

V.H.2 Durability Improvements Through Degradation Mechanism Studies

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Objectives

- Identification and delineation of individual component degradation mechanisms.
- Explore Nafion[®] structure and correlate different electrode structure to fuel cell tests:
 - Understand impact of structure electrode on durability and performance.
 - Define different production methods (especially solvents) on electrode structure.
- Quantify influence of operating environment on different component degradation.
- Make degradation measurements of components and component interfaces.

- Elucidation of component interactions, interfaces, operating conditions on cell degradation.
- Develop individual degradation models of all fuel cell components.
- Development and public dissemination of an integrated model of cell degradation.
- Development of advanced in situ and ex situ characterization techniques for analysis of fuel cell component degradation.
- Develop methods to mitigate degradation of components.

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/kWe)

Accomplishments

- Characterization of particle size growth after freeze operation and comparison to drive cycle operation data.
- Measurements of effect of catalytic ink solvent on electrode layer durability:
 - Comparison of electrochemical surface area (ECSA) and mass activity on performance durability.
 - Measurement of mass transport changes in electrode.
 - Characterization of polymer dispersion and electrode structure by small angle neutron scattering (SANS) and nuclear magnetic resonance (NMR).

- Measured water profile changes after severe catalyst carbon corrosion.
- In situ carbon corrosion measurements separating catalyst support, gas diffusion layer (GDL) microporous layer (MPL), and GDL substrate.



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. This team is headed by LANL and includes three other national laboratories (Argonne National Laboratory, Lawrence Berkeley National Laboratory and Oak Ridge National Laboratory), a university (University of New Mexico), a membrane/ionomer supplier (Ion Power), and a stack integrator (Ballard Power Systems).

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 [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

One of the major degradation issues involves the electrocatalyst, and has been studied in some detail [1] yet is not completely understood, nor have the durability issues been fully solved. The cost of the noble metal used in the catalyst makes this a crucial area that requires improvement in durability. For example, Pt particle size has been observed to increase especially during power cycling. Post-characterization of the cathode catalyst by techniques such as transmission electron microscopy (TEM) and X-ray diffraction (XRD) show particle size growth and particle agglomeration. An example of the change in platinum particle size distribution is shown in Figure 1a for operation with the US06 drive cycle.

Similarly, other types of operation show similar Pt particle degradation such as operation at freezing temperatures as shown in Figure 1b. This analysis shows that cathode catalyst coarsening observed over 2,000 hours of drive cycle operation is similar to a short period of operation with freeze cycles. The catalyst particle size is observed to rapidly increase compared with life testing at a constant potential. Also, the degree of particle size growth is dependent upon the amount of water in the system, with operation at 100% relative humidity (RH) showing a higher degree of particle growth (5.0 nm) compared to operation at 50% RH (4.2 nm), compared with an initial average particle size of 2.2 nm. This particle growth is attributed to dissolution and re-precipitation. In addition to the particle size growth, a change in the particle size distribution is occurring, as evidenced by the bi-modal shape observed especially with the 100% RH testing, observed at ~8 nm. This is evidence of particle coalescence, as particle growth by dissolution and re-precipitation should not show a change in the shape in the distribution. A short period of operation with freeze cycles shows a similar cathode catalyst coarsening (see Figure 1b). During freeze operation, significant coarsening of Pt on cathode was observed (from ~2.2 nm to ~4.2 nm) for both tested cells, no difference was observed in the Pt sizes and distributions between the two cells, however this Pt particle growth occurred in only a few hundred hours of operation but with the sub-freezing operation. Figure 2 shows TEM of how the electrocatalyst and the catalyst layer changes during

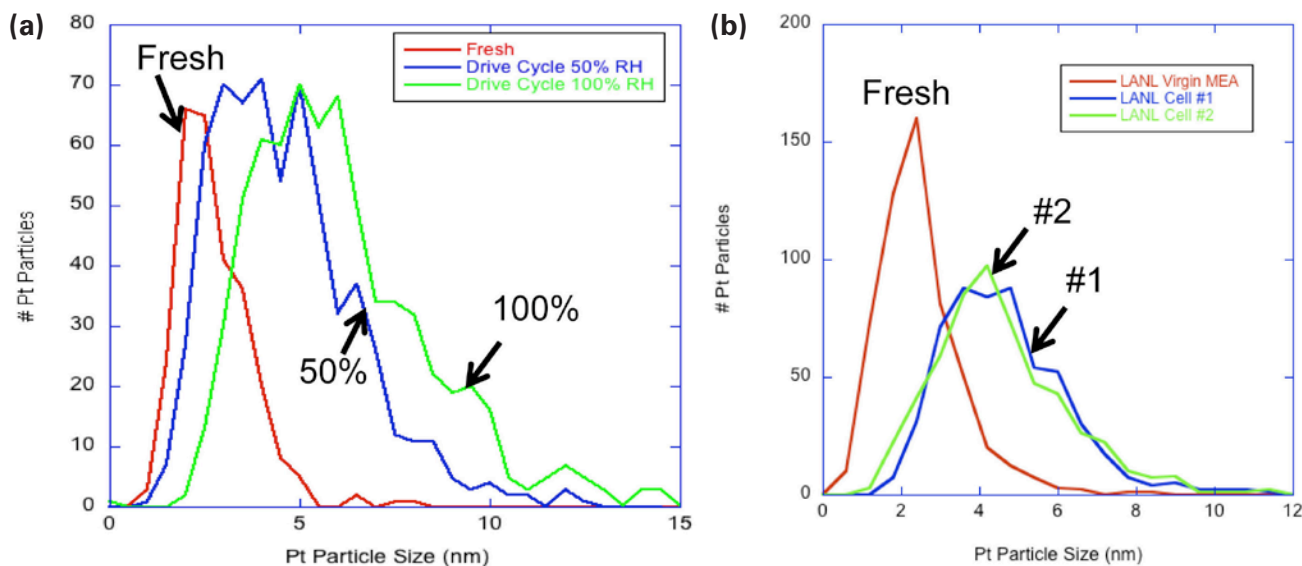


FIGURE 1. (a) Pt particle size distribution for fresh, and after 2,000 hours of simulated US06 drive cycle operation for 50% and 100% RH. Testing conditions are 50 cm^2 N112 single cell, Pt/Pt: 0.2 mg/cm^2 , Cell Temperature: 80°C , constant humidification and constant anode/cathode flowrates. (b) Pt particle size distribution after sub-freezing operation for 5 starts @ -10°C , 5 starts @ -20°C , 3 starts @ -40°C , 50 cm^2 N212 single cell, Pt/Pt: 0.2 mg/cm^2 [6].

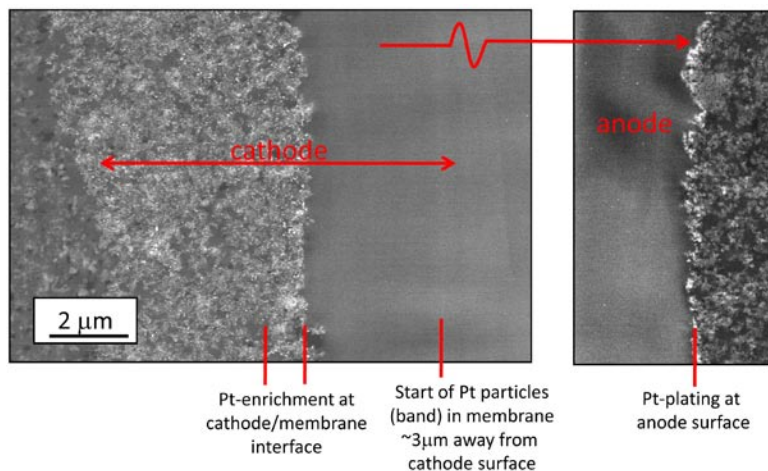


FIGURE 2. TEM images of Pt in the cathode, membrane and anode after sub-freezing operation. (After 5 starts @ -10°C ; 5 starts @ -20°C ; 3 starts @ -40°C .)

operation with freeze. Movement of Pt is observed from cathode to the cathode/membrane interface. Increased Pt agglomeration is observed near interface ($0.2\text{-}0.4 \mu\text{m}$). Pt-particles are observed across the remaining $47 \mu\text{m}$ to anode side however, no Pt particles are observed within $3 \mu\text{m}$ of cathode. Pt particles are also found in the center of the membrane, noting that Pt particles are observed continuously/homogeneously across the membrane starting $\sim 3 \mu\text{m}$ from cathode, with a nominal Pt particle size $\sim 15 \text{ nm}$ diameter. Pt particles are found across membrane up to anode/membrane interface, where the Pt “plates” the anode surface.

The main metrics for analysis of electrocatalyst durability have been ECSA, mass activity, and performance as measured by polarization curves. Post characterization by TEM and XRD has been most widely used to determine the particle size growth. Comparing mass activity and ECSA as a function of particle size can show a good correlation [1,5,6]. This correlation appears to be true for catalysts in certain types of MEAs. However in other types, the correlation can be poor, or even non-existent. An excellent example of this is shown by the polarization performance curves as a function of potential cycles in Figures 3a and 3b and the corresponding ECSA shown in Figures 4a and 4b. This work done by Christina Johnston and Yu Seung Kim at LANL explores the effect of different solvents on the electrode

structure performance and durability. 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. This examination was for identical cathode catalysts.

However, the lack of performance loss appears to not be associated with the catalytic surface area, as in Figure 4a vs. Figure 4b, the loss in catalyst surface area is essentially identical. For the case of electrodes made from a glycerol-based catalytic ink, there is essentially no

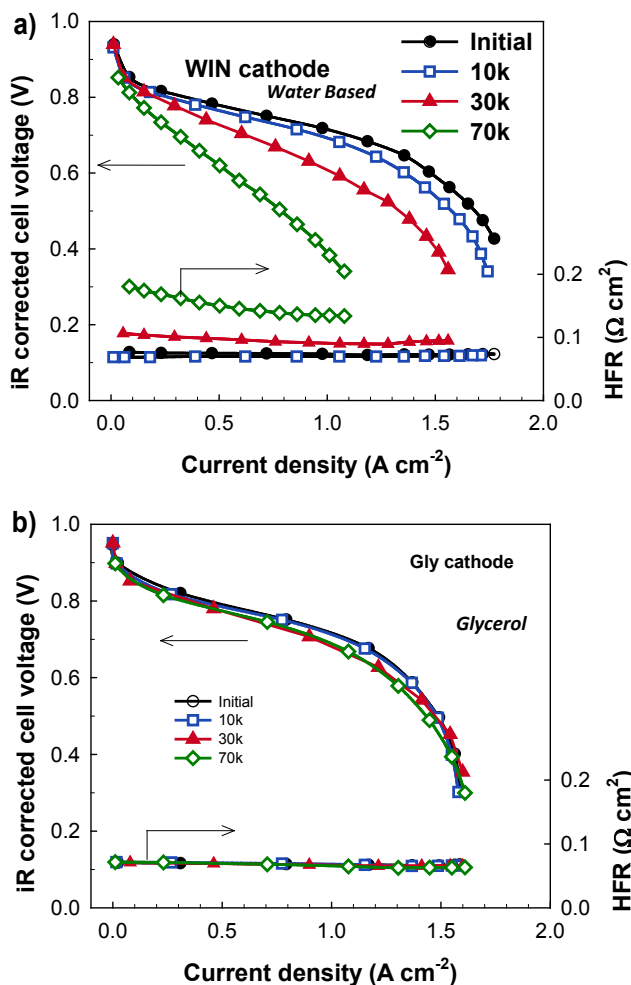


FIGURE 3. Polarization curves of electrodes vs. number of AST potential cycling for (a) water-based electrode and (b) glycerol-based electrode.

correlation between loss of ECSA and performance loss or catalytic mass activity.

Conclusions

To meet commercialization targets, improvements in durability are still required. Catalyst and electrode durability remains a primary degradation mode; catalyst particle growth occurs with potential cycling and with freeze testing/cycling. ASTs are used to rapidly evaluate component degradation, however the results such as ECSA and mass activity are sometimes easy to correlate, and sometimes difficult to correlate. Correlation of the results appears to depend upon the electrode layer structure, and the fabrication process used to produce the electrode. Tests which were developed to accelerate single components also affect the performance in other areas. Examples of this are tests to examine losses due to catalyst degradation and kinetics losses and also lead to losses in mass transport.

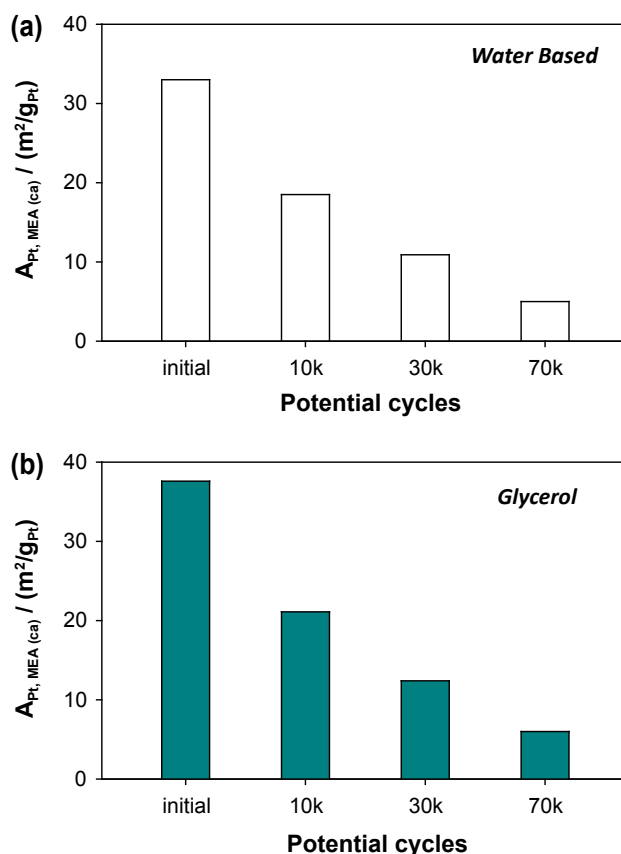


FIGURE 4. ECSA vs. number of potential cycles for (a) water-based electrode and (b) glycerol-based electrode.

Future Directions

- Fuel Cell Durability Testing and Performance Evaluation
 - Elucidation of single component degradation mechanisms:
 - Electrocatalyst, catalyst support, membrane, ionomer, MEA, GDL, metal bipolar plate, carbon bipolar plate, and seals.
 - Elucidation of multi-component degradation mechanisms.
 - Parametric aging studies:
 - Temperature, RH, transients (potential cycling), and shut-down/start-up,
 - Fuel cell testing on mixed MEAs:
 - Mixed Nafion[®]/hydrocarbon membranes and ionomer.
 - Characterization of Nafion[®] within aged electrode films.
 - Evaluation of water/Nafion[®] dispersions tendency to create weaker electrode structures.
- Fuel Cell Component Characterization

- SANS of electrode layers.
- XRD and TEM: higher crystallinity in aged electrodes.
- Neutron reflectivity measurements of swelling of Nafion® films on carbon substrates.
- NMR characterization of aged fuel cell components (membrane, catalyst and GDL).
- Development of in situ analytical techniques:
 - In situ Raman and infrared.
- Effect of film-forming properties on the electrode/membrane interface by X-ray tomography and scanning electron microscopy.
- Fuel Cell Degradation Modeling
 - Development of models for alternating current impedance data; heliox and 100% O₂ experiments.
 - Model membrane degradation:
 - Effect of mechanical loads on chemical degradation.
 - Effect of chemical degradation on mechanical properties.
 - Mechanical failure of the membrane due to RH cycling.
 - Aging of membrane in response to H₂O₂.
 - Model corrosion of the graphite and metallic bipolar plate.
 - Improve model for electrocatalyst degradation and catalyst support carbon corrosion:
 - Account for Pt band formation.
 - Model Pt agglomeration due to carbon corrosion.
 - Carbon oxidation due to potential cycling, startup/shutdown, and fuel starvation.
 - Effect of support loss on ECSA.
 - Model effect of GDL/MPL degradation:
 - Improve transport model to account for measurable properties such as surface energies, internal contact angles, pore size distributions.
 - Model effects of sealants and gaskets including impact of degradation products.

FY 2010 Publications/Presentations

1. Rodney L. Borup and Rangachary Mukundan, **PEM Fuel Cell Degradation**, submitted to 2010 ECS Transactions.
2. Bo Li, Yu Seung Kim, Rangachary Mukundan Mahlon S. Wilson, Cynthia Welch, James Fenton, and Rodney L. Borup, **Characterization of PEM Fuel Cell Ionomer Degradation by use of Hydrocarbon Ionomer and Membranes**, submitted to 2010 ECS Transactions.
3. Joseph Fairweather, Bo Li, Rangachary Mukundan, James Fenton, and Rodney Borup **In Situ and Ex Situ Characterization of Carbon Corrosion in PEMFCs**, submitted to 2010 ECS Transactions.
4. C.M. Johnston, Z. Ding, B. Choi, Y.S. Kim, **Effect of Ionomer on Electrode Performance Durability**, submitted to 2010 ECS Abstract.
5. C.M. Johnston, Y.S. Kim, K.-S. Lee, T. Rockward, D. Torrace, P. Zelenay; A. Labouriau, E. B. Orler, C. Welch, R. Hjelm; N. Mack; M. Hawley; K. More **Understanding and Optimization of Fuel Cell Electrode Structures at Multiple Length Scales**, 2009 Fuel Cell Seminar & Exposition Palm Springs, CA, USA Nov 16 – 19, 2009.
6. M.E. Hawley, Y.S. Kim, R.P. Hjelm, **Scanning Force Microscopy Study of Phase Segregation in Fuel Cell Membrane Materials as a Function of Solvent Polarity and Relative Humidity Treatment**, Materials Research Society Fall 2009 Meeting, Symposium T, Nov. 30, 2009, Vol. 1213E, Boston, MA.

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