V.E.1 Durability Improvements through Degradation Mechanism Studies

Rod Borup[1] (Primary Contact),
Rangachary Mukundan[1], Dusan Spernjak[1],
Roger Lujan[1], David Langlois[1], Fernando Garzon[1],
S. Michael Stewart[1], Rajesh Ahluwalia[2],
Xiaohua Wang[2], Adam Weber[3], Ahmet Kusoglu[3],
Karren More[4], Steve Grot[5]
[1]Los Alamos National Laboratory (LANL)
MS D429, P.O. Box 1663
Los Alamos, NM 87545
Phone: (505) 667-2823
Email: Borup@lanl.gov

DOE Manager
Nancy Garland
Phone: (202) 586-5673
Email: Nancy.Garland@ee.doe.gov

Subcontractors & Collaborators
[2] Argonne National Laboratory, Argonne, IL
[3] Lawrence Berkeley National Laboratory, Berkeley, CA
[4] Oak Ridge National Laboratory, Oak Ridge, TN
[5] Ion Power, New Castle, DE

Start Date: October, 2009
Project End Date: Project continuation and direction determined by DOE

Overall Objectives

- Identify and Quantify Degradation Mechanisms
  - Degradation measurements of components and component interfaces
  - Elucidation of component interactions, interfaces, and operations leading to degradation
  - Development of advanced in situ and ex situ characterization techniques
  - Discern the impact of electrode structure on durability and performance
    - Develop concepts for designing more stable 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
- Develop Methods to Mitigate Degradation of Components
  - Use degradation mechanisms to design new materials/structures to improve durability
  - Develop operating strategies to improve durability
  - Provide predictive comparisons for material durability related to operational aspects

Fiscal Year (FY) 2014 Objectives

- Quantify degree of cerium migration during fuel cell operation in membranes
- Quantify and compare the loss of pore volume after drive cycle tests of 0, 50, 100, 200, 400, and 1,000 hours
- Complete testing comparison of single type carbons and mixed carbons (high surface area carbon and graphitized) comparing the structure effect on mass transport losses
- Evaluate the effect of catalyst layer cracks on membrane durability during relative humidity (RH) cycling (wet/dry drive cycle tests)

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/kWe

✧ ✧ ✧ ✧ ✧

FY 2014 ACCOMPLISHMENTS

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, thereby 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 utilize 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, accelerated stress tests, 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

The cathode catalyst layer structure has been found previously in this project to change during operation. We have also experimentally shown that carbon corrosion exists at normal fuel cell operating conditions. This carbon corrosion (as measured by CO_2 evolution) is exacerbated by the voltage cycling inherent in the drive cycle. An example of how the cathode catalyst layer changes is shown by scanning transmission electron microscopy (STEM) in Figure 1 after utilizing a simulated drive cycle test prescribed by DOE/Fuel Cell Tech Team [3]; in this case the drive cycle test RH was held continuously at 100%. STEM post-analysis shows gradual thinning of the catalyst layer during operation. The reduction in catalyst layer width can be due to the loss of carbon through carbon corrosion or due to compaction; both effects likely lead to a loss of void volume. A sharp decrease in catalyst layer thickness is observed within the first 100 hours of operation (30%), eventually reaching ~50% of its thickness after 1,000 hours. The reduction in catalyst layer thickness leads to increases in mass transport resistance as well as contributing to the loss of Pt electrochemical surface area (ECSA). While the cathode has thinning/compression, there is little evidence for carbon corrosion from the microscopic analysis:

- The majority of the VULCAN® retains its meso-graphitic structure
- Structure of the carbon support is unchanged (observe abundant VULCAN® graphitic structure)
- Little densification (banding) until 1,000 h, and even then it is minimal
- The cathode catalyst layer structural changes during the drive cycle are very different than that which is observed during carbon corrosion holds at 1.2 V
- There is also an increased Pt migration into the membrane with increased drive cycle time

The loss of catalyst layer void volume is shown by digitized STEM images in Figure 2. The estimation of pore shape and (area) volume percent is made from two-dimensional image "slices" taken of the catalyst layer.

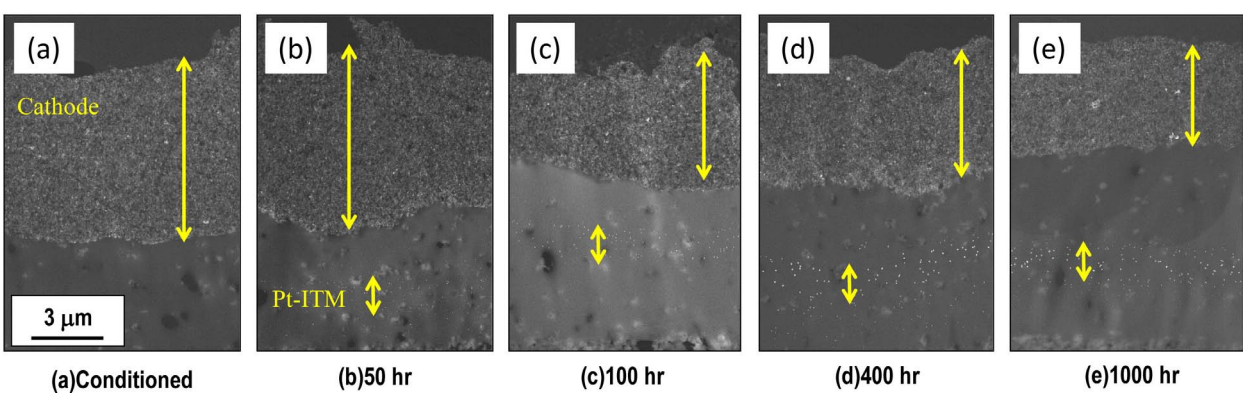


FIGURE 1. STEM images of the cathode catalyst layer and the membrane with VULCAN® Carbon (a) after conditioning (b) after 50 hours (c) after 100 hours (d) after 400 hours, and (e) after 1,000 hours of testing using the U.S. DRIVE Durability Drive Cycle Test operating at 100% RH.

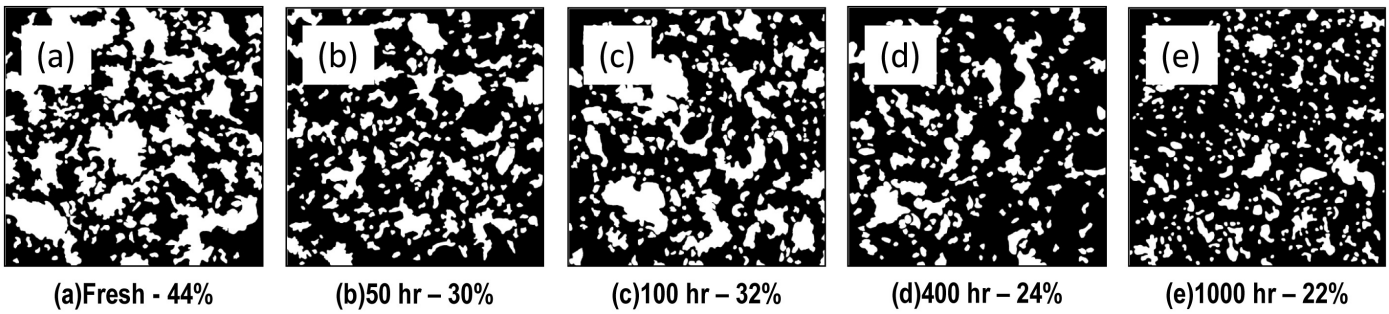


FIGURE 2. Digitized STEM images of the cathode catalyst layer examining the catalyst layer porosity with VULCAN® Carbon (a) after conditioning (b) after 50 hours (c) after 100 hours (d) after 400 hours, and (e) after 1,000 hours of testing using the U.S. DRIVE Durability Drive Cycle Test operating at 100% RH.

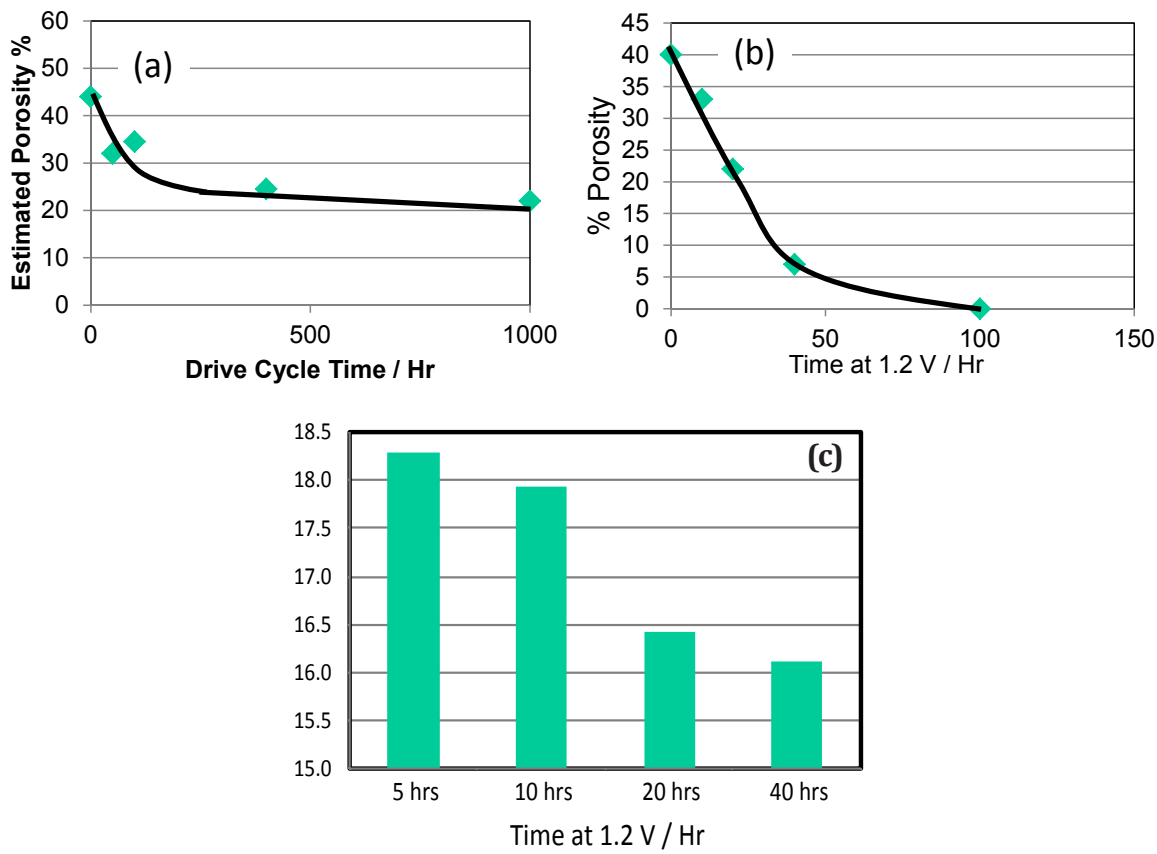


FIGURE 3. Cathode catalyst layer porosity during (a) drive-cycle operational time evaluated by STEM (b) during a carbon corrosion hold evaluated by STEM, and (c) during a carbon corrosion hold evaluated by MIP based on 0.01 to 0.2 micron pores.

The overall pore size and percent porosity decreases with increasing drive cycle time, with an initially large change followed by a gradual decline which appears to reach a limit. The void volume during the drive cycle time is shown in Figure 3a. An accelerated stress test (a potential hold of the cathode at 1.2 V inducing carbon corrosion) was used to evaluate the cathode support material Figures 3b and 3c show the changing catalyst layer porosity measured during carbon corrosion holds evaluated by digitized STEM images (3b) and mercury intrusion porosimetry (3c), where the void volume measured was limited to 0.01 to 0.2 micron sized pores. The mercury intrusion porosimetry (MIP) analysis was limited to these pore sizes as that is the predominant size of the pores in the electrode layer, as opposed to the membrane. Both the STEM and MIP show that the cathode catalyst layer porosity decreases rapidly during the carbon corrosion hold, contrasting to the initial rapid decrease but leveling off during drive cycle operations.

Cerium Migration

During the oxygen reduction reaction (ORR), whereby oxygen is converted to water, hydrogen peroxide and hydroxyl radicals are generated and are believed to be the principle cause of membrane chemical degradation. Cerium cations provide a viable option for inducing hydrogen peroxide decomposition as cerium plays a role in peroxide decomposition. Cerium cations can also facilitate the scavenging of radicals, which are generated during the decomposition process. We have measured the changes in the distribution of cerium cations during the lifetime of the fuel cell.

Figure 4a shows the initial cerium concentration in fresh DuPont™ XL membranes and how the cerium content of the membrane electrode assembly (MEA) decreases during operating time under OCV conditions (80°C and 100% RH). After 750 hours, only about 20% of the original cerium is left in the membrane. We have also observed that the cerium content decreases during normal fuel cell operation. The movement of cerium in the ionomer phase is quite quick as demonstrated by the results in Figure 4b where two Nafion® N211 membranes containing no cerium were hot/wet pressed with a DuPont™ XL membrane containing cerium. The cerium equilibrates between the N211 and XL membranes within the 10 minute pressing process at 90°C. During fuel cell operation, we have observed that cerium migrates from the membrane into both the anode and the cathode catalyst layer. Post-characterization shows that cerium in the cathode catalyst layer will migrate through the membrane to the anode catalyst layer, with little cerium remaining in the membrane.

CONCLUSIONS

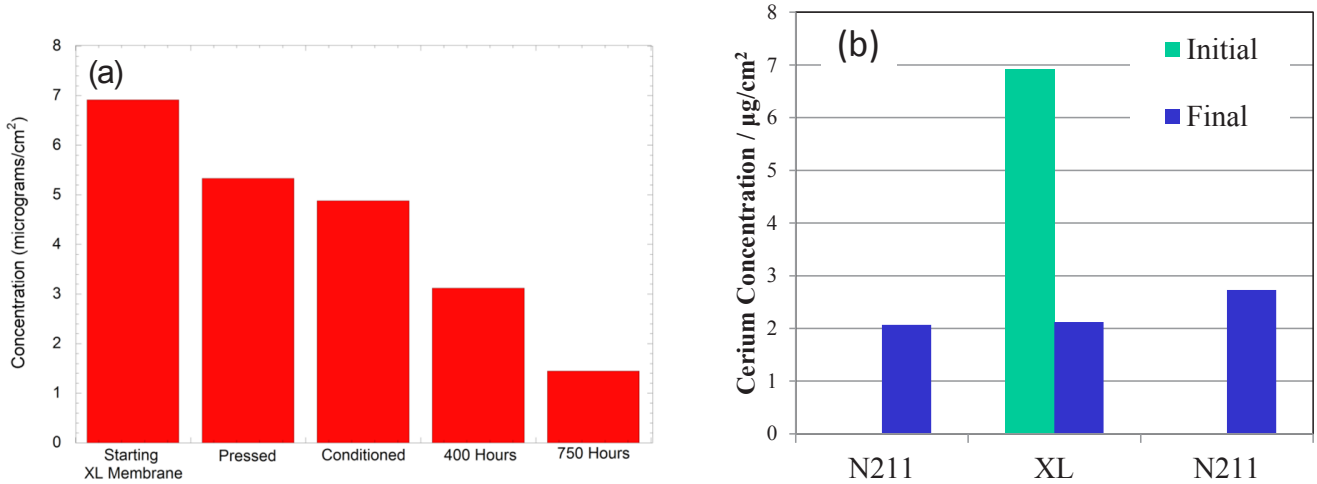
We have measured and quantified catalyst layer thinning during both accelerated stress tests (inducing carbon corrosion) and voltage cycle tests mimicking vehicle operation (drive cycle). Carbon corrosion is observed during the normal operating cycle potentials, although in a significantly smaller amount than is induced by start/stop cycles. During drive cycle operations the catalyst layer thins in width, which is not due solely to carbon corrosion, although carbon corrosion likely plays a role. Most of this thinning must be from compaction of the material in the catalyst layer. This reduction in thickness leads to the loss of catalyst layer porosity, which increases performance losses due to mass transport.

Cerium cations are effective at reducing the chemical degradation of proton conducting membranes. However, the cerium cations are not stable in terms of distribution within the membrane. Loss of cerium during operations has been measured and the changes in the distribution of cerium within the membranes are very quick, with equilibration occurring within 10 minutes during pressing tests at 90°C.

FUTURE DIRECTIONS

Catalyst layer morphology effect on durability

- Quantify the relationship between carbon corrosion and resulting changes in cathode catalyst layer structure
  - Quantification of Pt/pore distributions, Pt utilization, and ECSA
  - High vs. low surface area carbon structures and mixed formulations



(a)Change in cerium concentration for DuPont™ XL membrane

(b)Cerium Concentration Before/After 10 min Hot Press at 90°C

FIGURE 4. (a) Cerium concentration in DuPont™ XL membrane during operational time at open-circuit voltage conditions (80°C and 100% RH) (b) cerium concentration before and after pressing under hot/wet conditions for 10 minutes. Measured by X-ray diffraction.

- Effect of catalyst layer cracks and gaps; formation of cracks
  - Evaluate the effect of catalyst layer cracks on membrane durability
- Identify uniform methodology for measuring the real durability impact of start-up/shut-down and air cycling
  - Identify spatial/area performance variations over ageing

Durability evaluation of Pt alloys

- Define the effect of Pt and alloy migration on membrane durability
  - Experimentally define and model the dissolution of Pt at elevated temperatures and with a partial pressure of oxygen
  - Expand our previously developed models on Pt dissolution to incorporate alloy effects

Membrane structural changes and radical scavengers

- Effect of Ce (and other radical scavengers) movement on durability
  - Define best form of Ce for radical scavenging
  - Methods to stabilize Ce in both membrane and cell to prevent wash-out
- Evaluate changes in membrane crystallinity to determine both the durability effects and if these crystallinity changes affect more than water uptake.
- Examine membrane durability trade-offs with carbon corrosion
  - Compare membrane degradation at shut-down versus start-stop H_2 purging and carbon corrosion

Discern carbon/Nafion®/catalyst interactions and structure on durability

- Define catalyst layer porosity loss due to causes other than carbon corrosion
- Map the ionomer in the catalyst layer and define the ionomer chemical/structural changes in the catalyst layer
- Understand the structural effects of the catalyst layer on durability; different methods of forming catalyst layers
- Improve the durability/performance of low loaded MEAs (0.05 mg/cm^2)
  - Define the dependence of catalyst loading, MEAs, etc. on increases in mass transport resistance with fuel cell drive cycle testing

Mitigation of degradation

- Expand work on mitigation
  - Increasing catalyst layer transport and increase stability
    - Catalyst layer stability through the use of structure and stable materials
  - Stabilize cerium and/or other radical scavengers
  - Predict durability cost versus function of mitigation strategies

FY 2014 PUBLICATIONS/PRESENTATIONS

Publications

1. Ahluwalia, Rajesh K.; Arisetty, Srikanth; Peng, Jui-Kun; Subbaraman, Ram; Wang, Xiaoping; Kariuki, Nancy; Myers, Deborah J.; Mukundan, Rangachary; Borup, Rodney; Polevaya, Olga, Dynamics of particle growth and electrochemical surface area loss due to platinum dissolution, J. Electrochem. Soc. (2014), 161(3), F291-F304.

2. Papadias, Dionissios D.; Ahluwalia, Rajesh K.; Thomson, Jeffery K.; Meyer, Harry M., III; Brady, Michael P.; Wang, Heli; Turner, John A.; Mukundan, Rangachary; Borup, Rod, Degradation of SS316L bipolar plates in simulated fuel cell environment: Corrosion rate, barrier film formation kinetics and contact resistance, Journal of Power Sources (2014).

3. Dillet, J.; Spernjak, D.; Lamibrac, A.; Maranzana, G.; Mukundan, R.; Fairweather, J.; Didierjean, S.; Borup, R.L.; Lottin, O., Impact of flow rates and electrode specifications on degradations during repeated startups and shutdowns in polymer-electrolyte membrane fuel cells, J. Power Sources (2014), 250, 68-79.

4. Garzon, F., S. M. Stewart, R. Borup, M. Wilson, and A. Datye, Effects of Particles Size on Lifetime Improvement for Cerium (IV) Oxide in Hydrogen Fuel Cells, Accepted to J. Electrochem. Soc.

5. Stewart, S.M., R. Borup, M. Wilson, A. Datye, F. Garzon, Effects of Cerium (IV) Oxide Particle Size on Hydrogen Fuel Cell Durability During Accelerated Stress Testing, ECS Electrochemistry Letters (2014), 3(4), F19-F22.

6. Hwang G.S., H. Kim, R. Lujan, R. Mukundan, D. Spernjak, R.L. Borup, M. Kaviany M.H. Kim, and A.Z. Weber, Phase-Change-Related Degradation of Catalyst Layers in Proton-Exchange-Membrane Fuel Cells, Electrochimica Acta (2013), 95, 29-37.

7. Fairweather J., D. Spernjak, A.Z. Weber, D. Harvey, S. Wessel, D.S. Hussey, D.L. Jacobson, K. Artyushkova, R. Mukundan, and R.L. Borup, Effects of Cathode Corrosion on Through-Plane Water Transport in Proton Exchange Membrane Fuel Cells, J. Electrochem. Soc. (2013), 160(9), F980-F993.

8. Mishler, J.; Wang, Y.; Lujan, R.; Mukundan, R.; Borup, R.L., An experimental study of polymer electrolyte fuel cell operation at sub-freezing temperatures, J. Electrochem. Soc. (2013), 160(6), F514-F521.

9. Carnes, B.; Spernjak, D.; Luo, G.; Hao, L.; Chen, K.S.; Wang, C.-Y.; Mukundan, R.; Borup, R.L., Validation of a two-phase multidimensional polymer electrolyte membrane fuel cell computational model using current distribution measurements, J. Power Sources (2013), 236, 126-137.

10. Borup, R.L., R. Mukundan, J. Fairweather, D. Spernjak, D. Langlois, J. Davey, K. More, and K. Artyushkova, PEM Fuel Cell Catalyst Layer Structure Degradation During Carbon Corrosion, ECS Transactions (2013).

11. Rodgers M.P., L.J. Bonville, R. Mukundan, R. Borup, R. Ahluwalia, P. Beattie, R.P. Brooker, N. Mohajeri, H.R. Kunz, D.K. Slattery, J.M. Fenton, Perfluorinated Sulfonic Acid Membrane and Membrane Electrode Assembly Degradation Correlating Accelerated Stress Testing and Lifetime Testing, ECS Transactions (2013).

12. Fairweather J.D., D. Spernjak, J. Spendelow, R. Mukundan, D. Hussey, D. Jacobson, and R.L. Borup, Evaluation of Transient Water Content During PEMFC Operational Cycles by Stroboscopic Neutron Imaging, ECS Transactions (2013).

13. Abbou S., J. Dillet, D. Spernjak, R. Mukundan, J. Fairweather, R.L. Borup, G. Maranzana, S. Didierjean, O. Lottin, Time Evolution of Local Potentials during PEM Fuel Cell Operation with Dead-Ended Anode, ECS Transactions (2013).

14. Mukundan, R., J. Davey, K. Rau, D. Langlois, D. Spernjak, K. Artyushkova, R. Schweiss, and R.L. Borup, Degradation of Gas Diffusion Layers in PEM fuel cells during drive cycle operation, ECS Transactions (2013).

15. Hussey D.S., D. Spernjak, G. Wu, D.L. Jacobson, D. Liu, B. Khaykovich, M.V. Gubarev, J. Fairweather, R. Mukundan, R. Lujan, P. Zelenay, and R.L. Borup, Neutron Imaging Of Water Transport In Polymer-Electrolyte Membranes And Membrane-Electrode Assemblies, ECS Trans. (2013).

Presentations (Invited only)

1. Borup, Rodney L., Rangachary Mukundan, Yu Seung Kim, Dusan Spernjak, David Langlois, Karren More, R. Ahluwalia, S. Arisetty, G. Maranzana, J. Dillet and O. Lottin, (Invited) PEM Fuel Cell MEA Degradation During Drive Cycle Operation, Spring ECS May 2014.

2. Borup, Rodney L., Rangachary Mukundan, Dusan Spernjak, David Langlois, Dennis Torraco, Karren More, R. Ahluwalia, S. Arisetty Laure Guetaz, (Invited) Electrocatalyst Layer Degradation of PEM Fuel Cells, Fall ECS October 2014.

3. Rodgers, M.P., L.J. Bonville, R. Mukundan, R. Borup, S. Knights, R. Ahluwalia, P. Beattie, R.P. Brooker, N. Mohajeri, H.R. Kunz, D.K. Slattery J.M. Fenton, (Invited Keynote), Perfluorinated Sulfonic Acid Membrane and Membrane Electrode Assembly Degradation Correlating Accelerated Stress Testing and Lifetime Testing, Fall ECS October 2013.

4. Borup, R.L., et al., Degradation Mechanisms and Accelerated Testing in PEM Fuel Cells, (Invited), KIER – Korean Institute for Energy Research, October 2013.

5. Borup, R.L., R. Mukundan,J, Fairweather, D, Spernjak, D, Langlois, J, Davey and K, More, K. Artyushkova, R. Ahluwalia, S. Arisetty, (Invited), Electrode Morphology and Carbon Support Changes During Catalyst and Electrode Durability Tests, Joint DOE Durability/Catalyst Working Group Meeting, Golden Colorado, Dec. 2013.

6. Borup, Rod et al., Durability Improvements Through Degradation Mechanism Studies, (Invited), FC Tech Team, Detroit MI, September 18, 2013.

7. Borup, Rod et al., Durability Improvements Through Degradation Mechanism Studies, (Invited), DOE Fuel Cell Technologies Annual Merit Review, Arlington, Va, May 13–17, 2013.

8. Borup Rodney L., Rangachary Mukundan, Yu Seung Kim, Dusan Spernjak, David Langlois, Karren More, N. Mack, M. Hawley, C. Welch, (Invited) PEM Fuel Cells: Microstructural Design and Durability at the Microstructural Level, LANL Materials by Design Workshop, July 17, 2013.

9. Borup, R.L., et al, PEM Fuel Cells: Design and Durability at the Microstructural Level, 2014 Los Alamos National Lab, (Invited) Materials Capability Review.