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

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Fiscal Year (FY) 2012 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
  – Development of 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 $/kWₑ)

FY 2012 Accomplishments

• Detailed the catalyst degradation mechanism and dependency on loading
• Examined electrode structural changes for different electrode structures and processing techniques for low-loaded cathodes
• Measured chemical changes in catalyst layer ionomer and detailed differences between different types of ionomer
• Quantified carbon corrosion for different types of carbon and different operating parameters
• Modeled the parametric effects on carbon corrosion
• Identified carbon structural changes and localized corrosion
• Measured and modeled hydrogen crossover effect due to Pt particle migration into the membrane
• Measured and quantified surface chemistry changes of carbon bipolar plates
• Conducted parametric studies on metal bipolar plates and examined corrosion rates and increases in contact resistance

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 [1]. 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, accelerated stress tests [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

Correlating Electrode Structure to Durability

We have demonstrated that the solvents used can have a dramatic effect on the performance/durability of fuel cell electrodes, although the catalyst durability is unaffected. Examining the effect of loading on performance from membrane electrode assemblies (MEAs) made via decal process using a more traditional water/alcohol/glycerol mixture in the ink shows that the loading has a significant impact. Figure 1 shows the polarization performance during the potential cycling AST for Pt loadings of 0.25, 0.11 and 0.05 mg/cm². The electrochemical surface area (ECSA) change was similar for the different catalyst loadings at -55%, -56% and -74%, respectively. However, the performance change is substantially different. During potential cycling:

• The ultra-low loading cathode (0.05 mg/cm²) increased in performance
• The "high" loading (0.25 mg/cm²) decreased in performance
• The "low" loading (0.11 mg/cm²) stayed the same

The fact that the ECSA shows similar decreases during the potential cycling indicates that other changes in performance are occurring. Further measurements show that the mass transport resistance is decreasing during the potential cycling. Enhanced performance and impedance behavior of ultra-low loading cathode with potential cycling have similarity with performance improvement with HelOx (or air flow increase). Thus, electrode structural changes occur during potential cycling which favor oxygen diffusion, and lower mass transport resistance.

Noble Metal Loading Effect on Degradation Mechanism

Figure 2 shows how platinum particle size changes during accelerated testing of the catalyst and catalyst support for two different catalyst loadings. The MEAs for the two different ASTs (potential cycling from 0.6–1.0 V in Figure 2a, carbon corrosion AST hold at 1.2 V in Figure 2b) had identical loadings of 0.2 mg/cm² (20 wt% Pt) and 0.4 mg/cm² (40 wt% Pt). The Pt particle size distribution (PSD) growth is identical for the potential cycling AST from ~1.8 nm to ~2.2 nm (Figure 2a). This indicates that dissolution/precipitation particle-growth kinetics is unaffected by Pt particle concentration. However after a carbon support AST, greater Pt coarsening for the cathode with higher Pt loading is observed, showing that an increased concentration of Pt particles led to higher degree of agglomeration (Figure 2b). This demonstrates that rate of platinum agglomeration depends upon the relative loading; more particle agglomeration occurs at high Pt loadings.
Kinetics of Carbon Corrosion: Experimental Measurements and Model Development

Support corrosion leads to detachment and agglomeration of catalyst particles, while weakening of the carbon structure allows collapse of electrode pores and severely limits gas transport [1]. This report includes a summary of ongoing experimental work to improve existing models through inclusion of electrode aging effects. Some clarification will also be offered on the decay of corrosion rates over time under potentiodynamic conditions.

To illustrate typical observed oxidation patterns, potentiodynamic corrosion rates of two different electrodes are shown in Figure 3. Several features for the high surface area support are labeled: we use the peak naming convention

![Graphs and images related to corrosion and performance](image-url)

**Figure 1.** The polarization performance during potential cycling from 0.6–1.0 V for (a) 0.25 (b) 0.11 and (c) 0.05 mg-Pt/cm² cathode loadings. Anode: 0.2 mg-Pt/cm². Membrane: Nafion® 212; Cell: 80°C, 30 psig backpressure. Typical LANL decal process using water/alcohol/glycerol mixture in the ink.

**Figure 2.** Platinum particle size distribution (A) Pt PSD before and after 30,000 0.6–1.0 V cycles (B) Pt PSD before/after 1.2 V hold. Loadings of 0.2 mg/cm² (20 wt% Pt) and 0.4 mg/cm² (40 wt% Pt).
of Maass et al. [2] to describe such plots. Starting with the anodic sweep, peak II is closely related to CO stripping from Pt, or at least CO-like surface species oxidizing in close proximity to Pt.

\[
\text{Pt-CO}_{\text{ad}} + \text{Pt-OH}_{\text{ad}} \rightarrow \text{Pt}_2 + \text{CO}_2 + \text{H}^+ + e^- \quad [1]
\]

Peak IV is the Tafel-region electrochemical oxidation of carbon, increasing exponentially with overpotential.

\[
\text{C} + \text{H}_2\text{O} \rightarrow \text{C-O}_{\text{ads}} + 2\text{H}^+ + 2e^- \quad [2]
\]

\[
\text{C-O}_{\text{ads}} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 2\text{H}^+ + 2e^- \quad [3]
\]

Peak V, which initially appears as a shoulder to Peak IV and becomes prominent for aged electrodes (2), is thought to represent the oxidation of accumulated surface oxides, or equation 3 alone. Switching to the cathodic sweep, Peak III is similarly associated with surface oxides, likely catalyzed by the reduction of Pt oxides below 0.9 V. Peak I is thought to be due to the formation of hydrogen peroxide from trace oxygen, and subsequent chemical attack on carbon.

The role of Pt in corrosion rates has been of special interest. CO\text{2} release at high potentials is generally faster in the presence of Pt [2-4], and this is thought to be due to the catalyzing role of Pt surface oxides:

\[
\text{C-O}_{\text{ad}} + \text{Pt-OH}_{\text{ad}} \rightarrow \text{Pt} + \text{CO}_2 + \text{H}^+ + e^- \quad [4]
\]

However, most of the evidence for corrosion catalysis is under potentiodynamic conditions. For long holds at constant high potential, the effect may be much smaller [5], Peaks II and III only appear on catalyzed electrodes [3], and definitely involve Pt in the CO\text{2} release. Peak I, meanwhile, is much smaller when Pt is present [2], likely due to accelerated chemical decomposition of peroxide.

The Initial Model for Corrosion of High Surface Area Carbon considers:

\[
\text{C} + \text{H}_2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}^+ + 2e^- \quad [5] \\
\text{(Peroxide attack, low potentials)}
\]

\[
\text{C} + \text{H}_2\text{O} \leftrightarrow \text{C-O} + 2\text{H}^+ + 2e^- \quad [6] \\
\text{(Active surface oxide)}
\]

\[
\text{C-O} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 2\text{H}^+ + 2e^- \quad [7] \\
\text{(Electrochemical corrosion)}
\]

\[
x\text{C} + \text{H}_2\text{O} \leftrightarrow \text{C}_x\text{O} + 2\text{H}^+ + 2e^- \quad [8] \\
\text{(Passive surface oxide)}
\]

The model development predicts the effect of cell temperature, showing at higher temperatures, Peak I shifts to lower potentials and decreases in magnitude; Peak IV corrosion rate also increases. Modeling results of the effect of temperature on the carbon corrosion are shown in Figure 3b. At higher scan rates, the corrosion rates are generally higher and the curves lose their fine structure (Peaks II and III disappear). In agreement with equations 5-8, the corrosion rates are higher for higher relative humidity.
Carbon Corrosion shows Localized Structure Changes

Corrosion of catalyst-support carbon leads to numerous changes in the catalyst layer (CL): pore space collapse (lower porosity of the CL), lower electro-active surface area, lower catalyst connectivity, and less hydrophobic pore surface (2). Ex situ characterizations were performed to evaluate morphological changes in the catalyst layer and the gas diffusion layer (GDL) after operation. A surprising result observed by transmission electron microscopy (shown in Figure 4a) is the distinct interface between Pt/high surface area carbon cathode and micro-porous layer (MPL); the MPL carbon retains its meso-graphitic structure and porous network (even adjacent to the cathode surface) whereas the high surface area carbon directly at the interface is fully oxidized and loses its meso-graphitic structure.

In the absence of an MPL, the Pt/C cathode catalyst layer degrades faster due to higher water content during potential holds [5], exhibiting higher kinetic losses, faster Pt particle growth, and faster decrease of the active surface area. In the presence of an MPL, performance degradation is slower, however some cells suffered from mass-transport issues.

Influence of the cathode MPL on the cell degradation rate was investigated by aging cells in situ at 1.3 V (H₂/N₂) with GDL materials with and without an MPL, where two cathode CL materials were compared using (i) commercial carbon-supported Pt MEA supplied by W. L. Gore, and (ii) carbon-free MEA (Pt black). The X-ray tomography shown in Figure 4b illustrates a dramatic non-uniform cathode thinning due to the GDL fibers and water content of the structure, which is not observed for similar measurements for GDLs with MPLs.

Conclusions

Catalyst, support and electrode durability remain primary degradation modes. Measurements show that the degradation is dependent upon the electrode structure, which changes during durability tests, at least in some cases improving transport faster than the kinetics degrade. In other cases, the loading changes the Pt degradation mechanism from primarily dissolution/re-precipitation to include Pt particle agglomeration during support corrosion.

The structure of the support itself changes and is dependent upon the local environment. Loss of meso-graphitic structure of carbon is observed inside the catalyst layer, but not immediately adjacent in the GDL/MPL. The rates of degradation are dependent on many operating parameters including temperature and water content. Some of these were examined by parametric studies, and degradation modeling has modeled the various parameters in different sub-component models. These sub-component models are being integrated to develop an overall model to predict the performance degradation of fuel cells with various materials and operating parameters.

Future Directions

Identify and Quantify Degradation Mechanisms

- Continue examination of MEA materials to better define degradation mechanisms
  - Expand mixed hydrocarbon and PFSA materials for unambiguous chemical analysis
Electrode Structure

- Identify structural change of electrodes during potential cycling and operation
- Identify causes behind ionomer and solvent impact on MEA durability
  - Establish correlation of electrode structure durability to mechanical strength

Start-Up/Shut-Down (SU/SD)

- Series segmented cell SU/SD measurements comparing catalyst support materials
- Compare CO₂ during SU/SD to 1.2 V AST holds
- Compare the degradation mechanisms from the SU/SD to the ASTs

Carbon Corrosion

- Characterize corrosion rates of carbon supports with higher degree of graphitization during the aging process
- Measure and model the effect of aging on carbon corrosion rates:
  - Initial observations: high surface area carbon dropped by ~90%, carbon mass decreased by ~47%, yet the cell capacitance increased and the carbon corrosion rate did not slow down
- Measure and model the effects of carbon corrosion on growth of Pt particles, loss in ECSA and mass transfer overpotentials
- Define the hysteresis and age effect on carbon degradation (i.e. degradation rates: new vs. aged samples)

Component Interactions

- Metal bipolar plate evaluation and evaluation of interactions with MEA/GDL
  - Fuel cell testing of metal materials to correlate corrosion rate to metal cation contamination of membrane and proton conduction
- Composite (graphite) bipolar plate evaluation
  - Standardize surface evaluation improving data consistency to evaluate surface properties

Modeling

- Incorporate parametric studies of components into integrated model
- Water profile modeling during carbon corrosion comparing overpotential and hydrophobicity changes to water transport

FY 2012 Publications/Presentations

Journal Publications


4. 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. Mukundan, Rangachary, Greg James, Dana Ayotte, John Davey, David Langlois, Dusan Spernjak, Dennis Torraco, Sivagaminathan Balasubramanian, Adam Z Weber, Karren More, and Rodney L. Borup Accelerated testing of carbon corrosion and membrane degradation in PEM fuel cells, Submitted to ECS.

Invited Presentations


Contributed Presentations


References


