of porosity) associated with increased mass transport resistance. Figure 14b shows the decline in ECSA and MA over time for Pt/V during the 1.0–1.5 V cycling AST. A similar trend was observed for Pt/HSAC (E-carbon) and Pt/LSAC (EA-carbon).

Conclusions

Corrosion of the carbon used as the Pt electrocatalyst support leads to undesired changes in the CCL structure. We measured and quantified carbon oxidation/corrosion during wet drive cycle operation and as a variation of the upper and lower potential limits used in the wet drive cycle. Carbon corrosion is observed during normal operating cycle potentials, although significantly less than the carbon corrosion induced by start/stop cycles. During drive cycle operation, the CCL thickness is reduced, which is not due solely to carbon corrosion, although carbon corrosion plays a role. We conclude that much of this reduction in CCL thickness must be from compaction of the material in the catalyst layer, which leads to loss of catalyst layer porosity and increased performance losses due to mass transport limitations. The amount of carbon corrosion is exacerbated by the voltage cycling inherent in the drive cycle compared with constant potential operation. The potential gap between upper and lower potentials appears to be more important than the absolute operating potentials in the normal operating potential regime (0.40 V to 0.95 V).

Formation of surface oxides on carbon defect sites ($C^\#$) is related to the fact that the defect sites hydrolyze to form active oxides ($C^\#OH$) at cathode potentials (E) > 0.3 V. $C^\#OH$ converts to passive oxides ($C^\#O_x$) at $E > 0.6$ V. Carbon corrosion is catalyzed by PtOH, which begins to form at $E > 0.6$ V. PtOH converts to PtO at $E > 0.9$ V. Steady-state carbon corrosion showed that the corrosion rate peaks at ~ 0.6 V cathode potential, and was smaller at 0.95 V due to passivation. We find that spikes in corrosion rates while transitioning from high (0.95 V) to low cell potentials (0.4 V) are due to formation of $C^\#OH$ and its reaction with PtOH. Larger spikes in the carbon corrosion rates were observed while transitioning from low (0.4 V) to high cell potentials (0.95 V) and were due to accelerated oxidation of $C^\#OH$ by H_2O at elevated potentials. In general, the difference in transient corrosion rates for the three tested types of carbon was HSAC $\sim V \gg LSAC$.

Similar behavior to the drive cycle was observed during AST conditions at 1.2 V, where Pt/HSAC exhibited the best initial performance, but also showed the fastest degradation rate. Highly graphitized Pt/LSAC, on the other hand, had the lowest initial performance but also exhibited the lowest degradation rate. TEM analysis of the MEAs after corrosion testing indicated Pt particle size growth in all the CCLs in addition to significant a thickness reduction of the Pt/HSAC CCL. While Pt growth due to particle coalescence led to performance losses up to 40 mV, the greatest performance loss (up to 360 mV) was associated with mass transport losses resulting from compaction of the CCL and porosity reduction, primarily associated with the formation and sintering/densification of the oxidized carbon. The U.S. DRIVE FCTT AST that applied potential cycling between 1.0–1.5 V was evaluated and had an excellent ability to distinguish performance and durability between the different carbon supports. The cycling AST had a 10x faster carbon corrosion rate compared to the previous high potential hold (1.2 V) AST, and the ECSA, MA, and performance decays were also enhanced ~ 100 – $150\times$ for the new AST.

Acknowledgments

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Appendix

Table AI. Catalyst Support Cycle and Metrics Table Revised March 2, 2010.³⁴

Cycle	Hold at 1.2 V for 24 h; run polarization curve and ECSA; repeat for total of 400 h. Single cell 25–50 cm ²	
Total time	Continuous operation for 400 h	
Diagnostic frequency	24 h	
Temperature	80°C	
Relative Humidity	Anode/Cathode 100/100%	
Fuel/Oxidant	Hydrogen/Nitrogen	
Pressure	150 kPa	
Metric	Frequency	Target
Catalytic Activity*	Every 24 h	≤40% loss of initial catalytic activity
Polarization curve from 0 to > 1.5 A/cm ² **	Every 24 h	≤30 mV loss at 1.5 A/cm ² or rated power
ECSA/Cyclic Voltammetry***	Every 24 h	≤40% loss of initial area

*Mass activity in A/mg @ 150 kPa abs backpressure at 857 mV iR-corrected on 6% H₂ (bal N₂)/O₂{or equivalent thermodynamic potential}, 100% RH, 80°C normalized to initial mass of catalyst and measured before and after test.

**Polarization curve per Fuel Cell Tech Team Polarization Protocol in Tables V.

***Sweep from 0.05 to 0.6 V at 20 mV/s, 80°C, 100% RH.

Table AII. Catalyst Support Cycle and Metrics Table Revised January 14, 2013.³⁵

Cycle	Triangle sweep cycle: 500 mV/s between 1.0 V and 1.5 V; run polarization curve and ECSA; repeat for total of 400 h. Single cell 25–50 cm ²	
Number	5000 cycles	
Cycle time	2 s	
Temperature	80°C	
Relative Humidity	Anode/Cathode 100/100%	
Fuel/Oxidant	Hydrogen/Nitrogen	
Pressure	Atmospheric	
Metric	Frequency	Target
Catalytic Activity*	At beginning and end of test, minimum	≤40% loss of initial catalytic activity
Polarization curve from 0 to > 1.5 A/cm ² **	After 0, 10, 100, 200, 500, 1 k, 2 k, and 5 k cycles	≤30 mV loss at 1.5 A/cm ² or rated power
ECSA/Cyclic Voltammetry***	After 0, 10, 100, 200, 500, 1 k, 2 k, and 5 k cycles	≤40% loss of initial area

*Mass activity in A/mg @ 150 kPa abs backpressure at 857 mV iR-corrected on 6% H₂ (bal N₂)/O₂{or equivalent thermodynamic potential}, 100% RH, 80°C normalized to initial mass of catalyst and measured before and after test.

**Polarization curve per Fuel Cell Tech Team Polarization Protocol in Table A-5.

***Sweep from 0.05 to 0.6 V at 20 mV/s, 80°C, 100% RH.

ORCID

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Erratum: Carbon Corrosion in PEM Fuel Cells and the Development of Accelerated Stress Tests [*J. Electrochem. Soc.*, **165**, F3148 (2018)]

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Figure 14 on page F3158 contains an error in part a. The units of corroded carbon are given in (mgC/cm².h) but

should be given in (ugC/cm².h). The corrected figure is shown below.

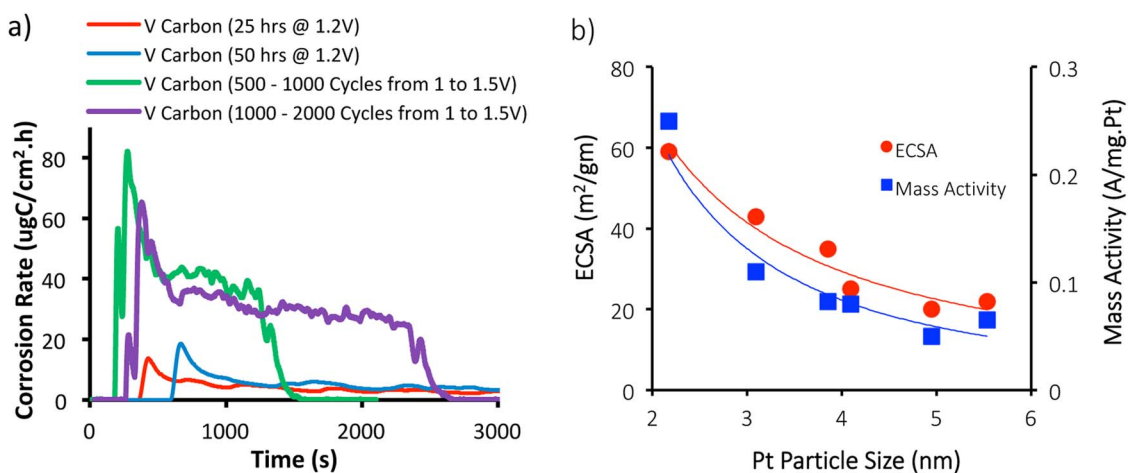


Figure 14. a. NDIR data for Pt/V over time during 1.0–1.5 V cycling and 1.2 V hold ASTs; b. ECSA and MA for Pt/V over time during new 1.0–1.5 V cycling AST; similar trend observed for Pt/HSAC (E-carbon) and Pt/LSAC (EA-carbon).