

V.E.2. Durability Improvements Through Degradation Mechanism Studies

Rod Borup¹ (Primary Contact),
Rangachary Mukundan¹, Yu Seung Kim¹,
Christina Johnston¹, John Davey¹, Roger Lujan¹,
Baeck Choi¹, Zhongfen Ding¹, Cynthia Welch¹,
Andrea Labouriau¹, Bo Li¹, Dusan Spornjak¹,
Joe Fairweather¹, Rex Hjelm¹, Bruce Orler¹,
Nathan Mack¹, Rajesh Ahluwalia²,
Xiaohua Wang², Adam Weber³, Ahmet Kusoglu³,
Karren More⁴, Mike Brady⁴, Sylvia Wessel⁵,
Paul Beattie⁵, Greg James⁵, Daniel Ramrus⁵,
Svetlana Loif⁵, Warren Williams⁵, Steve Grot⁶,
Kateryna Artyushkova⁷, Plamen Atanassov⁷,
Anant Patel⁷

¹Los Alamos National Laboratory (LANL)
MS D429, P.O. Box 1663
Los Alamos, NM 87545
Phone: (505) 667-2823
E-mail: Borup@lanl.gov

DOE Manager

HQ: Nancy Garland
Phone: (202) 586-5673
E-mail: Nancy.Garland@ee.doe.gov

Subcontractors:

- ² Argonne National Laboratory, Argonne, IL
- ³ Lawrence Berkeley National Laboratory, Berkeley, CA
- ⁴ Oak Ridge National Laboratory, Oak Ridge, TN
- ⁵ Ballard Power Systems, Burnaby, BC, Canada
- ⁶ Ion Power, New Castle, DE
- ⁷ University of New Mexico, Albuquerque, NM

Start Date: October 2009

Project End Date: 2013

Understand Electrode Structure Impact - Applied Science Subtask

- Better understand the electrode structural and chemical reasons for differences in durability.
- Understand impact of electrode structure on durability and performance.
- Correlate different electrode structures to fuel cell tests and durability.
- Define different fabrication effects (esp. solvents) on electrode structure.

Develop Models Relating Components and Operation 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.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Fuel Cell Technologies Program 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 2011 Accomplishments

- Performed all DOE Fuel Cell Tech Team recommended accelerated stress tests (ASTs) on a combination of

Fiscal Year (FY) 2011 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.

materials including ionomers, membranes, catalysts, and catalyst supports.

- Performed neutron imaging determining water profiles to determine effect of carbon corrosion on water management.
- Made durability comparison of electrode layers using Nafion[®] ionomer and a short-side-chained perfluorinated ionomer.
- Performed small angle neutron scattering determining long-range order effect of electrode solvents on electrode durability for ionomer in proton (H⁺) and sodium (Na⁺) forms.
- Measured Nafion[®] crystallinity changes with respect to electrode location.
- Measured component surface species change by X-ray photoelectron spectroscopy.
- Performed characterization of durability in segmented fuel cells.



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. Although there has been recent progress in improving durability, further improvements are needed to meet the commercialization targets. Past improvements have largely been made possible because of the fundamental understanding of the underlying degradation mechanisms. 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. Various factors have been shown to affect the useful life of PEM fuel cells [1-4]. Other issues arise from component optimization. Operational conditions (such as impurities in either the fuel and oxidant stream), cell environment, temperature (including subfreezing exposure), pressure, current, voltage, etc., or transient versus continuous operation, including start-up and shutdown procedures), represent other factors that can affect cell performance and 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, and modeling (component aging and integrated degradation modeling).

These areas have aspects that can be considered free-standing, but each benefit greatly from work performed in the other areas. 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, and through a US Fuel Cell Council task force on durability.

Results

Correlating Electrode Structure to Durability

In FY 2010, we demonstrated that the solvents used can have a dramatic effect on the performance durability of the fuel cell electrodes, although the electrochemical surface area (ECSA) of the catalyst was unaffected. Electrodes made from water-based catalytic inks show rapid performance degradation, whereas electrodes made from catalytic inks based on glycerol, show virtually no performance loss. Comparing mass activity and ECSA as a function of particle size normally shows a good correlation [1,5,6]. However, with other types of solvent-produced membrane electrode assemblies (MEAs), the correlation can be poor, or even non-existent. To define the effect of different solvents on the electrode structure performance and durability we conducted small angle neutron scattering (SANS) of both different electrode solvents and Nafion[®] in both H⁺ and Na⁺ form. The SANS for water/isopropanol is shown in Figure 1a and for glycerol in Figure 1b. A peak at a scattering intensity (Q) of ~ 0.04 indicates that the water/iso-propanol mixture shows more long-ranged order than does the glycerol/Nafion[®] mixture. Electrode mechanical strength measurements also suggest that glycerol-cast film shows better mechanical properties than water/isopropyl alcohol-cast films, suggesting that aggregation leads to lower mechanical properties and lower electrode durability.

The durability of electrodes formed with Nafion[®] ionomer was compared to similar electrodes made from Aquivion ionomer, which is ionomer with short-side chains with sulfonic acid. The comparison of the polarization performance during potential cycling ASTs is shown in Figure 2. The MEA using Aquivion ionomer at the cathode showed better stability than the MEA using Nafion[®] ionomer after 30K potential cycling test. The durability of these electrode structures show a similar disconnect between ECSA and performance for Pt/C reinforced as do electrodes made with the different solvents. Note that a reduction in ionomer content compared with MEAs made with Nafion[®] allowed for best performance without loss in potential cycling durability.

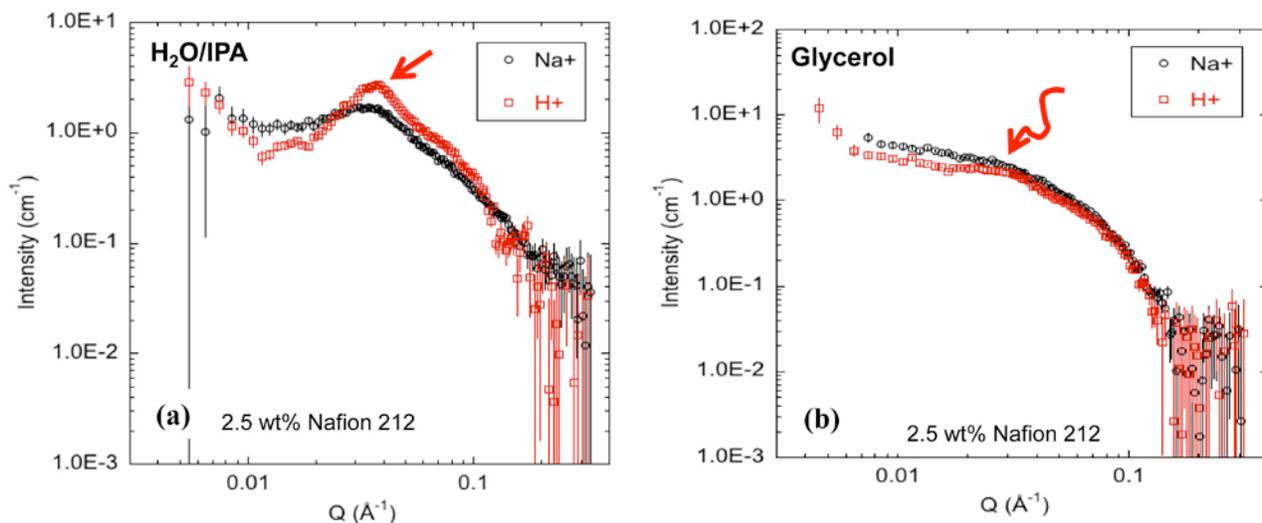


FIGURE 1. SANS of Nafion® dispersions with (a) water and iso-propanol as solvent and (b) glycerol solvent. Arrows identify location of SANS peak.

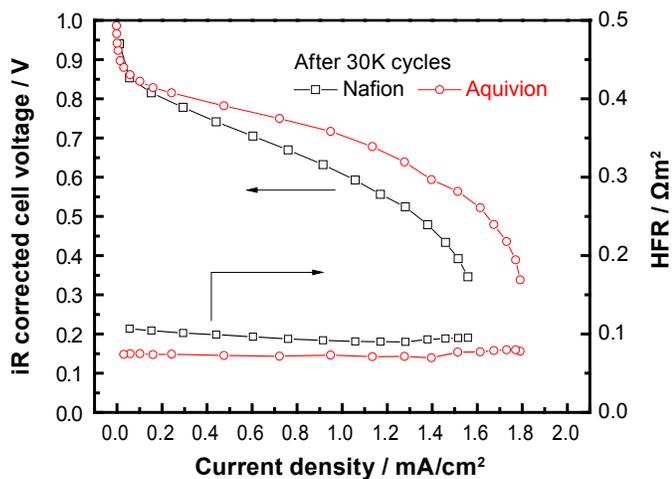


FIGURE 2. Polarization performance after 30,000 potential cycles of Nafion® and Aquivion electrodes. Catalyst, GDLs and membranes all identical.

Membrane Crystallinity Measurements

We previously have noted that the crystallinity of Nafion® during operation changes. To further investigate this phenomenon, we measured the conducted transmission electron microscopy (TEM) of fresh and AST-tested membranes. In fresh MEAs, small F-rich clusters are observed throughout the thickness of the membrane (from cathode to anode), see Figure 3a. Features exhibit some crystalline nature but are not highly crystallized nor have well-defined surfaces. After open-circuit voltage (OCV)-aging, these small F-rich clusters exhibited increased crystallinity on the cathode side without increasing in size (Figure 3b). The changes in Nafion® crystallinity were much more severe on the anode side of the membrane (Figure 3c).

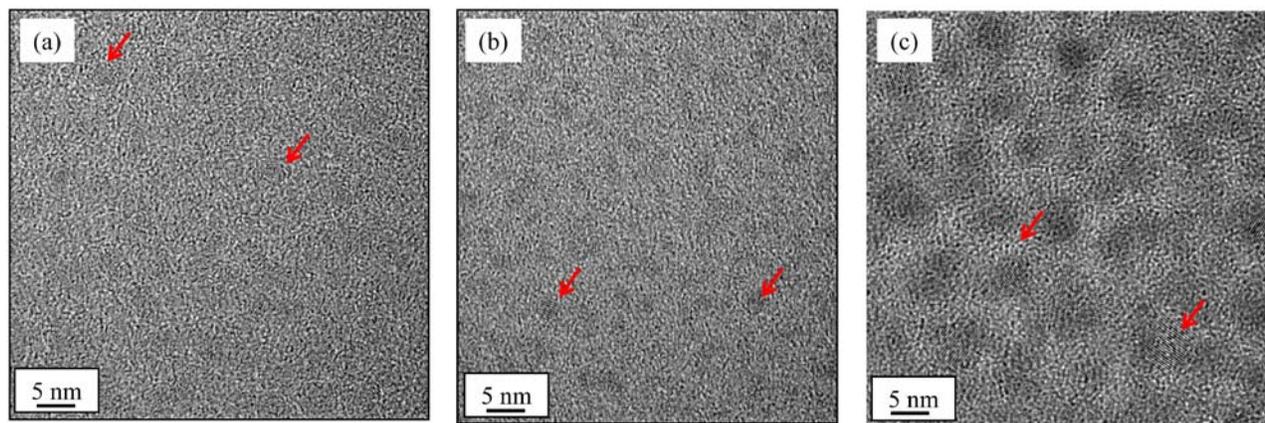


FIGURE 3. TEM of Nafion® membrane (a) fresh MEA membrane next to the cathode, (b) OCV-aged MEA membrane next to cathode and (c) OCV-aged MEA membrane next to anode. Arrows show fluorine-rich crystallites.

Durability Effects of Carbon Corrosion

To measure the effect of carbon corrosion on changes in catalyst and microporous layer hydrophobicity, the interaction of heat generation, and water retention in corroded PEM fuel cells, neutron imaging of water profiles was measured during carbon corrosion ASTs. Because of the importance of water content in determining corrosion rates, simultaneous high-resolution neutron imaging of the cells was used to calculate through-plane water profiles during the AST series. Polarization curves for a cell with 24BC cathode and anode gas diffusion layer (GDL) are shown in Figure 4a, taken after consecutive cathode holds at +1.3 V (vs. H₂ anode). The dramatic performance loss was typical for the highly oxidizing condition, as carbon loss in the cathode reduces catalytic activity and as pore space collapses. EIS at low and high overpotentials confirmed that both kinetic and mass transport resistances increased.

Water profiles at a constant current density of 0.8 A/cm² (constant water generation rate) are shown in Figure 4b. The consistent trend was of decreased water retention as the cell was increasingly corroded. Given the lowering of cell potential at constant current due to increasing resistances, we attributed the decreased water content to increasing internal heat generation and increasing transport from the MEA to channels. Surprisingly, we saw no evidence of increasing water holdup in the cathode, despite the tendency of corroded carbon surfaces to become more water-wetting [7]. Increased mass transport resistance during the AST was therefore attributed to collapse of porous pathways, instead of increased blockage by liquid.

Conclusions

Catalyst and electrode durability remains a primary degradation mode; however the durability of the electrode is also dependent upon the structure of the electrode. The structure of the electrode is dependent on the solvent structure of the electrode, and the ionomer used. The durability of the electrode may be related to ionomer long-range order and the mechanical strength of the electrode. Post-characterization of the membrane shows changes in crystallinity which are dependent upon relative location to the electrodes. Carbon corrosion induces decreased performance and changes in water content.

Future Directions

Identify and Quantify Degradation Mechanisms

Vary MEA materials to better define degradation mechanisms:

- Expand mixed hydrocarbon and perfluorinated sulfonic acid materials for unambiguous chemical analysis.

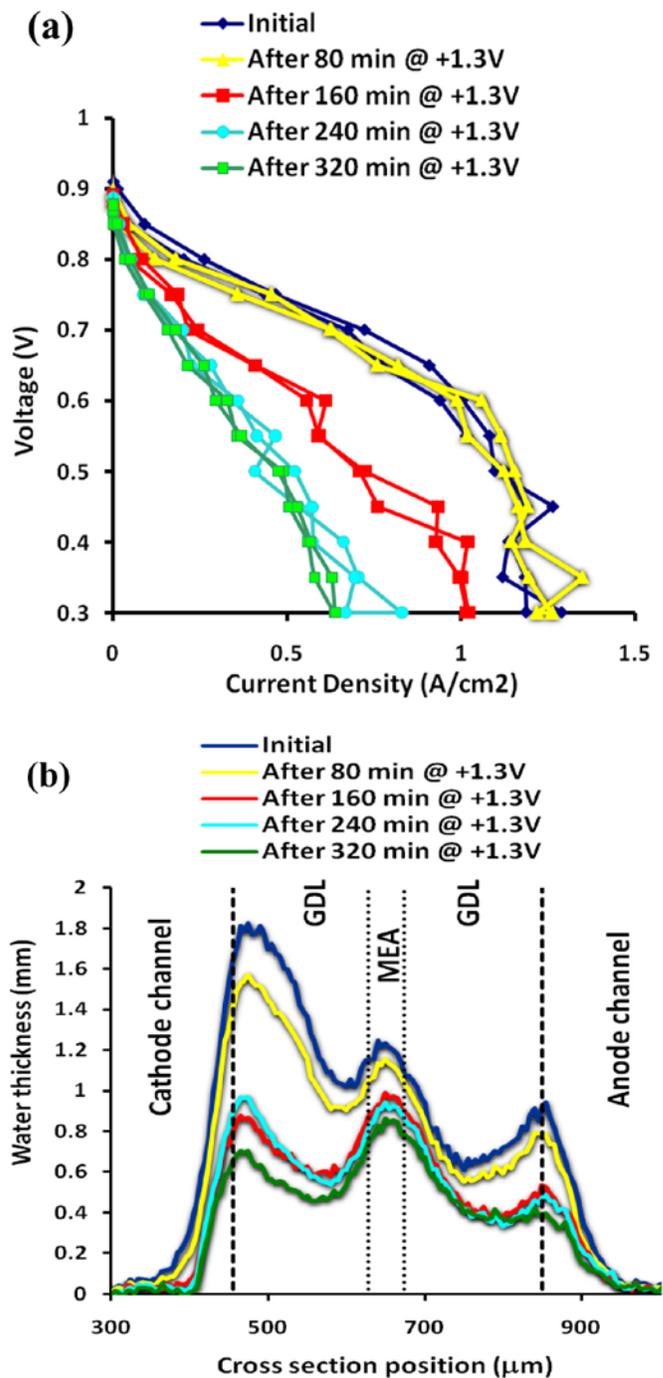


FIGURE 4. (a) Polarization curves for corrosion/imaging cell: 2.5 cm², Gore[®] 510 MEA, SGL[®] 24BC GDLs; H₂/Air, 80°C, 100% relative humidity (RH). (b) Through-plane water profiles for the above cell at a constant current density of 0.8 A/cm², 80°C, 100% RH. Profiles calculated from 20 min. neutron transmission images.

Evaluate degradation rates with MEA materials; guide integrated model development:

- Material variants include: ionomer, membrane, catalyst, support, electrodes.

- >30 MEA variants, >6 AST tests, >3 fuel cell durability tests.
- Incorporate DOE Durability Working Group protocols into testing shutdown/startup.
- Differential scanning calorimetry (DSC) of ionomer identifying changes in water bonding with age.

Electrode Structure

Identify causes behind ionomer and solvent impact on MEA durability:

- Combine microscopic, porosimetry, helox, O₂, and alternating current impedance information.
- Develop model for the SANS data already obtained from electrodes.

Establish correlation of electrode structure durability to mechanical strength:

- Assess mechanical properties and interface strength of electrode measurements.
- Correlate voltage-current-resistance durability by scratch testing of electrodes by nanoindentation.
- Develop test to be used to screen quality of dispersions intended for electrodes.

Assess short-side-chained ionomers using dispersion approach for potential cycling/OCV durability:

- Expand electrode structure durability testing to include fuel cell life testing.
- Extend study of electrode durability by characterization at various MEA life points.

Component Interactions

Five-cell short stack of ~2,000 hours with previously untested seal materials:

- Analyze product water for contamination over the test time.
- Link contaminant type from stack operation to that determined by leach investigation.
- DSC of aged material samples to see if their respective time to oxidation changes.

Metal bipolar plate evaluation and evaluation of interactions with MEA/GDL composite (graphite) bipolar plate evaluation:

- Surface evaluation improving data consistency to evaluate surface properties.

Correlate GDL properties and cell water profile measurements to surface property changes.

Modeling

Water profile modeling during carbon corrosion comparing overpotential and hydrophobicity changes to water transport. Correlate experimental data with detailed membrane modeling to allow prediction of synergistic effects on membrane degradation. Completion of Pt Dissolution Model and Pt Transport Model:

- Addition of impurity degradation.
- Inclusion of other component durability models into integrated model.

FY 2011 Publications/Presentations

1. *Invited talk*, Johnston, C.M; Kim, Y.S., **Ionomer Structure and Electrode Durability, Advances in Materials for Proton Exchange Membrane Systems**, Asilomar, CA, USA, February 20–23, 2011.
2. *Invited talk*, Johnston, C.M; Kim, Y.S., **Solvent Effects on Nafion Dispersion Morphology and Fuel Cell Electrode Structures**, W.L. Gore & Associates, Inc., Elkton, MD, USA, June 4, 2010.
3. *Oral paper*, Johnston, C.M; Ding, Z.; Choi, B; Kim, Y.S., **Effect of Ionomer on Electrode Performance Durability**, 214th Meeting of the Electrochemical Society, Las Vegas, NV, USA, October 10–15, 2010.
4. *Invited talk*, Borup, R.L., **Degradation Mechanisms and Accelerated Testing in PEM Fuel Cells**, Knowledge Foundation's Fuel Cells Durability & Performance, *December 9–10, 2010, Boston, MA*.
5. *Keynote Invited talk*, Borup, R.L., **PEM Fuel Cell Degradation**, 214th Meeting of the Electrochemical Society, Las Vegas, NV, USA, October 10–15, 2010.
6. *Oral Poster*, Bo Li, Yu Seung Kim, Rangachary Mukundan, Mahlon S Wilson, Cynthia Welch, James Fenton, and Rodney L. Borup, **Study of Ionomer Degradation within PEMFC Electrode**, 214th Meeting of the Electrochemical Society, Las Vegas, NV, USA, October 10–15, 2010.
7. *Oral paper*, Joseph Fairweather, Bo Li, Dusan Spornak, Rangachary Mukundan, James Fenton, and Rodney Borup, **In Situ and Ex Situ Characterization of Carbon Corrosion in PEMFCs**, 214th Meeting of the Electrochemical Society, Las Vegas, NV, USA, October 10–15, 2010.
8. *Oral paper*, Karren More, Kelly Perry, Miaofang Chi and Shawn Reeves, **Carbon Support Structural Degradation Observed in PEM Fuel Cell Cathodes**, 214th Meeting of the Electrochemical Society, Las Vegas, NV, USA, October 10–15, 2010.

References

1. Borup, R., J. Meyers, B. Pivovar, et al., *Chemical Reviews*; **107(10)**, 3904 (2007).
2. Chalk S.G.; Miller, J.F. *J. Power Sources* **2006**, 159, 73.
3. Fowler, M., Mann, R.F.; Amphlett, J.C.; Peppley, B.A.; Roberge, P.R., p. *In Handbook of Fuel Cells, Fundamentals, Technology and Applications, vol. 3, Fuel Cell Technology and Applications*, Vielstich, W., Gasteiger, H.A., Lamm A., Eds.; Wiley **2003**, 663.
4. Wilson, M.S., Garzon, F.H.; Sickafus, K.E., Gottesfeld, S.J. *Electrochem. Soc.* **1993**, 140, 2872.
5. Mukundan, R., In *2010 Fuel Cell Technologies Merit Review Meeting*, Washington, D.C., 2010.
6. Borup, R. In *2004 Hydrogen and Fuel Cells Merit Review Meeting*, Philadelphia, PA, 2004.
7. Kangasniemi, K.H., D.A. Condit, and T.D. Jarvi. *Journal of the Electrochemical Society*, 2004. **151(4)**: p. E125-E132.