V.B.5 FC-PAD: Modeling, Evaluation, Characterization

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Project End Date: September 30, 2020

Overall Objectives

- Demonstrate improved performance and durability of fuel cells.

- Develop and implement characterization techniques to better evaluate performance and durability of fuel cells.

- Develop and implement validated fuel cell models.

- Develop and optimize accelerated stress tests (ASTs) to rapidly evaluate durability of fuel cells.

- Quantify the effect of impurities on fuel cell performance and durability.

Fiscal Year (FY) 2016 Objectives

- Refine membrane and electrocatalyst ASTs.

- Evaluate the durability of state-of-the-art (SOA) alloy catalyst-based membrane electrode assemblies (MEAs).

- Quantify effect of sulfate poisoning on fuel cell performance.

- Develop models to address the mass transport limitation in low Pt loaded MEAs at high current densities.

- Develop new diagnostic capabilities including reference electrodes and segmented cells.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section (3.4) of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan.

(A) Durability

(B) Cost

(C) Performance

Technical Targets

See Table 1.

FY 2016 Accomplishments

- Developed a combined mechanical/chemical membrane AST and a more accelerated (5X) electrocatalyst AST.

- Discovered that alloy catalysts of ≥5.5 nm particle size do not show coarsening.

TABLE 1. Progress towards Meeting Technical Targets for Electrocatalysts and MEAs for Transportation Applications

Characteristic	Units	DOE 2020 Electrocatalyst and MEA Targets	Project Status (50 cm^2 cell, differential conditions)
Mass activity	A/mg$_{PGM}$ @ 0.9 mV$_{iR\text{-free}}$	≥0.44	≥0.44
PGM total loading	mg-PGM/cm$^2_{geo}$	≤0.125	0.1, cathode
MEA performance	mW/cm$^2_{geo}$ @ 600 mV	≥1,000	700–800
Electrocatalyst durability	% loss after 30,000 AST cycles (0.6 V to 0.95 V; 3 s square wave)	<40% loss in ECSA <40% loss in mass activity <30 mV loss @ 0.8 A/cm^2	<40% loss for electrocatalyst particle size ≥4.5 nm ≈50% loss in mass activity for PtCo$_x$ electrocatalyst >30 mV loss @ 0.8 A/cm^2

PGM – Platinum group metal; ECSA – Electrochemical surface area

- Quantified that $PtCo_x$ catalysts lose performance during catalyst potential cycling due to de-alloying, resulting in the loss of up to 70% of Co from the catalyst.

- Developed reference electrode hardware with assistance from National Physical Laboratory (United Kingdom).

- Developed three-dimensional fuel cell model to quantify mass transport losses in low loaded MEAs at high current densities.

- Quantified sulfate poisoning in low loaded MEAs.

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INTRODUCTION

The FC-PAD consortium was formed to advance performance and durability of polymer electrolyte membrane fuel cells (PEMFCs) to meet DOE targets and further enable their commercialization. The major challenge to be addressed by this consortium is to develop the knowledge base and optimize structures for more durable, high-performing PEMFC component technologies, while simultaneously reducing cost. In specific, we will develop validated models and advanced in situ and ex situ characterization techniques to further improve the performance and durability of fuel cells. We will also evaluate the performance and durability of SOA MEAs using both AST protocols and simulated durability drive cycle experiments. We will refine the AST protocols and adopt standardized hardware to accelerate the evaluation and incorporation of material advances.

APPROACH

The FC-PAD consortium incorporates national laboratory investigators with proven experience (developed in prior projects) related to durability, transport, and performance, and combines them into one highly coordinated effort. The effort is sub-divided into six thrust areas, including three materials related thrusts and three cross-cutting thrusts. This report summarizes some of the work performed in the three cross-cutting thrust areas of (1) Modeling and Validation, (2) Operando Evaluation: Benchmarking, ASTs, and Contaminants, and (3) Component Characterization and Diagnostics. The thrust areas of the consortium are highly integrated and the work performed related to the various specific components is presented in the reports of the three materials thrust areas.

The project will develop validated three-dimensional models that take into account the catalyst layer microstructure. The models will be validated using diagnostics from a standardized differential cell and advanced characterization techniques to resolve the oxygen transport resistance within the catalyst layer pores and ionomer thin films. The project will also benchmark the performance and durability of SOA MEAs provided by original equipment manufacturers and materials suppliers. Finally the project will apply in situ and ex situ characterization techniques to reveal the performance losses degradation mechanisms operational in fuel cells and propose strategies to improve performance and durability.

RESULTS

Two new ASTs were adopted by the DOE United States Driving Research and Innovation for Vehicle efficiency and Energy sustainability (U.S. DRIVE) Partnership's Fuel Cell Tech Team (FCTT) [1]. A combined mechanical/chemical degradation AST (relative humidity [RH] cycling under open circuit voltage at 90°C) and a square wave (0.6 V for 3 s and 0.95 V for 3 s) AST for catalyst durability. The combined chemical/mechanical AST provides an additional test that mimics the RH stress (as measured by the high frequency resistance) and the chemical stress (as measured by fluoride emission) of the existing two membrane ASTs in a single test. By combining these stressors in a single test, this AST is expected to closely resemble the conditions encountered in real world operations. Ex situ characterization of MEAs subjected to this AST revealed that the failure mechanism (extensive local thinning, some global thinning, and Pt band in the membrane) in this combined test is similar to that encountered in the FCTT durability protocol.

The durability of SOA PtCo/C alloy catalyst-based MEAs that meet the DOE mass activity target of 440 mA/mg.$_{Pt}$ were evaluated using the square wave AST. The results from two different MEAs using a 4.4 nm PtCo/C catalyst and a 5.5 nm PtCo/C respectively are presented in Figure 1. While the 4.4 nm PtCo/C showed ≈40% ECSA loss, the 5.5 nm PtCo/C showed no loss in ECSA (Figure 1a). However both these MEAs exhibiting identical mass activity loss (Figure 1b) and increased kinetic resistance (Figure 1c) indicating a loss in performance of the catalyst irrespective of ECSA. Moreover the mass transport resistance at high current density (Figure 1d) of the 5.5 nm PtCo/C catalyst was unchanged while that of the 4.4 nm PtCo/C increased by ≈50%. It should be noted that the Pt-loading of the 5.5 nm PtCo/C was 0.21 mg/cm^2 while that of the 4.4 nm PtCo/C was only 0.1 mg/cm^2. These results are indicative that this mass transport loss is associated with transport losses observed in highly active catalysts at very low loadings at high current densities and this loss can be exacerbated by a further decrease in catalyst surface area.

Transmission electron microscopy characterization (Figure 2) of this MEA revealed that both these catalysts were 5.5 nm after the test. The catalyst particle size distribution (Figure 2a, b) illustrated that the 5.5 nm PtCo/C did not grow during this test while the 4.4 nm PtCo/C grew consistent with the ECSA measurements. The Pt/Co ratio of
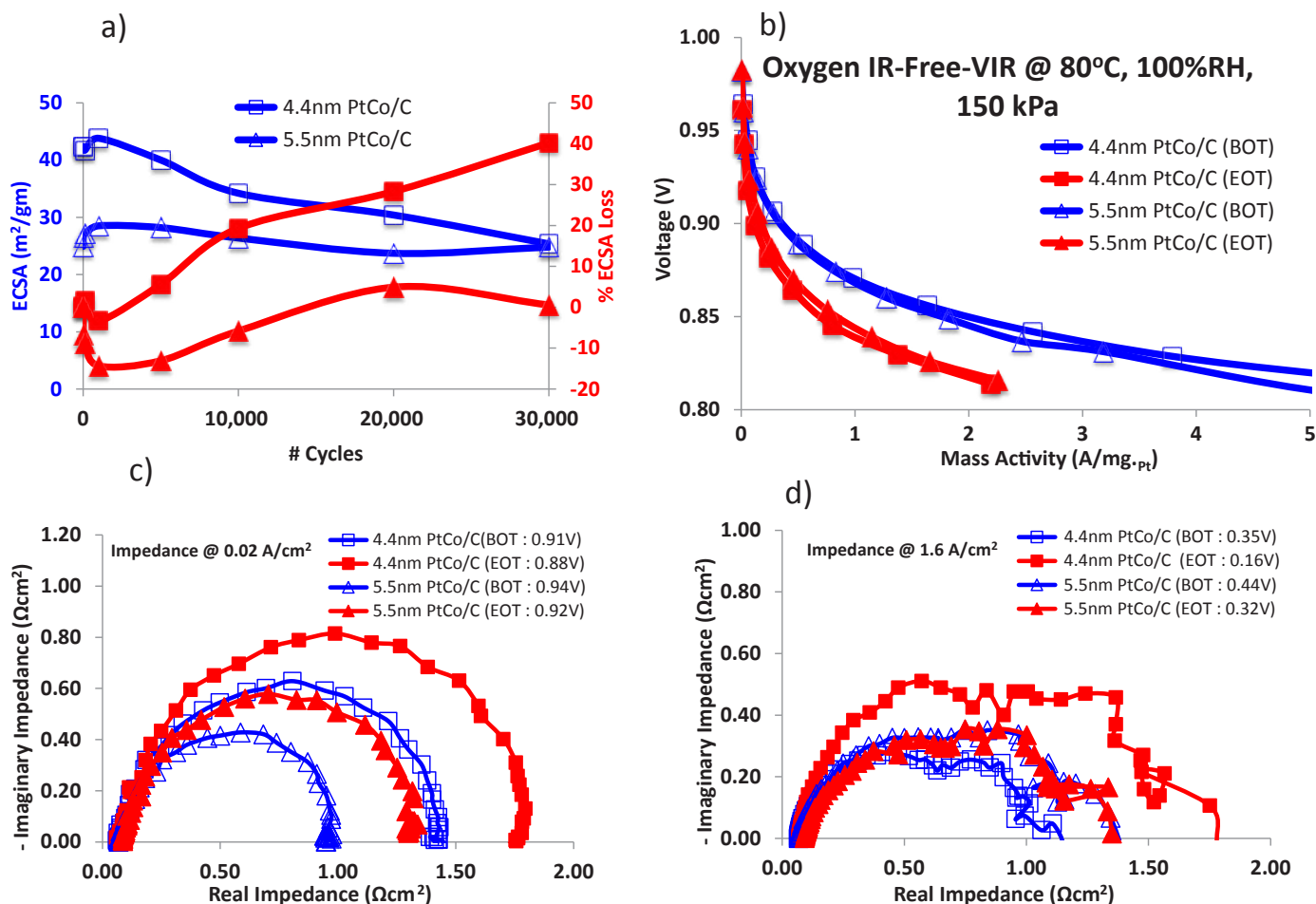
FIGURE 1. Evolution of (a) ECSA (measured at 80°C) and percent ECSA loss, (b) mass activity before (blue) and after (red) 30,000 cycles, (c) impedance at low current density (kinetic region) before (blue) and after (red) 30,000 cycles, and (d) impedance at high current density (mass transport region) of two PtCo/C catalyst-based MEAs during a 30,000 cycle square wave (3 s at 0.65 V and 3 s at 0.95 V) AST. Square = 4.4 nm PtCo catalyst at 0.1 mg$_{Pt}$/cm^2, and triangle = 5.5 nm PtCo catalyst at 0.21 mg$_{Pt}$/cm^2.

these two catalysts at various stages is illustrated in Figure 2c where both catalysts exhibited de-alloying and Co loss. This confirms that the ECSA loss is not the main degradation mechanism in these SOA alloy catalysts, which is controlled by mass activity loss due to de-alloying. The extent of Co loss was between 60–66% for the two MEAs and this Co was found primarily as Co ions throughout the membrane. Figure 2d illustrates this, where the Co was primarily concentrated in the catalyst layer in the fresh MEA whereas the Co was evenly distributed in the aged MEA. Further studies are underway to examine the effect of this Co in the membrane on performance and durability.

Full three-dimensional fuel cell models are being developed to quantify the various transport losses and these models are being validated using differential cell testing. A schematic of the three-dimensional cell used in the model is illustrated in Figure 3a where oxygen transport is by molecular diffusion in the gas diffusion layer, by Knudsen diffusion in the catalyst layer pores, and pressure

independent in the ionomer film. When the channel RH is 100% and the ionomer is saturated with water and the catalyst layer contains liquid water, the gas transport resistance is primarily controlled by gas diffusion limitation in the pores of the catalyst layer and gas diffusion layer. The transport resistance contribution from the gas channels and the ionomer film are significantly lower. Figure 3b shows the transport losses in the catalyst layer (R$_{cf}$) separated into ionomer component (R$_f$) and pore component (R$_c$) where the pore resistance dominates. These results are consistent with HelOx data obtained in the lab showing marked improvement in performance when air is replaced with HelOx.

Reversible degradation due to adsorption of membrane degradation fragments on the catalyst has been identified by the FCTT as one of the durability issues of concern in low loaded MEAs. Several studies have examined reversible degradation and suggested recovery methods [2,3]. However, a detailed understanding of this degradation mechanism is lacking and has been initiated in this project. To isolate
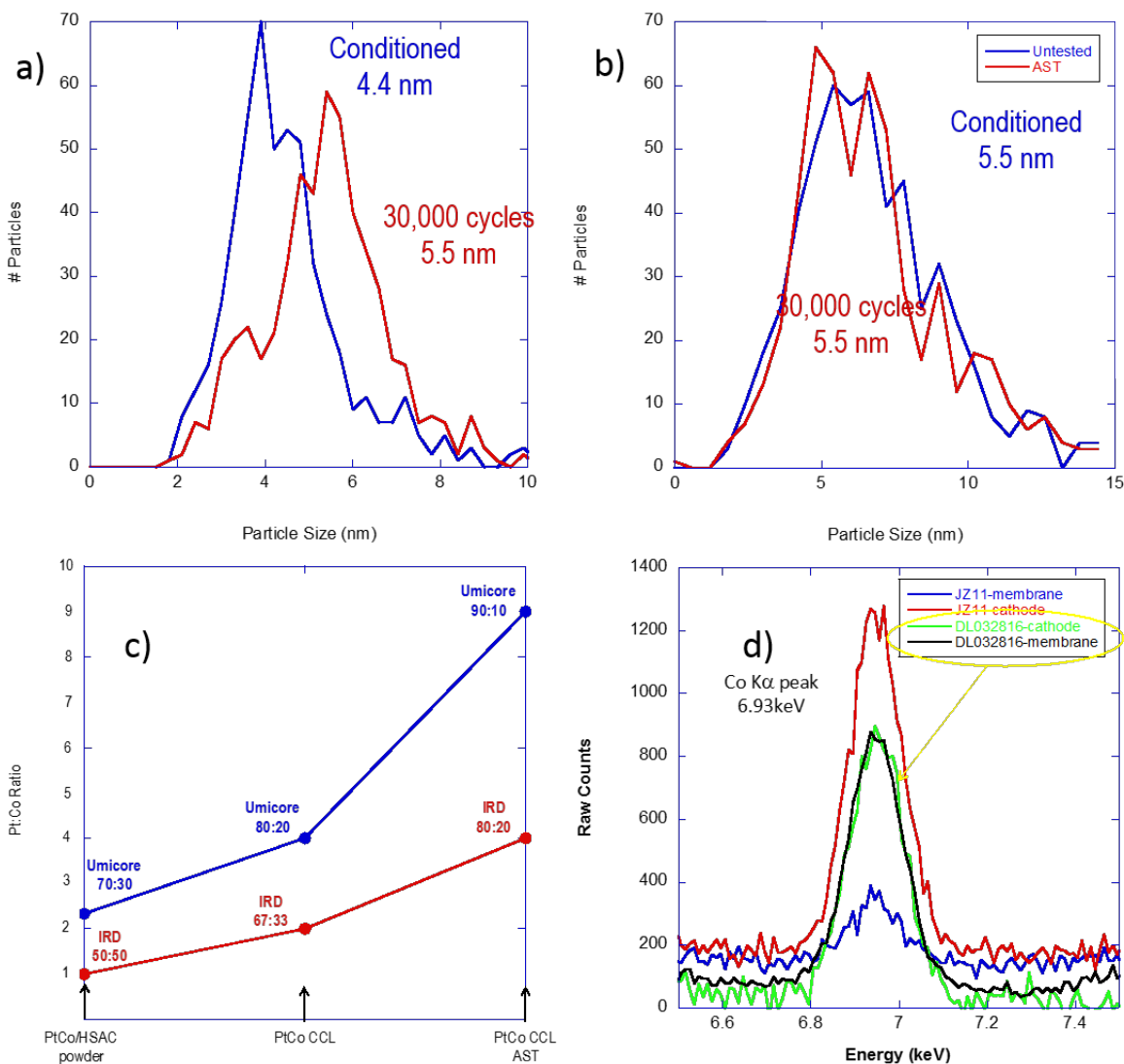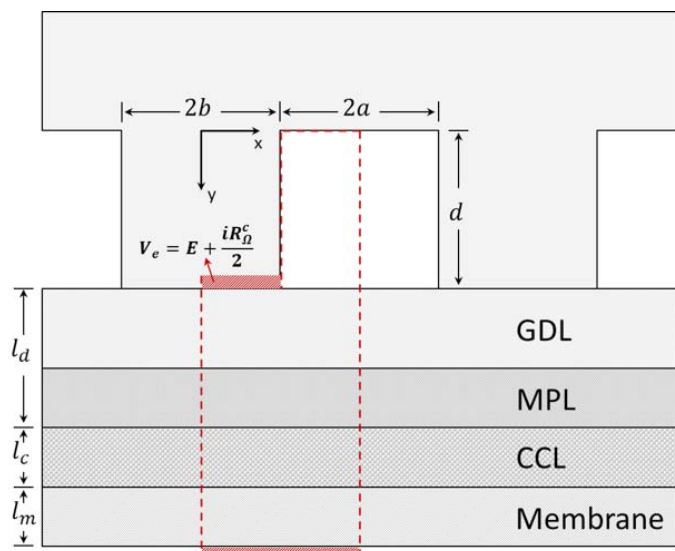
FIGURE 2. Comparison of transmission electron microscopy particle size distribution of two PtCo/C catalyst-based MEAs before (blue) and after (red) 30,000 cycles of a square wave potential cycle (3 s at 0.65 V and 3 s at 0.95 V) AST. (a) 4.4 nm PtCo catalyst at 0.1 mg$_{Pt}$/cm^2, and (b) 5.5 nm PtCo catalyst at 0.21 mg$_{Pt}$/cm^2. (c) Variation of the Pt/Co ratio of the 4.4 nm Pt/Co catalyst (blue) and the 5.5 nm Pt/Co catalyst (red) at various stages of testing. (d) Raw Co counts in beginning of test membrane (blue) and cathode catalyst (red) compared to the end of test membrane (black) and cathode catlalyst (green).

the effect of membrane degradation products, sulfate ions were deliberately introduced into the cathode gas stream by using dilute H$_2$SO$_4$ instead of water to humidify the cathode stream. At 10 mM concentration of H$_2$SO$_4$ infusion, no degradation was observed in high Pt-loaded catalysts (0.4 mg/cm^2) while significant voltage loss was observed at a cathode catalyst loading of 0.1 mg.$_{Pt}$/cm^2 (Figure 4a). Moreover, this voltage did not recover when the infusion was stopped (Figure 4a) but was fully recoverable (Figure 4b blue curve) after several cyclic voltammetric scans down to <0.1 V, where sulfate desorption can be expected. Further experiments are underway to quantify sulfate loss from

stabilized and unstabilized membranes to better quantify this degradation mechanism.

New diagnostic capability is being added within FC-PAD to better characterize the performance and durability of PEMFCs. One such technique is the use of multiple reference electrodes to accurately evaluate potential drops at the cathode and anode at various points in the flow-field. This technique was originally developed at National Physical Laboratory (United Kingdom) and researchers there have trained FC-PAD researchers in this technique and helped reproduce this experimental setup within FC-PAD. Preliminary results obtained at the National Physical Laboratory indicate that this technique can be a useful tool

$$V_e = E + \frac{iR_\Omega^c}{2}$$

$$V_i = -\frac{RT}{2F} \ln P_{H_2} - \frac{iR_\Omega^c}{2} - \eta_a^a$$

(a)

(b)

P: 1.5 atm
T: 80°C
Φ: 100%
Air: 3 slpm
H_2: 1 slpm

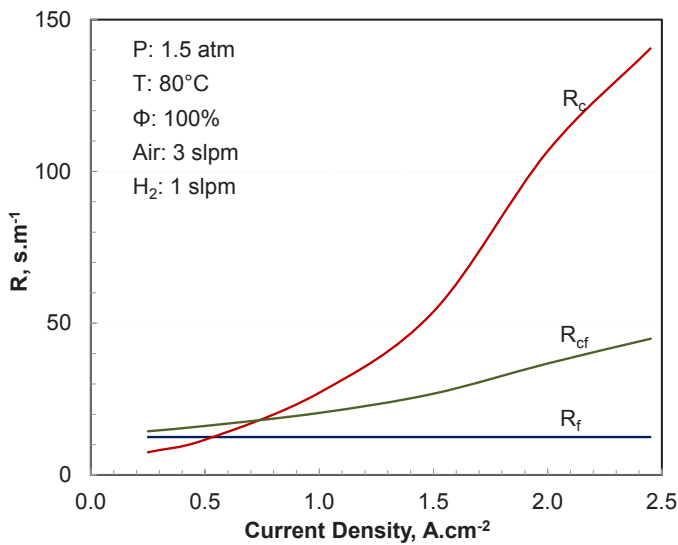GDL – Gas diffusion layer; MPL – Micro-porous layer; CCL – Cathode catalyst layer

FIGURE 3. (a) Schematic illustrating the dimensions of three-dimensional cell used in the model. (b) Example of calculated catalyst layer transport resistance at different current densities separated into ionomer component (Ri) and pore component (Rf).
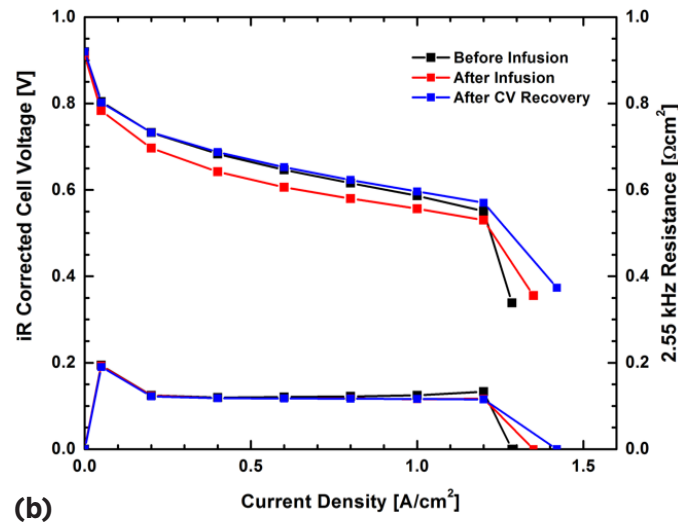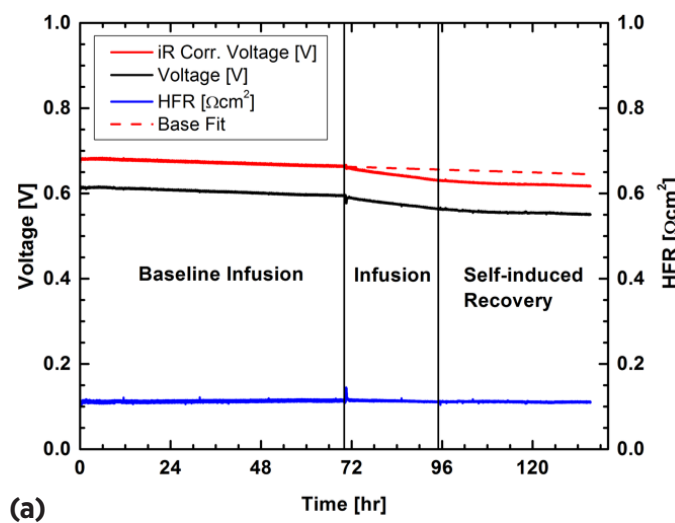

(a)

(b)

FIGURE 4. (a) Performance of a low loaded (0.1 mg/cm^2 cathode) Pt/C MEA at 0.6 A/cm^2 before during and after an infusion of 10 mM H_2SO_4. (b) Polarization curves before (black) and after (red) 10 mM sulfate infusion, and after a cyclic voltammetry (CV, between 0.05 and 1 V vs. reversible hydrogen electrode) recovery procedure (blue).

in the study of durability. Six different reference electrodes were embedded into the anode channel of a 50 cm^2 cell and their response was monitored when 50 ppm CO was introduced into the anode H_2 stream (Figure 5). When the CO is first introduced, the reference electrodes near the anode inlet immediately see a rise in potential corresponding to CO adsorption on the anode catalyst. Moreover the extent of

anode poisoning decreases with increasing distance from the anode inlet and there is a lag time before the anode outlet gets poisoned. However, when the CO is released, the desorption rate seems to be uniform from the inlet to the outlet. This experimental set up will be completed and used to examine other durability issues in the future.
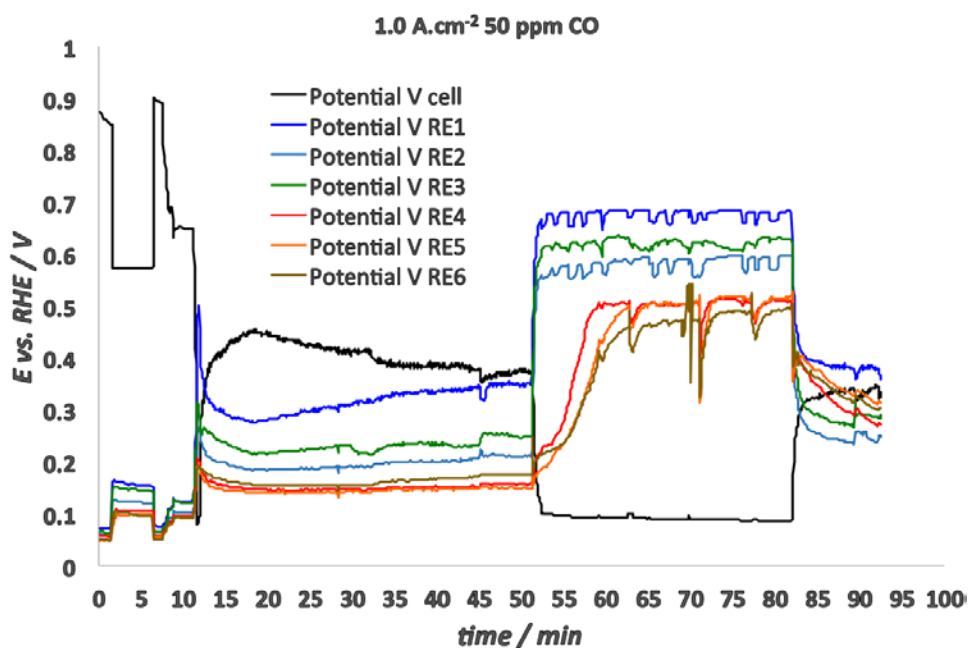
RHE – Reversible hydrogen electrode

FIGURE 5. Evolution of voltage at 1.0A/cm^2 at six different reference electrodes near the anode inlet (RE1, RE2, RE3) and anode outlet (RE4, RE5, RE6) of a 50 cm^2 fuel cell before (<10 min), during (≈10 min to ≈50 min) and after (>50 min) the injection of 50 ppm CO.

CONCLUSIONS AND FUTURE DIRECTIONS

New ASTs for membrane chemical/mechanical degradation and electrocatalysts were adopted by the U.S. DRIVE Partnership's FCTT. The main degradation mechanism in PtCo/C catalyst-based MEAs was the de-alloying of Co and the accompanying loss in mass activity. In low loaded MEAs using PtCo/C catalysts, additional increase in mass transport resistance due to decreased catalyst surface area was also observed. Models were developed to quantify the transport losses within GDLs, catalyst layers and ionomer films. A segmented cell and a reference electrode cell were developed for advanced diagnostics. The sulfate anion was also found to affect performance (reversible degradation) of low loaded MEAs.

The durability studies will be extended to MEAs utilizing de-alloyed PtNi/C catalyst and advanced carbons. The data from the electrocatalyst AST will be correlated to the data obtained from the durability protocol to confirm degradation mechanisms and quantify acceleration factors. The fuel cell models will be refined and validated utilizing data from a standardized differential cell. Extensive segmented cell evaluation of durability will be conducted and differential cell protocols will be proposed and adopted. Novel characterization of catalyst layer structures including ionomer mapping and ionomer interactions with catalyst will be developed.

FY 2016 PUBLICATIONS/PRESENTATIONS

1. Adam Weber, "Understanding Transport in Polymer-Electrolyte Fuel-Cell Ionomer," Colloquium, U. Kansas, 2015. (invited)

2. Iryna V. Zenyuk, Ezequiel Medici, Jeffrey Allen, and Adam Z. Weber, "Coupling continuum and pore-network models for polymer-electrolyte fuel cells," *International Journal of Hydrogen Energy*, 40, 16831–16845 (2015). doi: 10.1016/j.ijhydene.2015.08.009

3. Iryna V. Zenyuk, Ezequiel Medici, Jeffrey Allen, and Adam Z. Weber, "Coupling Continuum and Pore-Network Models in Polymer-Electrolyte Fuel Cells," *European Fuel Cell Technology & Applications Conference - Piero Lunghi Conference*, Naples, 2015.

4. Iryna V. Zenyuk and Adam Z. Weber, "Understanding Liquid-Water Management in PEFCs using X-ray Computed Tomography and Modeling," *ECS Conference*, Phoenix, 2015. (invited)

5. James A. Gilbert, A. Jeremy Kropf, Nancy N. Kariuki, Stacy DeCrane, XiaopingWang, Somaye Rasouli, Kang Yu, Paulo J. Ferreira, Dane Morgan,and Deborah J. Myers, "In-Operando Anomalous Small-Angle X-Ray Scattering Investigation of Pt$_3$Co Catalyst Degradation in Aqueous and Fuel Cell Environments," Journal of The Electrochemical Society, 162 (14) (2015) F1487-F1497.

6. D. Spernjak, R. L. Borup, D. S. Hussey, P. Zelenay, and R. Mukundan, "Imaging Fuel Cell Components: From Flow Field Channels to Catalyst Layers," Submitted to the 230th Meeting of the Electrochemical Society.

7. J.S. Spendelow, L. Castanheira, G. Hinds, T. Rockward, D.A. Langlois, R. Mukundan, and R.L. Borup, "Measurement of Local Electrode Potentials in an Operating PEMFC Exposed to Contaminants," Submitted to the 230th Meeting of the Electrochemical Society.

8. Iryna V. Zenyuk, Prodip K. Das, and Adam Z. Weber, "Understanding Impacts of Catalyst-Layer Thickness on Fuel-Cell Performance via Mathematical Modeling," *Journal of the Electrochemical Society*, 163, in press (2016). doi: 10.1149/2.1161607jes.

9. Iryna V. Zenyuk, Adrien Lamibrac, Jens Eller, Felix N. Büchi, and Adam Z. Weber, "Understanding Evaporation in Fuel-Cell Gas-Diffusion Layers with X-ray Computed Tomography," *Interpore: 8th International Conference on Porous Media*, Cincinnati, May 2016.

10. Rodney L. Borup, Rangachary Mukundan, Dusan Spernjak, David Langlois, G. Maranzana, A. Lamibrac, J. Dillet, S Didierjean, O. Lottin, L. Guetaz, D.D. Papadias, R. Ahluwalia and Karren More, "Material Degradation in PEM Fuel Cells," *MRS Meeting*, Phoenix, March 2016. (invited)

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