IV.I.3 PEM Fuel Cell Durability

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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
    - Corrosion products
  - 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:

- P. Durability
- Q. Electrode Performance
- O. Stack Material & Manufacturing Cost

Approach

Test durability of PEM fuel cells

- 5-cm^2, 50-cm^2 single cells and full-size active area (200 cm^2) 12-cell stack
- Testing: simulated vehicle drive cycle and steady-state testing
  - Polarization curve/cell impedance
  - Catalyst active area
  - Effluent water analysis

Conduct *in situ* and post characterization of membranes, catalysts, gas diffusion layers

- Electron spectroscopies for structural analysis: SEM/EDS and TEM
- Elemental analysis: XRF and ICP-MS
- Particle size distribution: XRD

- Electrochemical surface area: H_2 adsorption
- Carbon bonding interactions/polymer degradation: neutron scattering

Develop and test with off-line and accelerated testing techniques

- Potential sweep methods
- Environmental/leachate chamber
- Corrosion tests

Accomplishments

- Durability testing at steady-state conditions and simulating a vehicle drive cycle
- *In situ* characterization of membrane electrode assemblies (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

Future Directions

- Correlate potential cycling tests to drive cycle testing for accelerated testing
- Membrane/MEA degradation
  – Correlate F^- and SO_4^{-2} ions with hydrogen cross-over in membrane
  – Examine Nafion degradation via neutron scattering
  – Simulate membrane cross-over by inducing penetrations
- Gas diffusion layer (GDL)
  – Continue off-line testing determining hydrophobicity degradation
  – Determine poly-tetrafluoroethylene (PTFE)/graphite GDL bonding interaction changes
- Catalyst durability/characterization
  – Examine some Pt alloys for particle size growth
  – Conduct *in situ* XRD - real-time particle size analysis during simulated fuel cell operation

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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. 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. Simply acquiring 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. The individual components must be well characterized during durability testing to determine and quantify degradation mechanisms that occur over long periods [1]. Chemical degradation mechanisms in an operating environment are likely interconnected due to trace compounds that leach out of one component and subsequently affect another. For this reason, how each key component degrades separately must be well understood in order to understand its effect on the other components. 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 2004 technical progress in characterizing and quantifying the durability of fuel cell components and their degradation mechanisms to support the DOE target for 5000-hour fuel cell durability. We conducted steady-state durability testing of fuel cell stacks and single cells along with dynamic testing that would be more typical of transportation applications. Post-mortem characterization of the fuel cell components was conducted to identify changes in the catalyst and membrane and mechanisms of failure. We also developed off-line and accelerated testing experiments and applied those to examine the degradation mechanisms of single cells, gas diffusion layers, and bipolar plates.

Approach

PEM fuel cell durability tests are 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) 12-cell 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* 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 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 following the experiments.

Work is ongoing to use off-line 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 gas diffusion layer, are being investigated off-line with an environmental/leachate chamber.

Results

MEA Testing

Steady-state durability testing of MEAs was conducted in single cells operating with pure hydrogen. Figure 1 shows the performance of two N112 MEAs that operated at constant voltage (0.6 V) for 3500 hours before complete failure. MEA1 operated for 3000 hours with no decrease in current, while over the same time the current of MEA2 decreased at 2 microamps/hour. After 3000 hours, the current output of both MEAs decreased rapidly, probably due to the formation of small holes as detected by an increase in measured hydrogen cross-over. Final measurements of the MEA catalyst surface area showed an area reduction of 14% in the cathode and 0% in the anode for MEA1 and a reduction of 86% in the cathode and 75% in the anode of MEA2. The significant difference between the surface area reduction of the two MEAs is not due to catalyst particle size, as XRD analysis showed that the platinum particle size was the same for both

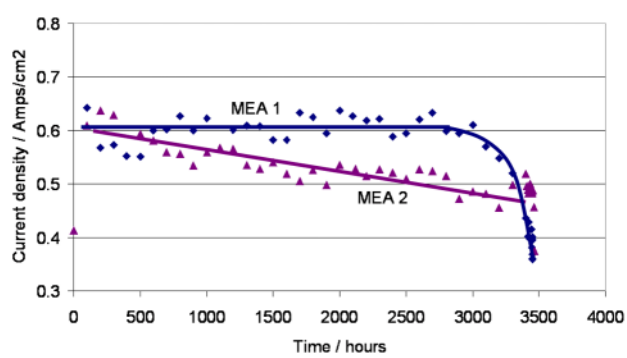

Figure 1. 3500-Hour Life Test of Two N112 MEAs (Active Area: 50 cm^2; Constant Voltage: 0.6 V; Platinum Loading: 0.2 mg/cm^2; Cell Temperature: 80ºC; Anode/Cathode Humidifier Temperature: 105/80°C; Anode/Cathode Gas Pressure: 15/15 psig)

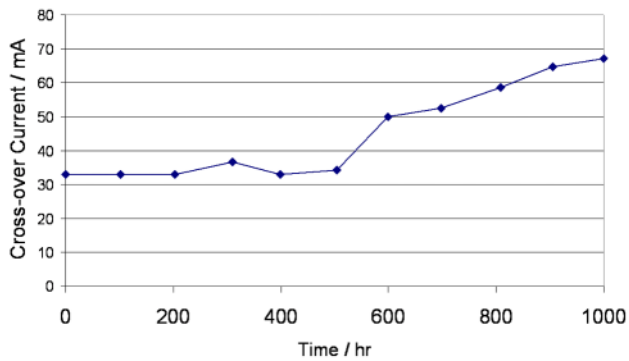

Figure 2. Measured Hydrogen Cross-Over Current during 1000-Hour Life Test (5 cm^2 active area)

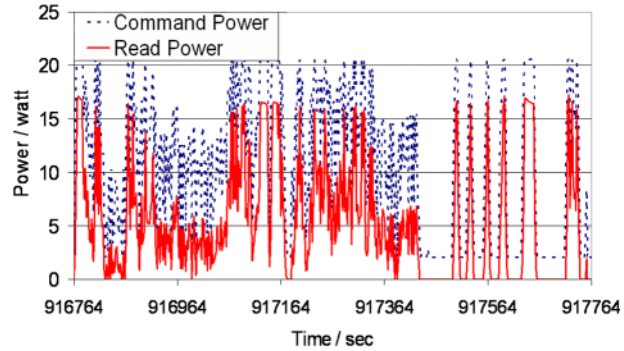

Figure 3. Comparison of the Commanded Power to the Actual Power Output for the Final Drive Cycle in a 1200-Hour Test (Testing conditions are 50-cm^2 N112 single cell, Pt/Pt: 0.2 mg/cm^2, Cell Temperature: 80ºC, constant humidification and constant anode/cathode flowrates)

MEAs at about 2.2 nm for the anode and 3.2 nm for the cathode.

During steady-state durability testing, electrochemical potential voltammograms are performed to quantify the electrode active surface area and membrane permeability. Figure 2 shows the measured hydrogen cross-over current for a 5-cm^2 single cell over a 1000-hour test. The hydrogen permeation rate remains constant for the first 500 hours, then increases after that. This increase in hydrogen cross-over may be due to a decrease in the thickness of the membrane, which eventually leads to hole formation and large hydrogen cross-over as seen in the test shown in Figure 1. During operation of the single cells, samples of water condensed from the anode and cathode exhaust were collected and analyzed for elemental content, ionic content and pH. Sharp increases in fluoride ion content and a decrease in the cathode effluent pH appear to coincide with the increased hydrogen cross-over and possible hole formation.

Dynamic durability testing was conducted on single cells using a drive cycle to vary the power output continuously over the life test. Cell voltage was computer-controlled to a 20-minute voltage drive cycle derived from the measured single cell polarization curve and a fuel cell power drive cycle provided by the National Renewable Energy Laboratory (NREL) [2]. Anode and cathode flow rates, humidification and temperature were held constant while the voltage was varied. Figure 3 compares the commanded power from the single cell with its actual power output over the final drive cycle of a durability test. The power output has decreased significantly from the peaks, whereas the actual power output tracked closely on the initial drive cycles. Single-cell MEA durability in drive-cycle testing, approximately 1200 hours, was shorter than that for steady-state testing (3500 hours) before MEA failure occurred, while operating conditions were similar.

Offline Testing and Characterization

Potential sweeping of an MEA was used as a potential accelerated testing technique. For this study, the anode was exposed to hydrogen while the cathode was exposed to nitrogen. The cathode potential was swept at 10 mV/sec from ~0.1 V to either 1.0 or 1.2 V. After intervals of 300 sweeps, the polarization curve of the MEA and the catalyst surface area were measured. Figure 4 shows the catalyst surface area as a function of potential sweep cycles for potential sweeps to 1.0 V and 1.2 V at temperatures of 60ºC and 80ºC. The electrochemical (EC) surface area decreased more rapidly with potential sweeps to 1.2 V than to 1.0 V. Operation at 80ºC decreased the surface area more rapidly than operation at 60ºC during cycling to 1.2 V.

X-ray fluorescence measurements of the quantity of platinum remaining on the MEA after potential sweep testing showed no loss in platinum. Therefore, either platinum sintering or loss of electronic and/or protonic connection to the cell caused the measured changes in platinum active surface area. Although platinum migration has been

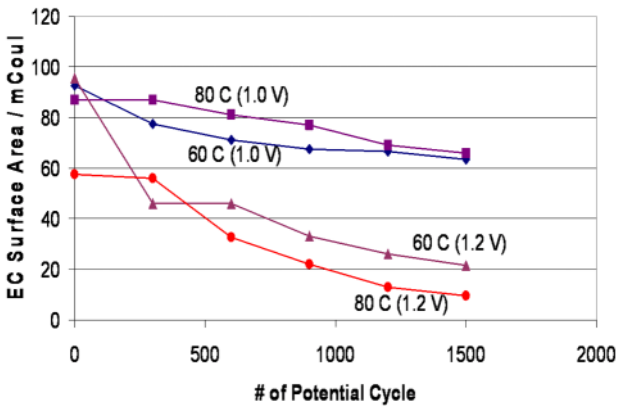

Figure 4. Measured Catalyst Surface Area as a Function of Number of Potential Cycles During Potential Cycling of the MEA Cathode (Voltage cycles from 0.1 V to 1.0 and 1.2 V, and at cell temperatures of 60ºC and 80ºC)

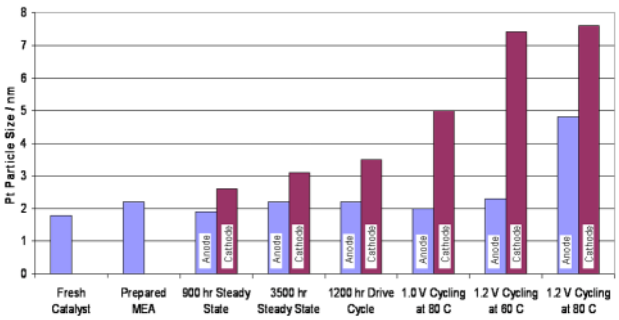

Figure 5. Summary of Electrocatalyst Particle Size by XRD Analysis of 20% Pt/XC-72R, Fresh Catalyst, Catalyst after Prepared MEA, 900-Hour Steady-State Test, 3500-Hour Steady-State Test, Cycling to 1.0 V (1500 cycles, 80ºC), 1200-Hour Simulated Vehicle Drive Cycle Testing, Cycling to 1.2 V (1500 cycles, 60ºC), and Cycling to 1.2 V (1500 cycles, 80ºC)

reported [1] and platinum has been measured in the fuel cell effluent water [3], the major fraction of the platinum remains on the MEA.

The catalysts were further analyzed by XRD to determine the degree of electrocatalyst sintering. Figure 5 summarizes these measurements. Anode catalyst size was nearly uniform at 2.2 nm for all experiments, except for significant growth to 4.8 nm in the potential sweep experiments at 1.2 V and 80ºC. In contrast, cathode particle size grew in all of the experiments, with the growth depending on

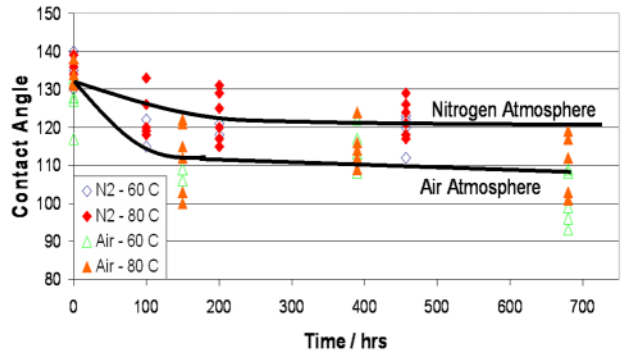

Figure 6. Contact Angle of GDL as a Function of Immersion Time in Deionized Water during Exposure to Nitrogen and Air

temperature, test length, and sweep potential. Growth of cathode catalyst particle size was greatest in the potential sweeping experiments and increased with the potential. In the single cell durability testing, the cathode catalyst particle size grew higher, to 3.5 nm, in the drive cycle experiments than in the steady-state experiments (particle sizes of 2.6 nm at 900 hours and 3.1 nm at 3500 hours).

Off-line testing of gas diffusion layers (GDLs) was conducted to measure changes in hydrophobicity. The GDLs were immersed in de-ionized water in the environmental/leachate chamber at two temperatures, 60ºC and 80ºC, and with either air or nitrogen sparging. Figure 6 shows the change in contact angle, a measure of the hydrophobicity, as a function of immersion time. The hydrophobicity of all samples decreased with time, but those exposed to air decreased further than those exposed to nitrogen.

Conclusions

Durability testing and accelerated testing have identified areas where improvement is needed to reduce the degradation of fuel cell components in order to achieve the durability goal of 5000 hours of operation. One area for improvement is reducing the loss of active catalyst surface area caused by both catalyst sintering and detaching of clusters from the catalyst layer surface, possibly by ionomer dissolution. The decrease in active area occurred primarily in the cathode catalyst and continued throughout a life test as determined by surface area and particle size measurements. Drive cycle testing and potential sweep testing increased the cathode

particle size growth rate, as did increasing the temperature from 60ºC to 80ºC.

Another needed improvement involves preventing the failure of MEAs due to hydrogen cross-over, which was observed to increase after a period of operation. Eventually, small holes in the membrane appear which decrease performance rapidly. Changes in fluoride ion and sulfate ion concentrations and the effluent pH may coincide with the hole formation in the membrane.

Gas diffusion layers show an initial decrease in their hydrophobicity, which levels out after a period of 100 to 150 hours, a relatively short period compared to the time scale of 5000 hours. Exposure to air decreased the hydrophobicity more than exposure to an inert nitrogen atmosphere.

References

1. J. P. Meyers and R. M. Darling, Abstract 1212, *The Electrochemical Society Meeting Abstracts*, Vol. 2003-1, Paris, France, April 27-May 2, 2003.

2. Tony Markel. National Renewable Energy Laboratory, private communication.

3. Jian Xie, David Wood, Douglas Blom, and Wayne Smith, Electrochemical Society Meeting, Fall 2003.

FY 2004 Publications/Presentations

1. Jian Xie, David L. Wood, III, David M. Wayne, Thomas A. Zawodzinski, Plamen Atanassov, and Rodney L. Borup, "Durability of Polymer Electrolyte Fuel Cells, at High Humidity Conditions", submitted to Journal of Electrochemical Society.

2. Jian Xie, David L. Wood, III, Karren L. More, Plamen Atanassov, and Rodney L. Borup, "Microstructural Changes of Membrane Electrode Assemblies During Polymer Electrolyte Fuel Cell Durability Testing at High Humidity Conditions", submitted to Journal of Electrochemical Society.

3. Jian Xie, David Wood, Douglas Blom, and Wayne Smith, "Correlation of MEA Structural Changes and Performance During the Life Test of a Polymer Electrolyte Fuel Cell", presented at the Electrochemical Society Meeting, Fall 2003.

4. Rodney L. Borup, Michael A. Inbody, David L. Wood, III, Susan D. Pacheco, Dennis R. Guidry, Jian Xie, José I. Tafoya, and Douglas Blom, "Fuel Cell Reformer and Stack Durability: Gasoline Reformate & Hydrogen – PEM Fuel Cell Durability", presented at the Fuel Cell Seminar, November 2003, Miami, FL.

5. David Wood, Jian Xie, Susan Pacheco, John Davey, Plamen Atanassov and Rodney Borup, "Durability Issues of the PEMFC GDL and MEA Under Steady-State and Drive-Cycle Operating Conditions", accepted to the 2004 Fuel Cell Seminar Meeting.

6. David Wood, Jian Xie, Susan Pacheco, John Davey, Plamen Atanassov, and Rodney Borup, "Long-Term Performance Characterization of Proton Exchange Membrane Fuel Cells", submitted to the Electrochemistry Society, Fall 2004 meeting.

7. David Wood, John Davey, Fernando Garzon, Plamen Atanassov, and Rodney Borup, "Effects of Long-Term PEMFC Operation on Gas Diffusion Layer and Membrane Electrode Assembly Physical Properties", submitted to the Electrochemistry Society, Fall 2004 meeting.

8. F. H. Garzon, R. Borup, D. Wood, J. Davey and E. L. Brosha, "Characterization of Nanocrystalline Fuel Cell Catalysts by X-ray Profile Fitting Methods", submitted to the Electrochemistry Society, Fall 2004 meeting.