VII.I.3 PEM Fuel Cell Durability

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Projected End Date: Project continuation and direction determined annually by DOE

Objectives

- Identify and quantify factors that limit polymer electrolyte membrane (PEM) fuel cell durability
  - Measure property changes in fuel cell components during long-term testing
    - Membrane-electrode structure
    - Electrocatalyst activity and stability
    - Gas diffusion layer hydrophobicity
  - Develop and apply methods for accelerated and off-line testing
- Improve durability of fuel cell components

Technical Barriers

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

- A. Durability
- B. Cost
- C. Electrode Performance

Approach

- Fuel cell membrane electrode assembly (MEA) durability testing and examination
  - Constant voltage/current/power and power cycling (drive cycle)
    - 5 cm^2, 50 cm^2 single cells and full-size active area (200 cm^2) stack
    - Voltage – current – resistance (VIR)/cell impedance
    - Catalyst active area
    - Effluent water analysis
  - Simulated vehicle drive cycle and steady-state testing
    - Polarization curve/cell impedance
    - Catalyst active area
    - Effluent water analysis
- *in situ* and post-characterization of membranes, catalysts, gas diffusion layers

- Electron spectroscopies for structural analysis: scanning electron microscopy (SEM)/energy dispersive spectroscopy (EDS) and transmission electron microscopy (TEM)
- Elemental analysis: X-ray fluorescence (XRF) and inductively coupled plasma mass spectrometry (ICP-MS)
- Particle size distribution: X-ray diffraction (XRD)
- Electrochemical surface area: hydrogen adsorption/desorption (HAD)
- Carbon bonding interactions and polymer degradation: neutron scattering
- Development and testing with off-line and accelerated testing techniques
  - Potential cycling
  - Environmental component testing and characterization (gas diffusion layer)
  - Component interfacial durability property measurements
  - Membrane thinning and analysis

Accomplishments

- Durability testing at steady-state conditions and simulating a vehicle drive cycle
- *in situ* characterization of MEAs by polarization curves, electrocatalyst surface area measurements, high-frequency resistance
- Post-characterization of tested MEAs by XRF, XRD, SEM/EDS, TEM
- Off-line testing of fuel cell components
  - Potential cycling evaluation of electrocatalyst
    - Examination of effects of potential range, time vs. number of cycles, humidity, loading, temperature
  - Environmental aging of components
  - Evaluation of hydrophobicity changes in gas diffusion layers (GDLs) and single fibers
  - Particle size correlated to electrochemical surface area

Future Directions

- Incorporate DOE durability test protocol into testing
  - Vary parameters of standard test protocol to advance protocol
  - Incorporate shut-down/start-up and thermal cycles into durability protocol
  - Correlate accelerated testing protocols to fuel cell testing
- Measure membrane/MEA degradation
  - Simulate membrane cross-over by inducing penetrations
  - Develop methods to measure peroxide formation
- Study gas diffusion layer
  - Conduct off-line testing determining hydrophobicity degradation
  - Determine poly-tetrafluoroethylene (PTFE)/graphite bonding interaction changes
- Conduct catalyst characterization and durability testing
  - Examine some Pt alloys for particle size growth with *in situ* XRD
  - Analyze particle size in real time during simulated fuel cell operation
  - Model platinum particle growth
  - Examine carbon corrosion during simulated shut-down scenario

Introduction

The durability of PEM fuel cells is a major barrier to the commercialization of these systems for stationary and transportation power applications. Commercial viability depends on improving the durability of the fuel cell components to increase the system reliability and to reduce the system lifetime cost by reducing the stack replacement frequency. Durability is difficult to quantify and improve not only because of the quantity and duration (*i.e.*, up to several thousand hours or more) of testing required, but also because the fuel cell stack is a system of components, electrocatalysts, membranes, gas diffusion layers, and bipolar plates, for which the degradation mechanisms, component interactions and effects of operating conditions are not fully understood. The acquisition of 5000 hours of durability test data on a fuel cell stack or single cell will not lead to a comprehensive understanding of the degradation mechanisms. To improve fuel cell component durability, and thus fuel cell stack durability, the individual components must be well-characterized to determine and quantify degradation mechanisms that occur. This requires development of *in situ* diagnostics and unique experiments to characterize the performance and properties of components as a function of time. Using these measurements, along with extensive post-mortem characterization, degradation mechanisms can be delineated to help develop more durable fuel cells and fuel cell components.

This report describes our FY 2005 technical progress in characterizing and quantifying the durability of fuel cell components and their degradation mechanisms to support the DOE target for 5000 hr durability of PEM fuel cell systems. We conducted fuel cell testing, coupled with accelerated off-line testing. Post-mortem characterization of the fuel cell components was conducted to identify changes in the catalyst and membrane and mechanisms of failure.

Approach

Our approach to improving PEM fuel cell durability is to define and understand the degradation mechanisms of fuel cell components to allow the design of improved fuel cell materials and

components This approach also will define operating conditions that promote degradation, which will identify operational constraints to improve durability.

PEM fuel cell durability testing is performed on single cells with active areas of 5 cm^2 and 50 cm^2, and on a full-size active area (200 cm^2) stack. Tests are conducted with steady-state conditions (both constant voltage and constant current) and with dynamic conditions using power cycling to simulate a vehicle drive cycle. Measurements of polarization curves, membrane resistance, hydrogen cross-over and electrochemical surface area are made *in situ* by measuring hydrogen adsorption/desorption (HAD) periodically during the durability test to characterize those fundamental properties changing as a function of time. Effluent water analysis (elemental analysis, ionic content and pH) is conducted to monitor for degradation products. Scanning electron microscopy/energy dispersive x-ray spectroscopy (SEM/EDS), X-ray fluorescence (XRF), X-ray diffraction (XRD), transmission electron microscopy (TEM), and neutron scattering are used to characterize changes in the membrane and catalyst after the durability test.

Work is ongoing to use offline testing and characterization to develop accelerated testing techniques and to differentiate the contributions of fuel cell components such as the electrocatalyst and membrane to the degradation of the overall performance. A potential sweep method is applied to single cells to investigate its use as an accelerated testing technique. Degradation mechanisms of individual components, initially the gas diffusion layer, are being investigated off-line with an environmental/leachate chamber.

Results

Electrocatalyst Characterization and Cycling

Previous results have shown that the active surface area of the fuel cell electrocatalyst decreases faster during drive cycle operation than during constant potential or current testing [1]. Potential cycling of an MEA was used to examine the operating conditions leading to loss of electrocatalyst surface area. In addition, potential cycling was
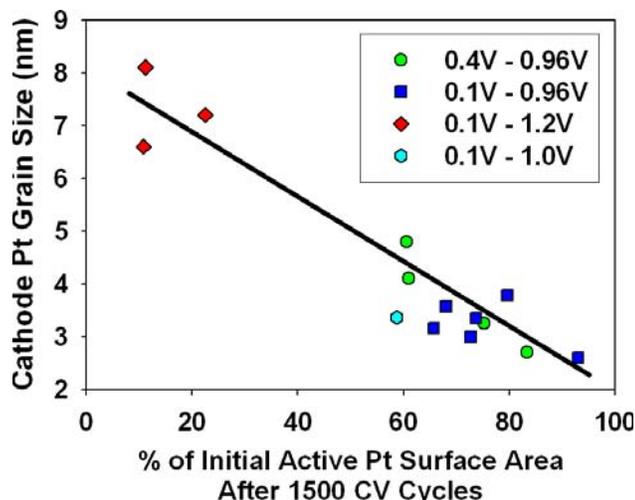
Figure 1. Particle Size as Determined by XRD and Measured Electrochemical Active Surface Area for Various Cycling Experiments

examined as a possible accelerated testing method for electrocatalysts. During potential sweeping, the anode was exposed to hydrogen while the cathode was exposed to nitrogen. The cathode potential was swept linearly from an initial voltage (usually 0.1 V) to an upper limit voltage. After cycling intervals, the polarization curve of the MEA and the catalyst surface area were measured. After the cycling experiment was completed, post-characterization was performed by XRD, SEM and TEM.

The use of XRD analysis to determine the degree of electrocatalyst sintering was validated by comparing the particle size with the measured electrochemically active surface area (Figure 1). As expected, there is a linear relationship between the platinum particle size and the measured catalytic surface area. This verifies that the XRD post-mortem measurement of platinum particle size is correlated to platinum surface area loss, i.e., growth in particle size leads to catalyst surface area loss.

Previous results showed that the cathode particle size increased with increasing potential. However, use of a linear sweep rate increased the time at the high potentials. To identify whether the time at potential or the number of cycles caused the particle size growth, cycling was conducted at different sweep rates: 10 mV/sec and 50 mV/sec. This comparison is shown in Figure 2. The electrochemical surface area is plotted for the two
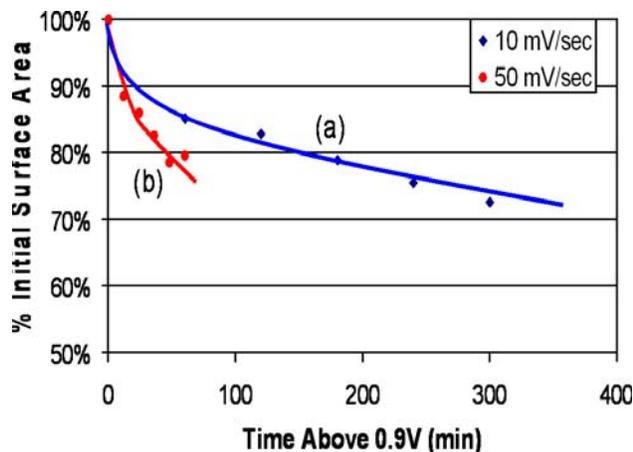
Figure 2. Electrocatalyst Surface Area During Cycling Experiments Comparing Scan Rates of (a) 10 mV/sec and (b) 50 mV/sec (Plotted as a function of time above 0.9 V. Cycling conditions: 0.4 mg/cm^2, 0.1 V - 0.96 V, T_{cell} = 80°C, $T_{anode\ humidifier}$ = 105°C, $T_{cathode\ humidifier}$ = 80°C.)
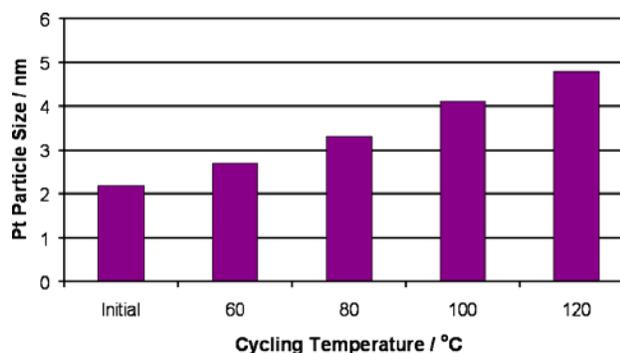
Figure 3. Platinum Particle Size after Cycling from 0.1 V – 0.96 V as a Function of Operating Cell Temperature

sweep rates as a function of time over 0.90 V. As seen in the comparison, the number of cycles is responsible for the vast majority of the effect in loss of platinum surface area. Time at high potential shows a secondary effect compared with the number of cycles.

The effect of operating temperature was examined during potential cycling and is shown in Figure 3. An increase in operating temperature correlates with increasing particle size. The effect of catalyst loading also was examined, using loadings of 0.40 mg/cm^2 and 0.2 mg/cm^2 of 20% Pt/C. The

change in loading did not cause a difference in platinum particle size growth.

Platinum particle size growth appears to be a function of many parameters. The XRD analysis of the particle size distribution provides insight into the mechanism. As the catalyst ages, it retains the log normal particle size distribution it had as a fresh catalyst. This is an indication that the growth mechanism does not occur by long-range Ostwald ripening. TEM images of the catalyst materials before and after testing [2] provide further evidence of the mechanism. These images indicate that many platinum particles are not sufficiently anchored to the carbon support, and they move into the ionomer layer in the catalyst layer. These particles seem to show a more rapid tendency to coalesce into larger particles.

Additional evidence for the mechanism for platinum particle growth comes from the platinum solubility in acidic solution [3]. Platinum solubility is a function of potential, with the solubility changing over two orders of magnitude from 0.7 to 1.0 V. Thus, as a fuel cell is tested during cycling conditions, especially between ~0.7 V to open circuit (~ 0.96 V), platinum solubility indicates that platinum will go into solution at the high potential of open circuit, then be forced to precipitate back out as the potential is decreased.

The corrosion of the electrocatalyst support is an additional issue with durability. This was measured for various operating conditions by comparing the relative XRD signals of platinum and carbon and comparing the signals with the initial material. The same conditions were examined as for platinum particle sintering, including sweep rate, potential, humidity, catalyst loading and temperature. Shown in Figure 4 are the platinum/carbon XRD signals for potential and relative humidity (RH). With increasing potential, a decrease in the carbon signal was measured, indicating carbon corrosion occurred. Similarly, at low RH, carbon corrosion occurred. Temperature, sweep rate, and catalyst loading did not show an effect on carbon corrosion under the condition tested.

Gas Diffusion Media Characterization

In order to quantify GDL hydrophobicity loss, the RH fingerprint is used as a function of durability testing time and for before/after comparison of an
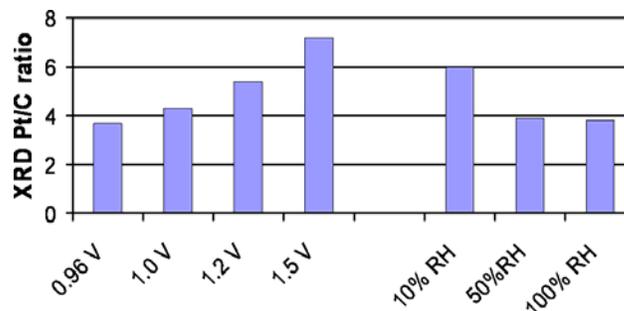
Figure 4. Carbon Corrosion as Measured by Relative XRD Pt/C Ratio after Cycling as a Function of Potential and Humidity (Cell temperature = 80°C, Sweep rate = 10 mV/sec. Humidification as in Figure 2 except where stated. Potential to 0.96 V, except where stated.)
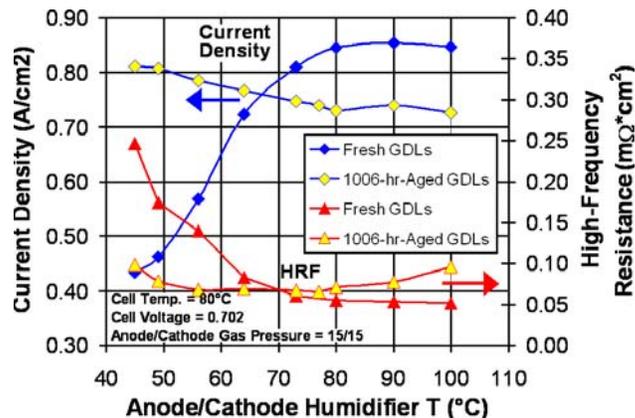
Figure 5. Comparison of RH-Sensitivity Scans between Unaged GDLs and GDLs Aged for ~1000 hr in 80°C Deionized Water with Air Sparging

accelerated/aging experiment. Figure 5 shows the results of two different cells with identical components (3M MEA and Sigri Great Lakes Technologies GDL 24BC at both sides) during the early stages of life testing. GDL 24BC is a paper substrate (~200 μm) with 5 wt% PTFE in the substrate and 23 wt% in the microporous layer (MPL) (~40 μm). One set of GDLs was aged for ~1000 hr in 80°C de-ionized water with air sparging, while the other set was not aged. The two GDL sets exhibit entirely different RH sensitivities, with the unaged GDLs showing the RH fingerprint of the "classic" hydrophobic GDL (fluoropolymer impregnation of the substrate and single-sided MPL coating). In this experiment (see Figure 5), the conventional type of hydrophobic GDL is sensitive to dry conditions, showing low performance and
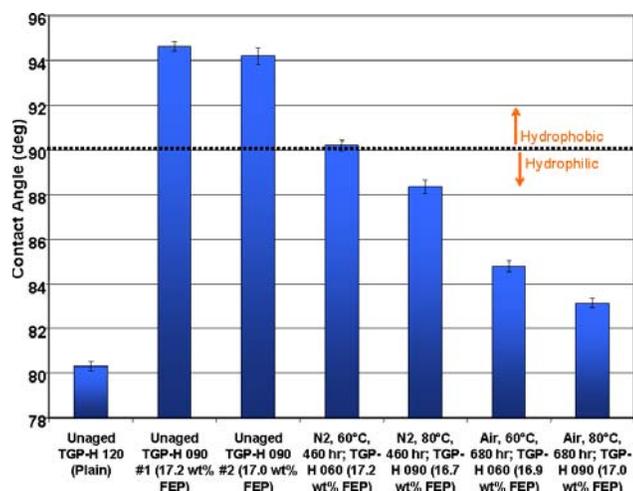
Figure 6. Single-Fiber Contact Angle Measurements of GDL (a) Untreated Toray Fiber: 80.3°, (b) Toray TGP-H090 17.2 wt% FEP aged: 94.6°, (c) Toray TGP-H-090 16.7 wt% FEP - 460 hr in N_2 80°C: 88.4°, (d) Toray TGP-H-060 17.0 wt% FEP - aged 680 hr in Air 80°C: 83.2°

unstable high-frequency impedance (HFR) readings, and demonstrates excellent management of excess liquid water (high performance at high RH values). The aged GDLs show an RH fingerprint resembling a less hydrophobic (or even hydrophilic) GDL, characterized by higher cell performance under dry conditions and lower cell performance under wet conditions (due to flooding). Less hydrophobic and mildly hydrophilic GDLs typically exhibit less sensitivity to inlet water vapor as well, as evidenced by the flatter RH-sensitivity profile of the aged GDLs.

Figure 6 shows the single-fiber Wilhelmy contact angles for aged samples. The plain Toray graphite paper – high conductivity (TGP-H) fibers exhibit hydrophilic behavior. Once 17-wt% fluorinated ethylene propylene (FEP, Teflon®) is added, corresponding to a common bulk hydrophobic treatment, the single-fiber contact angle sharply increases from 80.3° to 94.4°. As the aggressiveness of the aging conditions was elevated, *i.e.*, the temperature of the water was increased by 20°C and the presence of dissolved O_2 was added, the contact angles measured at the end of each experiment decreased slightly. Aging conditions of 60°C and N_2 sparging brought the single-fiber contact angle down

to the hydrophilic/hydrophobic threshold (90.2°), and conditions of 80°C and air sparging brought the contact angle down to nearly the value of the plain, unaged graphite fiber (83.2° and 80.3°, respectively).

Conclusions

- Electrocatalyst surface area loss is due to the growth in platinum particle size.
- Particle size growth is exacerbated by potential cycling.
- Particle size growth occurs more rapidly at higher potentials.
- Increased temperature increases particle growth.
- Low RH decreases particle growth.
- Carbon corrosion increased with increasing potential and decreasing humidity.
- The hydrophobicity of GDL materials was measured to decrease rapidly with aging with air.
- Aged GDL materials show dramatically different humidification performance fingerprints.

Special Recognitions & Awards

1. 2004 Fuel Cell Seminar (San Antonio) Best Poster Presentation Award
2. 2005 DOE Hydrogen Program R&D Award

FY 2005 Publications/Presentations

1. Microstructural Changes of Membrane Electrode Assemblies during PEFC Durability Testing at High Humidity Conditions, Xie et al., *Journal of The Electrochemical Society,* **152** 5 A1011-A1020 2005

2. Durability Study of Polymer Electrolyte Fuel Cells at High Humidity Conditions, Xie et al., *Journal of The Electrochemical Society*, **152** A104-A113 2005

3. Effects of Long-Term PEMFC Operation on Gas Diffusion Layer and Membrane Electrode Assembly Physical Properties, Wood et al., 206th Meeting of The Electrochemical Society, Honolulu, Hawaii, October 5, 2004

4. Long-Term Performance Characterization of Proton Exchange Membrane Fuel Cells, Wood et al., 206th Meeting of The Electrochemical Society, Honolulu, Hawaii, October 5, 2004

5. Characterization of Nanocrystalline Fuel Cell Catalysts by X-ray Profile Fitting Methods, Garzon et al., 206th Meeting of The Electrochemical Society, Honolulu, Hawaii, October 5, 2004

6. Durability Issues of the PEMFC GDL and MEA Under Steady-State and Drive-Cycle Operating Conditions, Borup et al., 2004 Fuel Cell Seminar, San Antonio, Texas, November 1-5, 2004

7. PEM Electrocatalyst Durability Measurements, Borup et al., The Electrochemical Society, Las Vegas, Nevada, June 12-17, 2005

8. Mass-Transport Phenomena and Long-Term Performance Limitations in H_2-Air PEMFC Durability Testing, Wood et al., To be presented at the Fuel Cell Seminar, 2005, Palm Springs, California, November 14-18, 2005

9. PEM Fuel Cell Durability, Borup et al., 2005 DOE Hydrogen Program Review, Arlington, Virginia, May 25, 2005

References

1. R. Borup, M. Inbody, J. Davey, D. Wood, F. Garzon, J. Tafoya, J. Xie and S. Pacheco, "PEM Fuel Cell Durability," DOE Hydrogen Program, FY 2004 Progress Report.

2. K.L. More and K.S. Reeves, "Microstructural Characterization of PEM Fuel Cell MEAs," 2005 DOE Hydrogen Program Review, Arlington VA, May 25, 2005.

3. Xiaoping Wang, Romesh Kumar, and Deborah Myers, "Cathode Electrocatalysis: Platinum Stability and Non-Platinum Catalysts," 2005 DOE Hydrogen Program Review, Arlington VA, May 25, 2005.