

V.D.1 Durability Improvements Through Degradation Mechanism Studies

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Project End Date: 2013

Overall Objectives

- Identify and Quantify Degradation Mechanisms
 - Degradation measurements of components and component interfaces
 - Elucidation of component interactions, interfaces, operation leading to degradation
 - Development of advanced in situ and ex situ characterization techniques
 - Quantify the influence of inter-relational operation between different components
 - Identification and delineation of individual component degradation mechanisms

- Understand Electrode Structure Impact—Applied Science Subtask
 - Better understand the electrode structural and chemical effects on durability
 - Understand impact of electrode structure on durability and performance
 - Correlate different electrode structures to fuel cell performance and durability
 - Define different fabrication effects (esp. solvents) for high-durability electrode structures
- Develop Models Relating Components and Operating Conditions to Fuel Cell Durability
 - Individual degradation models of individual fuel cell components
 - Development and dissemination of an integrated comprehensive model of cell degradation
- Methods to Mitigate Degradation of Components
 - New components/properties, designs, operating conditions

Fiscal Year (FY) 2013 Objectives

- Refine Degradation Model
 - Incorporate carbon corrosion effects
 - Incorporate membrane and catalyst layer ionomer effects
 - Model metal bipolar plate corrosion and contact resistance
- Characterize Degradation Mechanisms of Components
 - Carbon corrosion and effects on catalyst layer structural changes
 - Membrane degradation by measuring changes to water uptake and membrane structure
 - Metal bipolar plate corrosion

Technical Barriers

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

- (A) Durability
- (B) Cost

Technical Targets

- Transportation Durability: 5,000 hours (with cycling)
 - Estimated start/stop cycles: 17,000
 - Estimated frozen cycles: 1,650
 - Estimated load cycles: 1,200,000
- Stationary Durability: 40,000 hours
 - Survivability: stationary -35°C to 40°C
 - Cost (\$25/kW_e)

FY 2013 Accomplishments

- Measured carbon corrosion and completed initial development of carbon corrosion model:
 - Measured carbon corrosion rates for Pt-catalyzed corrosion of Ketjen[®] black (E-type), Vulcan[®] XC72 (V-type), and graphitized carbon (EA-type) supports
 - Examined mixing more stable catalyst supports and showed mixture retains more of the pore structures and maintains transport properties better during a carbon corrosion accelerated stress test (AST)
 - Post-characterization revealed increasing graphitic content and increasing oxygen concentration in the catalyst layer
 - Modified catalyst durability model to account for changes due to carbon corrosion
 - Determined the effect of aging on the specific surface area of carbon (S_c , m²-C/g-C)
 - Characterized the percent change in Pt particle size to be much greater for Pt supported on E-carbon in surface layer than Pt particles supported on EA-carbon in inner layer
- Measured and modeled membrane and ionomer degradation, including gas crossover during membrane degradation:
 - Modeled open-circuit voltage (OCV) data to show Pt particles deposited in aged membrane promote reaction between H₂ crossing over from anode and O₂ crossing over from cathode
 - Demonstrated that Pt particle migration affects the membrane H₂ crossover
 - Developed a component model for chemical/mechanical membrane durability and validated prediction of changing H₂O uptake based on nanostructure degradation
 - Modeled catalyst layer ionomer degradation as contributing cause to electrochemical surface area (ECSA) loss

- Measured corrosion properties of metal bipolar plates, contact resistance and corrosion products:
 - Developed model for SS 316L and G35 metal bipolar plates
- Characterized membrane electrode assembly (MEA) structure degradation:
 - Demonstrated that the durability response of low-loaded cathodes (0.05 mg/cm²) is significantly different than that of higher-loaded cathodes (>0.10 mg/cm²)
 - Attributed differences in catalyst layer degradation from different casting solvents to Nafion[®] relaxation in catalyst layer



INTRODUCTION

The durability of polymer electrolyte membrane (PEM) fuel cells is a major barrier to the commercialization of these systems for stationary and transportation power applications. By investigating component and cell degradation modes, defining the fundamental degradation mechanisms of components and component interactions, new materials can be designed to improve durability. To achieve a deeper understanding of PEM fuel cell durability and component degradation mechanisms, we have assembled a multi-institutional and multi-disciplinary team with significant experience investigating these phenomena.

APPROACH

Our approach to understanding durability and degradation mechanisms within fuel cells is structured in three areas: fuel cell testing (life testing, ASTs, ex situ aging), characterization of component properties as a function of aging time, and modeling (component aging and integrated degradation modeling). The modeling studies tie together what is learned during component characterization and allow better interpretation of the fuel cell studies. This approach and our team give us the greatest chance to increase the understanding of fuel cell degradation and to develop and employ materials that will overcome durability limitations in fuel cell systems. This work is also being coordinated with other funded projects examining durability through a DOE Durability Working Group.

RESULTS

Electrode Structural Changes and Carbon Corrosion

The structural change of the catalyst layer can cause changes in the PEM fuel cell performance due to loss of

catalyst utilization, electronic/protonic conductivity, and changes in the mass transport of the gases. A primary cause for changes in the structure of the catalyst layer is the corrosion of carbonaceous electrode supports leading to electrode collapse, reduced active catalyst area, and increased surface hydrophilicity. Figure 1 shows comparisons of cathode catalyst layers after 389 hours of the DOE/U.S. DRIVE Durability Drive Cycle Test (including wet/dry cycles). The fresh catalyst layer (Figure 1a) shows a non-compacted catalyst layer of about 7-8 microns thick, while after testing (Figure 1b) the catalyst layer shows about 30% compression/thinning due to either loss of carbon or due to loss of the pore structure of the catalyst layer.

Catalyst layer thinning is regularly observed due to carbon corrosion, which is accelerated at high potentials that are produced during shut-down/start-up transients. Carbon corrosion measurements were made for three different types of carbon, E-carbon (high surface area carbon), V-carbon (Vulcan) and EA-carbon (graphitized carbon). Figure 2 shows scanning transmission electron microscopy (STEM) images of the cathode catalyst layer as a function of time during 1.2 V holds for E-Carbon. The fresh catalyst layer had a catalyst layer thickness of 25 microns, whereas after

only 20 hours of potential hold, the catalyst layer thickness was reduced to about 15 microns, 8 microns at 40 hours, and 5 microns at 100 hours. Mass transport losses associated with significant cathode “thinning” >50% after only 20 hours at 1.2 V were observed. Post characterization (X-ray photoelectron spectroscopy) after the carbon corrosion AST shows that both graphitic content (as percent) and oxygen content increases. The graphitic content increase is likely due to a decrease of amorphous carbon due to corrosion, while the increasing oxygen content is likely on the carbon surface and has the tendency to change the hydrophobic properties of the catalyst layer and can affect the mass transport due to changing catalyst layer water content.

Measurements indicate that the performance loss is due to both kinetic losses arising from loss of active surface area and due to increases in mass transport resistance. To minimize the losses due to mass transport resistance, mixtures of E and EA carbon were made to measure the effect on mass transport resistance, to determine if by stabilizing the catalyst layer void volume, a portion of the performance loss can be prevented. Figure 3 shows a bar plot of mass activity and ECSA (Figure 3a) and associated polarization performance (Figure 3b) for E-carbon, EA-carbon, V-carbon, and an MEA made of a mixture of E- (60%) and EA- (40%) carbon. Figure 3c shows impedance spectra for the samples measured at 1 A/cm². The post-aging transport losses of the E-carbon are very large (blue squares), whereas when mixed with the EA-carbon, the transport losses were minimized (green squares). However, the overall performance of the EA-carbon after 400 hours of the AST was the highest.

Nanostructure of Degraded Membrane

We have previously observed that the membrane structure changes during aging, with the crystallinity of the membrane being more pronounced (transmission electron microscopy [TEM] inserts in Figure 4b). In FY 2013, small angle X-ray scattering (SAXS) was used to quantify these changes for Nafion[®] 212 (Figure 4a). The results for the Nafion[®] 212 membrane show that upon aging, the SAXS

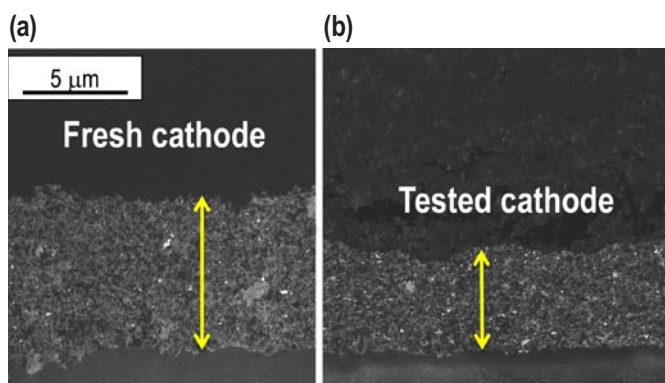


FIGURE 1. STEM images of the cathode catalyst layer with HSAC (high surface area carbon) (a) fresh, and (b) after 389 hours of testing using the U.S. DRIVE Durability Drive Cycle Test.

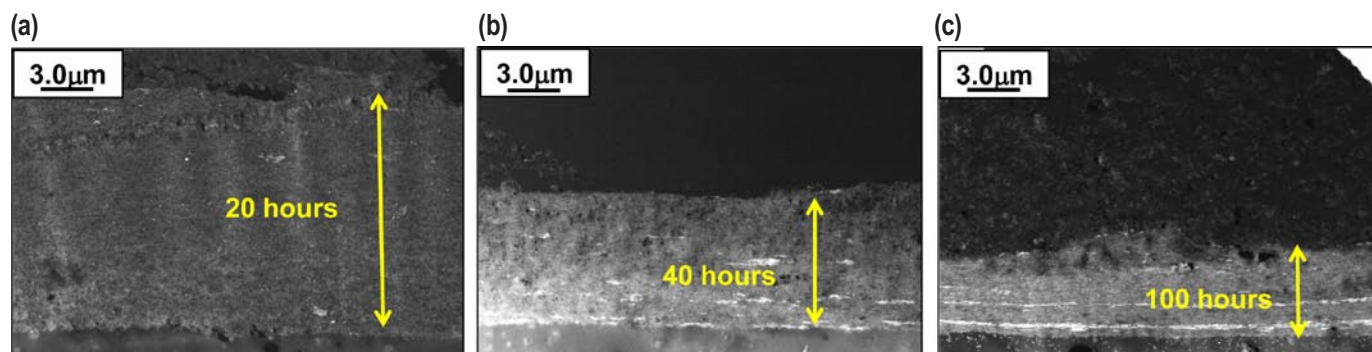


FIGURE 2. STEM images of the cathode catalyst layer with HSAC after carbon corrosion AST hold at 1.2 V for (a) 20 hours, (b) 40 hours and (c) 100 hours.

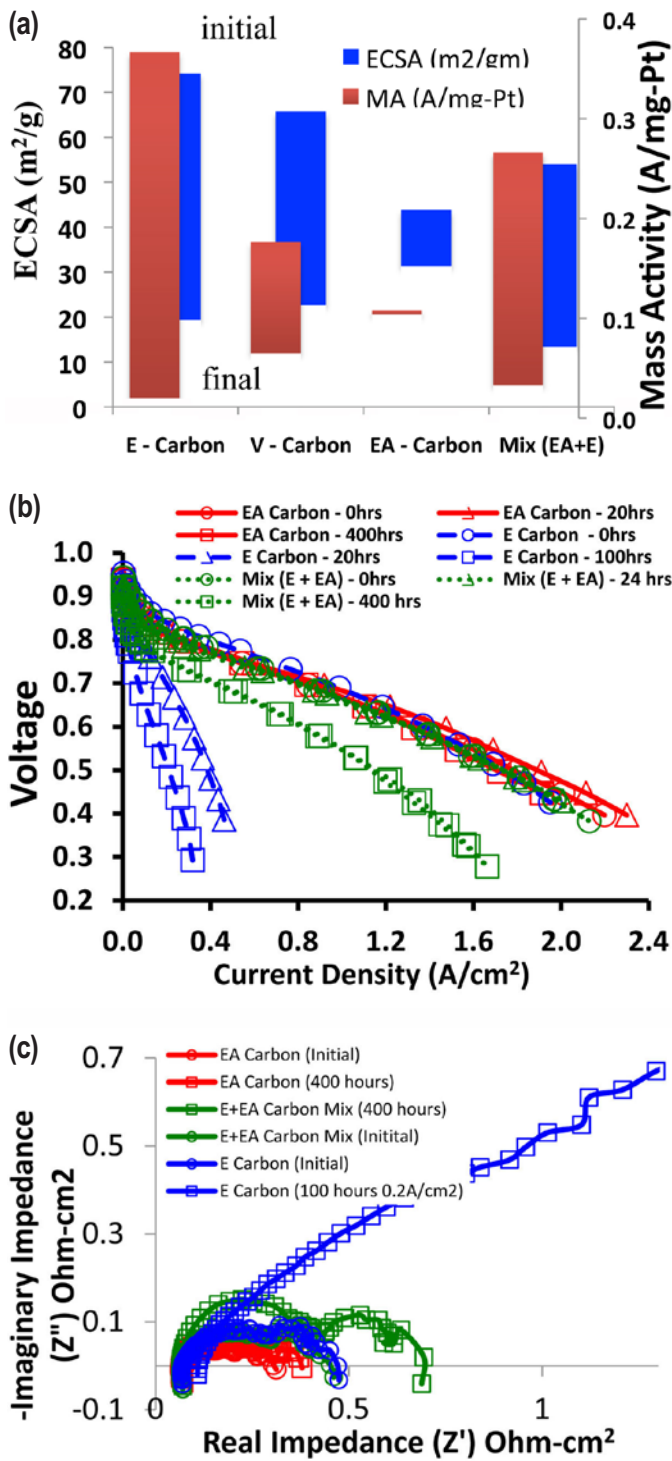


FIGURE 3. For catalyst layers comprised of Pt supported on carbon, with E-carbon (HSAC), Vulcan carbon, EA-carbon (graphitized), and a catalyst layer with a mixture of EA+E carbon: (a) bar plot with initial and final ECSA and mass activities, (b) polarization curves as a function of time during a 1.2 V carbon corrosion AST hold, and (c) impedance spectra at 1.0 A/cm². Note: MEA Pt loadings were 0.15 mg/cm² (E)/0.15 mg/cm² (EA+E)/0.25 mg/cm² (EA).

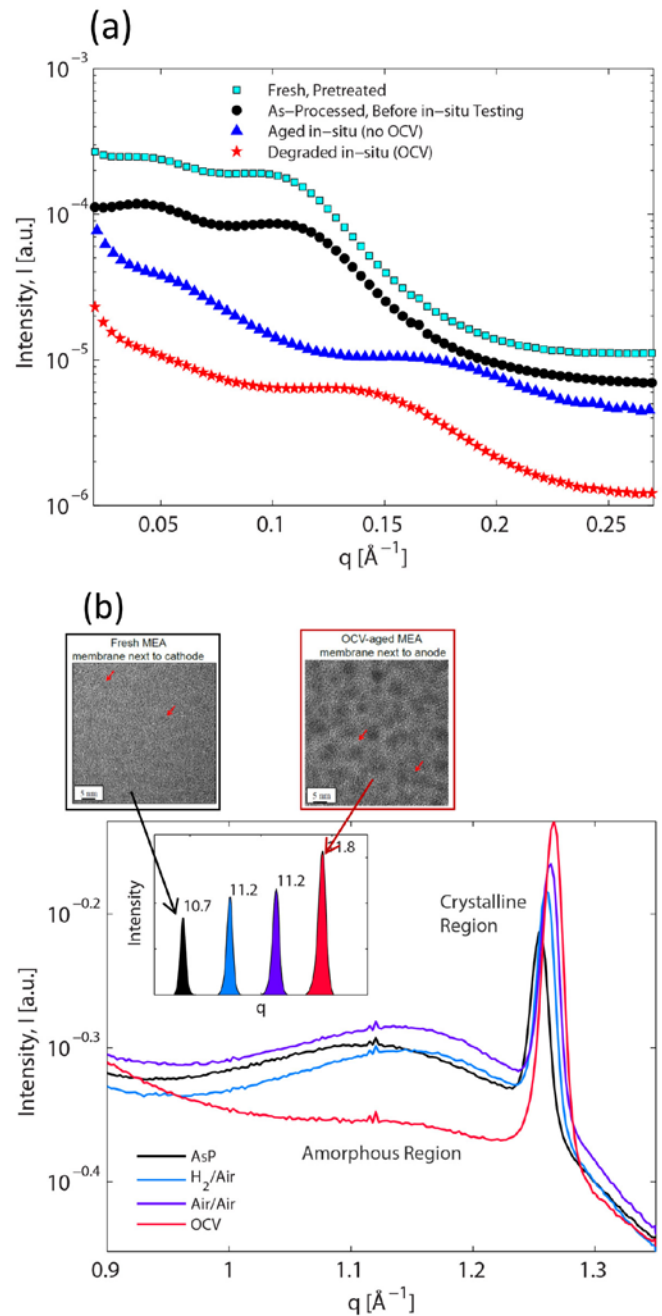


FIGURE 4. Characterization of Nafion[®] 212 membrane fresh and with different aging treatments by (a) SAXS and (b) WAXS.

peak indicative of membrane/water structure occurs at a much larger scattering vector ($q \approx 0.18$ vs. 0.1 for fresh); upon boiling of the aged membrane, d-spacing increases. However, this is still lower than fresh membrane. Increased crystallinity of the membrane was measured by wide angle X-ray scattering (WAXS) and is shown in Figure 4b. The crystallinity of the membrane was lowest in the fresh sample (AsP), and increased with aging treatment, with the highest crystallinity observed after OCV testing. These higher

crystallinity/aging measurements correspond to lower water uptake in the membrane.

CONCLUSIONS

Testing and advanced characterization were conducted to determine component degradation; testing included drive-cycle tests, start-up/shut-down tests, and available ASTs, with varying conditions and materials. Advanced characterization techniques included a) TEM and scanning electron microscopy (SEM) measurements that identified the corrosion of different types of carbons during AST and fuel cell operation and its effect on catalyst layer structure; b) SAXS and WAXS characterization of the changes to membrane structure and crystallinity and correlating nanostructural changes to membrane water-uptake; c) advanced electrochemical impedance spectroscopy that measured the effect of metal bipolar plate corrosion and changes to internal contact resistance, and delineated mass transport losses from electrode structure changes; and d) atomic force microscopy studies that revealed changes to catalyst layer ionomer relaxation with different solvent manufacturing techniques and their effect on mass transport properties.

The degradation modeling was refined to include advanced component models. These included a) incorporation of a carbon corrosion model into the catalyst durability model; b) development of a membrane degradation model for combined chemical/mechanical membrane durability and validating the prediction of changing H₂O uptake based on nanostructure degradation; c) modeling the effect of Pt incorporation into the membrane on gas crossover and membrane/ionomer degradation, and quantifying ionomer degradation contributions to ECSA loss; and d) modeling metal bipolar plate corrosion and contact resistance increase during aging.

FUTURE DIRECTIONS

Component Interactions

- Measure transport of dissolved cations through catalyst ionomer and membrane
- Further quantitate relationship between ionomer relaxation, carbon corrosion, and resulting changes in carbon catalyst layer structure (Pt/pore distributions, Pt utilization, ECSA, catalyst supports and mixtures)
- Incorporate component membrane model into integrated model
- Model refinement incorporating data on advanced materials and better delineated degradation mechanisms; incorporate transport of dissolved cations through catalyst ionomer and membrane from carbon plates, seals, and metal bipolar plates

Understand Carbon/Nafion®/Catalyst Structure and Durability Effects

- Understand the effect of catalyst layer structure on durability, different methods of forming catalyst layers
- Improve durability/performance of low-loaded MEAs (0.05 mg/cm²)
- Identify ionomer degradation source for fluoride emission rate (catalyst layer vs. membrane)

Define Effect of Carbon Corrosion on Catalyst Layer Structure and Transport Losses

- Quantify relationship between carbon corrosion and changes in catalyst layer structure
- Identify uniform methodology for measuring real durability impact of start-up/shut-down, air cycling
- Spatial/areal performance variations over aging remain largely undetermined

Catalyst Durability

- Reduce solubility of Pt via increasing support interactions, alloying
- Understand/model dissolution of Pt at elevated temperatures and in oxygen
- Understand effect of Pt transport and band formation

Component Surface Properties

- Understand effects of changing surface chemistry on bipolar plates, catalysts, gas diffusion layers

Mitigation of Degradation

- Increase catalyst transport, stability through use of stable structures and stable materials

ISSUED PATENTS

1. Advanced membrane electrode assemblies for fuel cells, USP 8,227,147 (2012).
2. Non-Aqueous liquid composition of ion exchange polymers, USP 7,981,319 B2 (2011), USP 8,236,207 B2 (2012), USP 8,394,298 (2013).

FY 2013 PUBLICATIONS/PRESENTATIONS

Publications

1. Hussey, D.S.; Spornjak, D.; Weber, A.Z.; Mukundan, R.; Fairweather, J.; Brosha, E.L.; Davey, J.; Spendelow, J.S.; Jacobson, D.L.; Borup, R.L. **Accurate measurement of the through-plane water content of proton-exchange membranes using neutron radiography**, Journal of Applied Physics (2012), 112(10).

2. Spornjak, Dusan; Fairweather, Joseph; Mukundan, Rangachary; Rockward, Tommy; Borup, Rodney L., **Influence of the microporous layer on carbon corrosion in the catalyst layer of a polymer electrolyte membrane fuel cell**, *Journal of Power Sources* (2012), 214, 386-398.
3. Mishler, Jeffrey; Wang, Yun; Mukundan, Rangachary; Spendelow, Jacob; Hussey, Daniel S.; Jacobson, David L.; Borup, Rodney L., **Probing the water content in polymer electrolyte fuel cells using neutron radiography**, *Electrochimica Acta* (2012), 75, 1-10.
4. J. Chlistunoff, J.R. Davey, K.C. Rau, R. Mukundan, and R.L. Borup, **PEMFC Gas Diffusion Media Degradation Determined by Acid-Base Titrations**, *ECS Transactions* (2012).
5. Rangachary Mukundan, Greg James, Dana Ayotte, John Davey, David Langlois, Dusan Spornjak, Dennis Torrace, Sivagaminathan Balasubramanian, Adam Z Weber, Karren More, and Rodney L. Borup, **Accelerated testing of carbon corrosion and membrane degradation in PEM fuel cells**, *ECS Transactions* (2012).
6. J.D. Fairweather, D. Spornjak, R. Mukundan, R.K. Ahluwalia, S. Arisetty, R.L. Borup, **Time Resolved Corrosion of Electrode Supports in PEM Fuel Cells**, *ECS Transactions* (2012).
7. Joseph Fairweather, Dusan Spornjak, Adam Z. Weber, David Harvey, Silvia Wessel, Daniel S. Hussey, David L. Jacobson, Kateryna Artyushkova, Rangachary Mukundan, and Rodney L. Borup, **Effects of Cathode Corrosion on Through-Plane Water Transport in Proton Exchange Membrane Fuel Cells**, *Journal of the Electrochemical Society*, **160** (9) F980-F993 (2013).
8. Gi Suk Hwang, Hyoungchul Kim, Roger Lujan, Rangachary Mukundan, Dusan Spornjak, Rodney L. Borup, Massoud Kaviani, Moo Hwan Kim, and Adam Z. Weber, **Phase-Change-Related Degradation of Catalyst Layers in Proton-Exchange-Membrane Fuel Cells**, *Electrochimica Acta*, Volume 95, pp 29-37 (2013).
9. Arisetty, S.; Wang, X.; Ahluwalia, R. K.; Mukundan, R.; Borup, R.; Davey, J.; Langlois, D.; Gambini, F.; Polevaya, O.; Blanchet, S., **Catalyst Durability in PEM Fuel Cells with Low Platinum Loading**, *Journal of the Electrochemical Society* (2012), 159(5), B455-B462.
10. Mishler, Jeffrey; Wang, Yun; Mukherjee, Partha P.; Mukundan, Rangachary; Borup, Rodney L., **Subfreezing operation of polymer electrolyte fuel cells: Ice formation and cell performance loss**, *Electrochimica Acta* (2012), 65, 127-133.
11. C. Welch, A. Labouriau, R. Hjelm, B. Orlor, C. Johnston, Y.S. Kim, **Nafion in Dilute Solvent Systems: Dispersion or Solution?** *ACS Macro Letters*, 1, 1403-1407 (2012).
12. J. Dillet, D. Spornjak, A. Lamibrac, G. Maranzana, R. Mukundan, J. Fairweather, S. Didierjean, R.L. Borup, O. Lottin, **Impact of flow rates, Pt loading, and carbon support on performance, CO₂ evolution, and active surface area during repeated startups and shutdowns in polymer-electrolyte membrane fuel cells**, submitted to *J. Electrochem. Soc.*

Invited Presentations

1. R.L. Borup, R.K. Ahluwalia, K.L. More, C.J. Johnston, and R. Mukundan, **Degradation Mechanisms in PEM Fuel Cells**, 222th ECS Meeting – Honolulu, Hawaii, October 7 – October 12, 2012.
2. Rod Borup, **PEM Fuel Cells: Microstructural Design and Durability at the Microstructural Level**, *Materials by Design Workshop*, 2013 Los Alamos National Laboratory Materials Summer Research Group (SRG).
3. Borup, Rod et al., **Durability Improvements Through Degradation Mechanism Studies**, FC Tech Team, Detroit MI, September 12, 2012.

Contributed Presentations

1. A. Lamibrac, J. Durst, D. Spornjak, G. Maranzana, J. Dillet, S. Didierjean, O. Lottin, F. Maillard, L. Dubau, M. Chatenet, R. Mukundan, and R.L. Borup, **Internal Currents, CO₂ Emissions and Decrease of the Pt Electrochemical Surface Area during Fuel Cell Start-Up and Shut-Down**, 222th ECS Meeting – Honolulu, Hawaii, October 7 – October 12, 2012.
2. J.D. Fairweather, D. Spornjak, R. Mukundan, R.K. Ahluwalia, S. Arisetty, and R.L. Borup, **Time Resolved Corrosion of Electrode Supports in PEM Fuel Cells**, 222th ECS Meeting – Honolulu, Hawaii, October 7 – October 12, 2012.
3. D.S. Hussey, D. Jacobson, B. Khaykovich, M.V. Gubarev, D. Spornjak, J.D. Fairweather, R. Mukundan, R. Lujan, and R.L. Borup, **Neutron Imaging PEMFCs with ~1 μm Spatial Resolution**, 222th ECS Meeting – Honolulu, Hawaii, October 7 – October 12, 2012.
4. R. Mukundan, G. James, D. Ayotte, J. Davey, D. Langlois, D. Spornjak, D. Torrace, S. Balasubramanian, A. Weber, K.L. More, and R.L. Borup, **Accelerated Testing of Carbon Corrosion and Membrane Degradation in PEM Fuel Cells**, 222th ECS Meeting – Honolulu, Hawaii, October 7 – October 12, 2012.
5. J. Chlistunoff, K.C. Rau, R. Mukundan, and R.L. Borup, **PEMFC Gas Diffusion Media Degradation Determined by Acid-Base Titrations**, 222th ECS Meeting – Honolulu, Hawaii, October 7 – October 12, 2012.
6. D. Spornjak, J.D. Fairweather, T. Rockward, K.C. Rau, R.L. Borup, and R. Mukundan, **Influence of In Situ and Ex Situ Aging of Gas Diffusion Layers on Fuel Cell Performance Degradation**, 222th ECS Meeting – Honolulu, Hawaii, October 7 – October 12, 2012.
7. D. Spornjak, R. Mukundan, P. Wilde, R. Schweiss, K.L. More, D. Langlois, J.D. Fairweather, and R.L. Borup, **PEM Fuel Cell Performance and Durability with Different Treatments of Microporous Layer**, 222th ECS Meeting – Honolulu, Hawaii, October 7 – October 12, 2012.
8. Borup, Rod et al., **Durability Improvements Through Degradation Mechanism Studies**, DOE Fuel Cell Technologies Annual Merit Review, Arlington, VA, May 13–17, 2013.