V.G.4  PEM Fuel Cell Durability

Objectives

Identify and quantify factors that limit proton exchange 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 barrier from the Fuel Cells section (section 3.4.4.2) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

(A) Durability

Technical Targets

Durability with cycling: 5,000 hrs

Accomplishments

- Durability testing simulating a vehicle drive-cycle with shut-down/start-up cycling.
  - Development of start-stop testing protocol

- Comparison of 50% and 100% inlet relative humidity (RH) during drive-cycle testing
- In situ characterization of membrane electrode assemblies (MEAs) by polarization curves, electrocatalyst surface area measurements, high frequency resistance.
- Post-characterization of tested fuel cell components by x-ray fluorescence (XRF), x-ray diffraction (XRD), scanning electron microscopy (SEM/EDS), transmission electron microscopy (TEM), inverse gas chromatography (IGC), contact angle and porosimetry measurements.
- Modeling of mass-transport losses extrapolated to ‘over-potential’
  - Method for analyzing performance losses (voltage loss due to resistance, iR; oxygen reduction reaction, ORR; mass transport; MT)
- Neutron Reflectivity of Nafion® and polytetrafluoroethylene (PTFE) on carbon
- Measurements of gas diffusion layer (GDL), MEAs and membrane pore size distribution
  - Total porosity, delineation between hydrophobic and hydrophilic pores
- Measurements of hydrophobicity changes of aged membrane materials
- Modeling of Pt particle growth.
  - Kinetic growth
  - Convection/diffusion
  - Brownian dynamics (Molecular Dynamics++)

- Off-line durability testing of fuel cell components.
  - Potential cycling evaluation of electrocatalysts
    - Operational variable effects on particle growth
  - Environmental aging of components
  - RH effect on surface energy of GDL materials
    - Dispersive Energy (non-polar interactions)
    - Specific Energy (polar interactions)

Introduction

In this project, Los Alamos National Laboratory is identifying and quantifying factors that limit PEM fuel cell durability by measuring property changes in fuel cell components during long-term testing (membrane-electrode durability, electrocatalyst activity and stability, gas diffusion media hydrophobicity, and corrosion products) and developing and applying methods for
accelerated and off-line testing. The overall objective is to meet the 2010 DOE target of 5,000 hours simulating automotive operating conditions.

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 a fuel cell is a system of components; electrocatalysts, membranes, gas diffusion layers, and bipolar plates; for which degradation mechanisms, component interactions and effects of operating conditions are not fully understood. Development of in situ diagnostics and unique experiments to characterize the performance and properties of components as a function of time are required to speed understanding of fuel cell degradation mechanisms. With these measurements and 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 2006 technical progress in characterizing and quantifying the durability of fuel cell components and their degradation mechanisms to support the DOE target for 5,000 hours of durability.

Approach

Our approach to improving PEM fuel cell durability is to define the degradation mechanisms to allow the design of improved fuel cell materials and components. This approach also helps to define operating conditions that promote degradation which will identify operational constraints to improve durability.

PEM fuel cell durability testing is typically performed on single cells with active areas of 5 cm² and 50 cm². 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 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. SEM/EDS, XRF, XRD, TEM, and neutron scattering are used to characterize changes in the membranes, gas diffusion layers and catalyst after durability testing. Porosimetry measurements of MEAs, membranes and gas diffusion layers are used to define structural changes in material properties. IGC is used to identify relative humidity effects on the hydrophobic nature of gas diffusion layers. Contact angle measurements are used to monitor material hydrophobicity/hydrophillicity changes of materials. Off-line testing to develop accelerated testing techniques is used to help differentiate the contributions of individual fuel cell components to the degradation of the overall performance.

Results

Durability Testing Simulating Automotive Drive Cycles

To best understand fuel cell durability for transportation applications, we have tested fuel cells simulating the power cycling observed in vehicles. Testing of this type is crucial, as previous results have shown the active surface area of fuel cell electrocatalyst decreases faster as the potential is cycled compared to constant potential or current testing [1,2]. In addition, other work has shown that fuel cell start/stop operations can have detrimental durability effects [3]. Figure 1 shows the energy production per cycle and high frequency resistance (HFR) during testing utilizing a 6 minute drive cycle defined by DOE, modified to include shut-down cycles every 10 cycles. Automated shut-down/start-up operation was conducted with air purge of both the anode and cathode to limit shut-down potentials and peroxide/radical formation. A similar rate of performance degradation was measured for parallel operating cells with and without the shut-down operation. These results suggest that fast dry air purge may be an acceptable method to limit fuel cell component degradation upon shut-down.

Figure 2 shows the cathode platinum particle size distribution after testing utilizing an automotive drive cycle, (US06 ~ 20 minutes per cycle) for ~2,000 hrs of operation. The cathode Pt particle size showed an increase in the particle size distribution by both
XRD and TEM post-characterization. An average spherical particle size diameter of 5.0 nm was observed, however, there was a substantial particle population at significantly higher particle sizes. The particle size distribution changed from initially being log normal, to having a bi-modal Pt particle distribution. The bi-modal distribution shows a log normal distribution coupled with a large shoulder at higher particle sizes. During this testing, separate tests were conducted at 50% and 100% RH; the anode and cathode flow rates, humidification and temperature were held constant while the voltage was varied.

Several candidate mechanisms appear responsible for the loss of Pt surface area. Oxidation of the Pt occurs at voltages near the peak potential of a typical drive cycle. There is a corresponding change in solubility of Pt that leads to dissolution and re-precipitation and the catalyst potential is changed. Simple Brownian motion with an accompanying particle coalescence is also a Pt particle growth mechanism. A theoretical investigation has been initiated to elucidate the operative mechanisms at a molecular/atomistic resolution with the goal of providing insight for new designs to mitigate their effects. To model the bimodal distribution of catalyst particle growth, the particle growth was simulated with a kinetic rate in particle growth coupled to particle coalescence by particle Brownian motion in an ionomer matrix. Figure 3 shows an example of the types of particle size distribution that are obtained utilizing coupled kinetic and coalescence particle growth. Modeling shows particle growth with bi-modal particle distributions, not unlike experimental measurements.

Characterization of Changes in Chemical Properties of GDLs and MEAs

We previously have shown that GDLs change during operation in fuel cells [4]. To help identify the losses due to mass transport effects from changing GDL properties, we have modeled the losses during testing to quantify losses due to mass transport limitations. This modeling is based on calculating losses due to various components of the fuel cell, such as in equation (1):

\[
V_{cell} = E_{eq}(T, \rho_{H_2}, P_{O_2}) - \eta_{\text{ORR}} - \eta_{\Omega, \text{HFR}} - \eta_{\text{tx,elec}} - \eta_{\text{GDL-FF}} \quad (1)
\]

Where: the \( \eta_{\text{ORR}} \) represents all kinetic and catalytic sources of the cathode activation polarization, \( \eta_{\Omega, \text{HFR}} \) is the total ohmic resistance of the single cell (sum of anode, cathode, and membrane), \( \eta_{\text{tx,elec}} \) is losses within the cathode catalyst layer, and \( \eta_{\text{GDL-FF}} \) is mass-transport losses within the cathode GDL/flow-field. These losses are modeled in Figure 4 for a 1,000-hour steady-state test conducted. As observed in Figure 4, the losses due to changes in mass transport at high current densities can be significant, and is likely due to chemical changes in GDL materials. Modeling of mass-transport losses extrapolated to over-potential provides a method for analyzing performance losses (iR, ORR, MT) to quantitatively define losses to due changing mass-transport (changes in the GDL). This modeling allows for better understanding of long-term fuel cell test data, with definition of components leading to performance degradation.

To help understand the chemical changes that fuel cell carbon materials undergo, we have studied these materials and their properties by a number of methodologies. Figure 5 is an example of a fundamental study examining the interface between carbon and an ionomer coating of Nafion® by use of neutron scattering.
This simulates catalyst support material interactions with typical coatings used in fuel cells. As shown in Figure 5, the carbon-oxide substrate layer thickness increases during aging in an air humidified environment. Increasing the carbon-oxide substrate increases the carbon surface hydrophilicity [5], thus helping explain why during aging GLD materials become more hydrophilic.

Other material property changes due to aging effects have been measured in membranes and MEAs, including changes in porosity and hydrophobicity. Figure 6 shows contact angle measurements of cast Nafion® membrane before and after aging. The contact angle (θ) increases after aging – the membrane surface becomes more hydrophobic. In addition, the contact-angle slope magnitude decreases after aging (⇒ decreased hydrophilicity); this indicates slower water uptake in the membrane. The spread between initial pre-aging θ values increased after aging suggests localized chemical effects (possible loss of sulfonate sites).

**Conclusions**

- Fast air purge during shut-down/start-up appears to limit fuel cell performance degradation.
- Electrocatalyst surface area loss is due to the growth in platinum particle size.
  - Platinum particle size distribution can exhibit bi-modal particle size distributions after extended testing simulating automotive drive cycles.
  - Bi-modal particle size distributions can be simulated with a kinetic rate in particle growth coupled to particle coalescence by particle Brownian motion.
  - Particle size growth is exacerbated by operating with power cycling, compared with constant voltage operation.
  - Particle size growth occurs more rapidly at higher potentials.
- Hydrophobicity of GDL materials was measured to decrease rapidly with aging with air.
  - Modeling of GDL mass transport losses is an effective method of systematically quantifying individual component performances losses.
Growth of a carbon-oxide surface layer has been measured by neutron reflectivity and is likely partially responsible for changes to GDL hydrophobicity.

Membranes show changing hydrophobicity and water uptake rates upon aging.

**Future Directions**

- Testing Utilizing Drive Cycle Operation
  - Examine shut-down/start-up effect on durability.
  - Examine durability with variable RH/(pressure) operation during drive cycles.
  - Measure carbon corrosion effects during shut-down/start-up, with water condensation and during cycling operation.
  - Make segmented cell measurements of durability during operation.

- Off-line and Accelerated Testing and Characterization
  - Membrane and GDL aging characterization (porosity, hydrophobicity).
  - *In situ* XRD - catalyst particle size evaluation.
  - Examine 2010/2015 low loadings of electrocatalysts.

- Membrane Degradation and Radical (Peroxide) Formation
  - Measure peroxide/radical formation including operational effects such as RH, temperature, pressure, drive cycle, and electro-catalysts.

**FY 2006 Publications/Presentations**


**References**


**Special Recognitions & Awards**