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PEM Fuel Cell Degradation

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The durability of PEM fuel cells is a major barrier to the commercialization of these systems for stationary and transportation power applications. While significant progress has been made in understanding degradation mechanisms and improving materials, further improvements in durability are required to meet commercialization targets. Catalyst and electrode durability remains a primary degradation mode, with much work reported on understanding how the catalyst and electrode structure degrades. Accelerated Stress Tests (ASTs) are used to rapidly evaluate component degradation, however the results are sometimes easy, and other times difficult to correlate. Tests that were developed to accelerate degradation of single components are shown to also affect other component's degradation modes. Non-ideal examples of this include ASTs examining catalyst degradation performances losses due to catalyst degradation do not always well correlate with catalyst surface area and also lead to losses in mass transport.

Introduction

The durability of 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 or 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 examine degradation mechanisms and define differences in durability arising from operating characteristics of components, researchers have evaluated both stationary and automotive operating conditions. Most long-term testing is carried out at a given set point or group of set points to simulate stationary conditions, where the voltage or current density is held for hundreds or thousands of hours at a time. However, long-term testing is costly and relatively slow in terms of evaluating materials and understanding degradation mechanisms.

Rapid materials evaluation requires relevant Accelerated Stress Tests (ASTs), the design of which relies on understanding the degradation mechanism. The need for ASTs is apparent given the target lives for fuel cell systems: 5000 hours (~ 7 months) for automotive, and 40,000 hrs (~ 4.6 years) for stationary systems. Thus testing methods that enable more rapid screening of individual components to determine their durability characteristics are needed for evaluating new component durability in a reasonable turn-around time. This allows proposed material improvements in a component to be evaluated rapidly and independently, subsequently allowing rapid advancement in PEM fuel cell durability. These tests are also crucial to developers in order to make sure that they do not sacrifice durability while making improvements in costs (e.g. lower

precious metal loading) and performance (e.g. thinner membrane or a GDL with better water management properties).

Experimental

Life testing was conducted in 50 cm² hardware from Fuel Cell Technologies. Various experimental conditions were used to define the durability in relation to the fuel cell operating conditions, including steady-state potentials, and dynamic operating simulated drive cycles. Dynamic durability testing was conducted on single cells using a modified US06 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. Anode and cathode flow rates, humidification and temperature were held constant while the voltage was varied. Figure 1 shows an example voltage profile during the life testing voltage cycle of a durability test.

Figure 1. Voltage cycling profile for life testing based on the US06 drive cycle.

Accelerated life testing was conducted using an AST developed by the Fuel Cell Technical Team of the FreedomCAR and Fuel Partnership, or prior variations thereof. The primary protocol discussed in this paper (or variation of) is shown in Table 1.

Durability testing including operation at subfreezing conditions was conducted by first operation at 0.6 – 0.8 V at 80 °C with air and H₂ at either 100% or 50% inlet RH and 25 psi back pressure. Single cells were then purged using N₂ gas (< 5000 cc/min for < 3 minutes) and cooled down to sub-freezing temperatures. Dry H₂ and dry air were then introduced into the anode and cathode of the cells respectively and their performance was monitored isothermally at various sub-freezing temperatures (-40°C < T < -10°C) at various constant current densities. The voltage and high frequency resistance were monitored during these isothermal operations at sub-freezing temperatures.

Cells during durability tests, and ASTs were characterized in situ by cyclic voltammograms (CVs) to determine the catalyst surface area, polarization curves (VIRs) were obtained under standard conditions in order to track the durability of the cells, full impedance spectra from 1 kHz to 100 mHz was obtained at the beginning and end of fuel cell operations in order to help identify the various degradation mechanisms (IR, charge transfer and mass transport). Polarization curves with high frequency resistance measurements (VIRs) and AC impedance spectra were performed using a fuel cell test station from Fuel Cell Technologies Inc.

Cathode CVs (from 0.1 to 1.0 V @ 20 – 60 mV sec⁻¹) were performed using either Pine or PAR potentiostats at 500 cm³ min⁻¹ of N₂ and H₂ at the cathode and anode respectively.

Table 1 Electrocatalyst Cycle and Metrics Revised April 2008		
Cycle	Triangle sweep cycle: 50 mV/s between 0.6 V and 1.0 V. Single cell 25-50 cm ²	
Number	30,000 cycles	
Cycle time	16 s	
Temperature	80°C	
Relative Humidity	Anode/Cathode 100/100%	
Fuel/Oxidant	Hydrogen/N ₂ (H ₂ at 200 sccm and N ₂ at 75 sccm for a 50 cm ² cell)	
Pressure	Atmospheric pressure	
Metric	Frequency	Target
Catalytic Mass Activity*	At Beginning and End of Test minimum	≤40% loss of initial catalytic activity
Polarization curve from 0 to ≥1.5 A/cm²**	After 0, 1k, 5k, 10k, and 30k cycles	≤30 mV loss at 0.8 A/cm ²
ECSA/Cyclic Voltammetry	After 10, 100, 1k, 3k, 10k, 20k and 30k cycles	≤40% loss of initial area

*Mass activity in A/mg @ 150 kPa abs backpressure at 857 mV iR-corrected on 6% H₂ (bal N₂)/O₂ {or equivalent thermodynamic potential}, 100%RH, 80°C normalized to initial mass of catalyst and measured before and after test.

**Polarization curve per USFCC "Single Cell Test Protocol" Section A6 expanded to 1.5 A/cm²

Table 1. Fuel Cell Tech Team AST for electrocatalyst.⁵

Results and Discussion

One of the major degradation modes 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 such as from Figure 1. Post-characterization of the cathode catalyst by techniques such as TEM and XRD show particle size growth and particle agglomeration. An example of the change in platinum particle size distribution is shown in Figure 2a for operation with the US06 drive cycle.

Similarly, other types of operation show similar Pt particle degradation such as operation at sub-freezing temperatures as shown in Figure 2b. This analysis shows that cathode catalyst coarsening observed over 2000 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% RH showing a higher degree of particle growth (5.0 nm) compared to operation at 50% RH (4.2 nm), when starting 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 of the distribution.

Figure 2. (a) Pt particle size distribution for fresh, and after 2000 hours of simulated US06 drive cycle operation at 50% and 100% RH. Testing conditions are 50 cm² N112 single cell, Pt_a/Pt_c: 0.2 mg/cm², 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, and 3 starts @ -40°C. 50 cm² N212 single cell, Pt/Pt: 0.2 mg/cm².⁶

The particle coarsening and agglomeration is clearer in the TEM image shown in Figure 3. There are localized regions where Pt particle migration has occurred, forming regions of highly populated large Pt particles.

Figure 3. TEM image after 2000 hours of drive cycle operation. (Courtesy Karren More, ORNL)

A short period of operation with freeze cycles shows a similar cathode catalyst coarsening (see figure 2b). 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 anode Pt sizes and distributions between the two cells, however this Pt particle growth occurred in only a few hundred hours of operation with the sub-freezing operation.

During freeze operation, significant migration of Pt particles was also observed. Figure 4 shows TEM of how the electrocatalyst and the catalyst layer changes during operation with freeze. Movement of Pt is observed from the cathode to the cathode/membrane interface. Increased Pt agglomeration is observed near the interface of the catalyst layer and membrane (0.2-0.4 μm).

Pt-particles are observed across the remaining 47 μm to anode side, however no Pt particles are observed within 3 μm of cathode.

Figure 4. 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 . (Courtesy Karren More, ORNL)

Figure 5. TEM image of Pt in the membrane and anode after sub-freezing operation. After 5 starts @ -10°C ; 5 starts @ -20°C ; 3 starts @ -40°C . (Courtesy Karren More, ORNL)

Figure 5 shows the distribution of Pt particles in center of membrane – note 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.

To rapidly examine cathode catalyst degradation, ASTs have been implemented to quickly observe the relative degree to which the catalyst degrades, and how operational conditions affect the catalyst degradation. Potential cycling of an MEA is used as an accelerating testing technique. For this study, the anode is exposed to hydrogen while the cathode is exposed to nitrogen. An example of the effect on catalyst durability is shown in Figure 6. For this example, the cathode potential was swept at 10 mV/sec from 0.1 V to 1.2 V. After intervals of 300 sweeps, the polarization curve of the MEA and the catalyst surface area were measured. The performance polarization curves in Figure 6a show the rapidly decreasing performance. Figure 6b shows the catalyst surface area as a function of the number of potential sweep cycles. The electrochemical surface area decreases rapidly with potential sweeps.

Figure 6. (a) Performance polarization and (b) measured catalyst surface area as a function of number of potential cycles during potential cycling of the MEA cathode. Voltage cycling was from 0.1 V to 1.2 V at a cell temperature of 80 °C.⁶

Since the work done in Figure 6, cathode electrocatalyst durability has been increased by use of different carbon support materials and in some cases use of platinum alloys. In addition, the metric of mass activity has been found to be more useful in evaluating electrocatalyst durability.⁷ Figure 7a shows the kinetic region as a function of potential cycles as per reference 5 and Table 1 over 30,000 cycles, and Figure 7b shows the corresponding ECSA loss and loss in activity as defined by performance voltage loss at 0.8 A/cm².

Figure 7. (a) The kinetic region of the polarization curve as a function of number of potential cycles. (b) % ECSA loss and voltage loss from the polarization curve measured at 0.8 A/cm² vs. number of potential cycles.⁸

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. As shown in Figure 8, comparing Mass Activity and ECSA as a function of particle size can show a good correlation.

Figure 8. Electrochemical surface area and mass activity vs. Platinum particle size measured from MEAs before and after the AST cycling protocol.

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 9 a,b and the corresponding ECSA shown in Figures 10 a,b. This work done by Christina Johnston and Yu Seung Kim at Los Alamos National Lab⁹ explores the effect of different solvents on the electrode structure performance and durability. Electrodes made from catalytic inks based on water and iso-propanol (WIN) show rapid performance degradation, whereas electrodes made from catalytic inks based on glycerol, show virtually no performance loss. This examination was for identical cathode electrocatalysts.

Figure 9. Polarization curves of electrodes vs. number of AST potential cycling for (a) water based electrode and (b) glycerol based electrode. (Courtesy of Christina Johnston and Yu Seung Kim, LANL).

However, the lack of performance loss appears to not be associated with the catalytic surface area, as in Figure 10 a vs. Figure 10 b, 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 correlation between loss of ECSA and performance loss or catalytic mass activity.

Figure 10. Electrochemical active surface area vs. number of potential cycles for (a) water based electrode and (b) glycerol based electrode. (Courtesy of Christina Johnston and Yu Seung Kim, LANL).

Impedance measurements to help define the performance losses show that voltage cycling does effect more than the catalyst activity. Impedance for the potential cycling for Figures 7 and 8 show highly increased charge transfer resistance (by 138% at 0.87 V) and small increases in mass transport resistance (40% at 50A). See Figure 11.

For other AST testing, such as a carbon corrosion AST, which is a potential hold at 1.2 V, more dramatic changes in impedance are observed (Figure 12). Significant increase in charge transfer resistance is observed. After 144 hours: the Charge Transfer resistance at 0.85V increased by 866 % and Mass Transport Resistance at 0.1 A/cm² is greater than the initial MT resistance at 1 A/cm² indicating a huge increase in the MT resistance due to the carbon corrosion, and changes in the electrode structure.

Figure 11. Impedance spectra before and after catalyst cycling AST.

Figure 12. Impedance spectra before and after carbon corrosion AST (potential hold at 1.2V).

Conclusions

Significant progress has been made in understanding degradation mechanisms and improving materials. Electrocatalyst and electrode durability remains a primary degradation mode, with much work on understanding how the catalyst and electrode structure degrades. Accelerated Stress Tests (ASTs) are used to rapidly evaluate component degradation, however the results 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 effect the performance in other areas. Examples of this are tests to examine losses due to catalyst degradation and kinetics losses can also lead to losses in mass transport. Other durability tests can induce rapid degradation of components, such as fuel cell potential cycling vs. steady-state operation, and sub-freezing operation inducing rapid particle size growth comparable to thousands of hours of power cycling.

To meet commercialization targets, improvements in materials durability and characterization techniques are still required. Needed advances in PEM fuel cell durability can be summarized:

- Identification of individual component degradation mechanisms
- Elucidation of component interactions, interfaces, operating conditions leading to cell degradation
- Correlation of fuel cell operating conditions to degradation rates and degradation. (Including: temperature, relative humidity, power/voltage transients, current density, start-up/shut-down and freezing operation).
- Correlation of ASTs to fuel cell operation.
- Development of advanced ASTs, which accurately gauge in situ component behavior.
- Development of advanced in situ and ex situ characterization techniques for analysis of fuel cell component degradation

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