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Title: Degradation Mechanisms and Accelerated Testing in PEM Fuel Cells

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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 and 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.

The need for Accelerated Stress Tests (ASTs) can be quickly understood 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, such as off-line environmental testing, are needed for evaluating new component durability in a reasonable turn-around time. This allows proposed 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 platinum group metal [PGM] loading) and performance (e.g. thinner membrane or a GDL with better water management properties).

To achieve a deeper understanding and improve PEM fuel cell durability LANL is conducting research to better define fuel cell component degradation mechanisms and correlate AST measurements to component in 'real-world' situations.

Results

One of the major degradation 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. 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 1 for operation

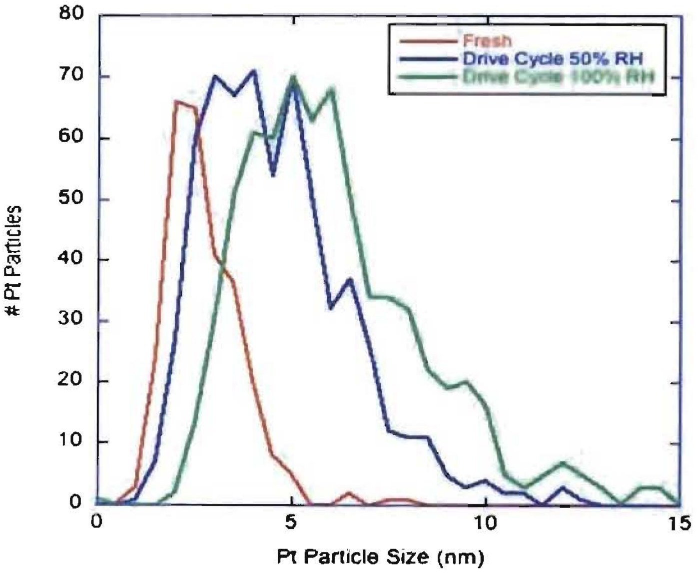

Figure 1. Pt particle size distribution for fresh, and after 2000 hours of simulated US06 drive cycle operation for 50% and 100% RH. Testing conditions are 50 cm^2 N112 single cell, Pt/Pt: 0.2 mg/cm2, Cell Temperature: 80°C, constant humidification and constant anode/cathode flowrates.

with the US06 drive cycle.

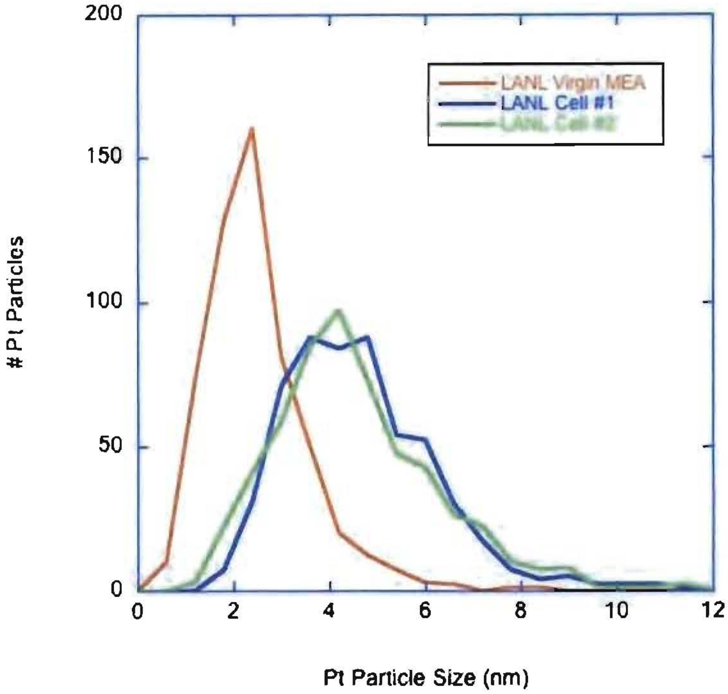

Figure 2. Pt particle size distribution after sub-freezing operation for 5 starts @ -10°C, 5 starts @ -20°C, 3 starts @ -40°C. 50 cm^2 N212 single cell, Pt/Pt: 0.2 mg/cm^2.

Similarly, other types of operation show similar Pt particle degradation such as operation at freezing temperatures as shown in Figure 2. 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), compared 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 in the distribution. A short period of operation with freeze cycles shows a similar cathode catalyst coarsening (see figure 2). 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 Pt sizes and distributions between the two cells, however this Pt particle growth occurred in only a few hundred hours of operation but with the sub-freezing operation. Figure 3 shows TEM of how the electrocatalyst and the catalyst layer changes during operation with freeze. Movement of Pt is observed from cathode to the cathode/membrane interface. Increased Pt agglomeration is observed near interface (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. Pt

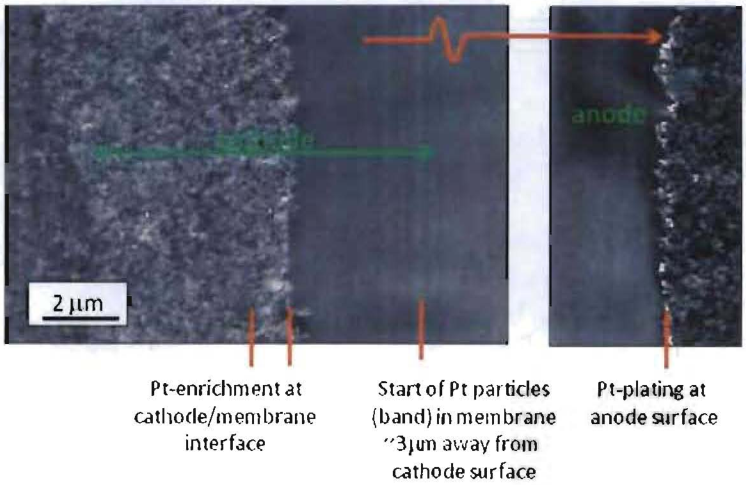

Figure 3. TEM Images of Pt in the cathode, membrane and anode after sub-freezing operation. After 5 iso-thermal starts at -10C, 5 starts at -20C and 3 starts at -40C.

particles are also found in the center of the membrane, notint that Pt particles are observed continuously/homogeneously across the membrane starting ~3 μm from cathode, with a nominal Pt particle size ~15 nm diameter. Pt particles are found across membrane up to anode/membrane interface, where the Pt "plates" the anode surface.

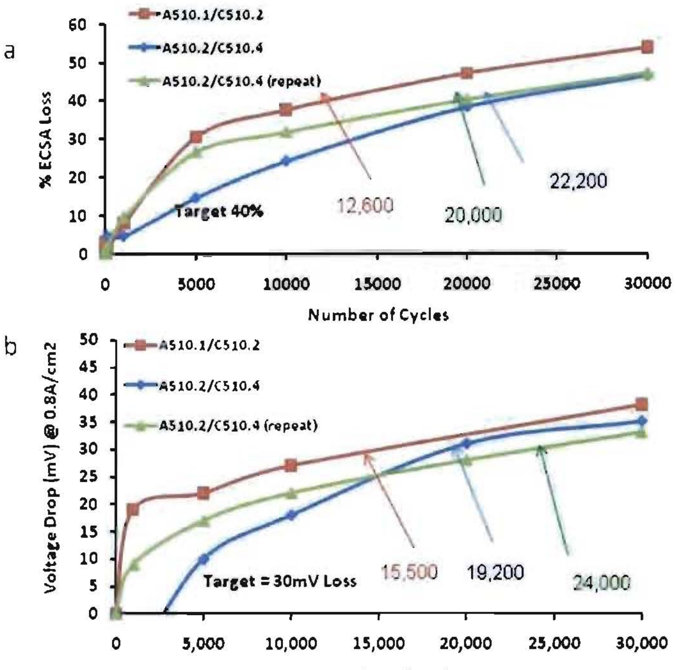

Figure 4. AST performance metrics of Gore® Primea™ MEAs during potential cycling (according to reference 6) with 2 different cathode Pt loadings (0.2 and 0.4 mg-Pt/cm^2) (a) % ECSA loss and (b) mV loss at 0.8 A/cm^2. The number of cycles for the AST metrics to reach their target degradation rate is indicated in the figures.

Accelerated Stress Testing (AST) of catalyst layers was conducted in accordance with the published Fuel Cell Tech Team protocols.[5] The results from the potential cycling AST are illustrated in Figure 4, which shows the degradation in ECSA and performance as a function of the number of potential cycles. There is reasonable agreement in the ECSA and performance loss targets with the lower loaded (0.2 mg-Pt/cm^2 @ cathode) MEA showing a 40% loss in ECSA after 12,500 cycles and a 30 mV loss in performance after 15,500 cycles. Moreover, the higher loaded (0.4 mg-Pt/cm^2 @ cathode) MEA exhibited better durability with the 40% ECSA loss target occurring after 20,000 cycles. Figure 5 illustrates the impedance of an MEA before and after the potential cycling test. The Nyquist plot shows two semi-circles with the low frequency semi-circle corresponding to mass transport losses and the high frequency semi-circle corresponding to kinetic losses. The potential cycling introduces a significant increase in the charge transfer resistance, and also results in an increase in the mass transport losses. This result indicates that the upper potential for the cycling that is presently 1.0 V may need to be lowered in order to avoid any carbon corrosion and make this test truly representative of the electro-catalyst alone.

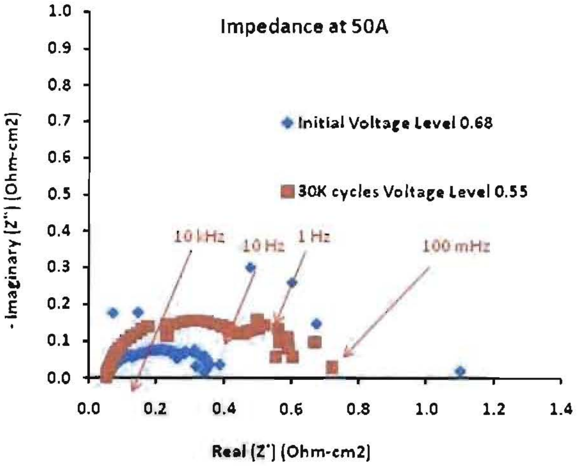

Figure 5. The impedance curves obtained at a current density of 1A/cm^2 in H_2/Air at 80 °C and 100% inlet RHs, for a Gore® Primea™ MEA, before and after 30,000 potential cycles from 0.6V to 1.0V.

Performance degradation due to catalyst support corrosion during a 1.2 V constant potential hold is illustrated in Figure 6. It is seen that two identical MEAs showed very similar performance losses indicating the excellent reproducibility of the tests. Fig. 6a shows that by doubling the cathode catalyst loading to 0.4 mg-Pt/cm^2, the loss of ECSA can be delayed significantly. The target 40% ECSA loss is reached after 61 hours instead of 29 hours. Fig. 6b confirms that this translates to a slower loss of performance at 1.5 A/cm^2. However, the 30 mV target for this metric is still passed within the first ≈ 12 hours. This illustrates that there is significant loss in performance due to mass transport losses that is not captured in the ECSA measurements and therefore the ECSA metric may not be very relevant for this constant potential hold AST.

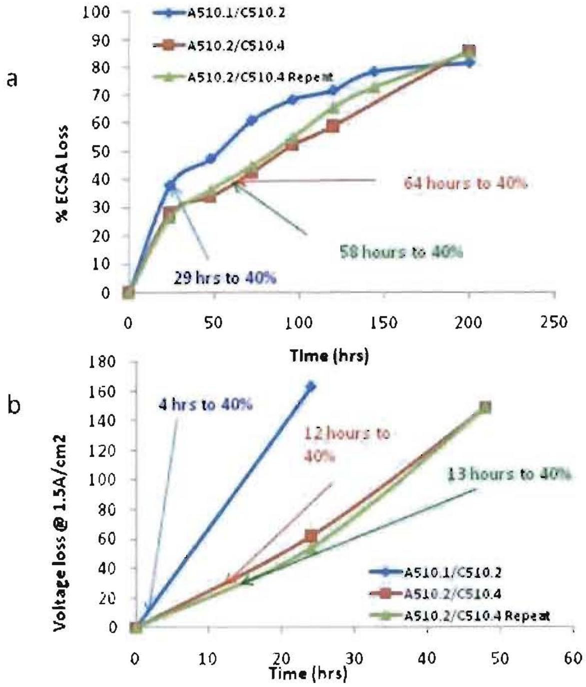

Figure 6. Carbon corrosion AST performance metrics during constant potential with 2 different cathode Pt loadings (0.2 and 0.4 mg-Pt/cm^2) (a) % ECSA loss and (b) mV loss at 1.5 A/cm^2. Number of hours for Target AST metrics is indicated in the figures.

The main metrics for analysis of electro-catalyst durability have been ECSA, mass activity, and performance as measured by the kinetic region of polarization curves. Post characterization by TEM and XRD has been most widely used to determine the particle size growth. As shown in Figure 7, comparing MA and ECSA as a function of particle size (determined by XRD) can show a good correlation. Here, the fresh cathode catalyst had a spherical particle size of 2.7 nm that grew to ≈ 6.5 nm after 30,000 potential cycles and to ≈ 10 nm after 200 hours of 1.2 V potential hold. Although the mechanism of Pt particle growth is expected to be completely different in these 2 tests, it is important to note that the average Pt particle size can be used as an excellent marker to track performance loss in both "real-world" and AST testing of PEM fuel cells.

Conclusions

To meet commercialization targets, improvements in durability are still required. Catalyst and electrode durability remains a primary degradation mode; catalyst particle growth occurs with potential cycling and with freeze testing/cycling. Accelerated Stress Tests (ASTs) are used to rapidly evaluate component degradation. Tests which were developed to accelerate single components also effect the performance in other areas.

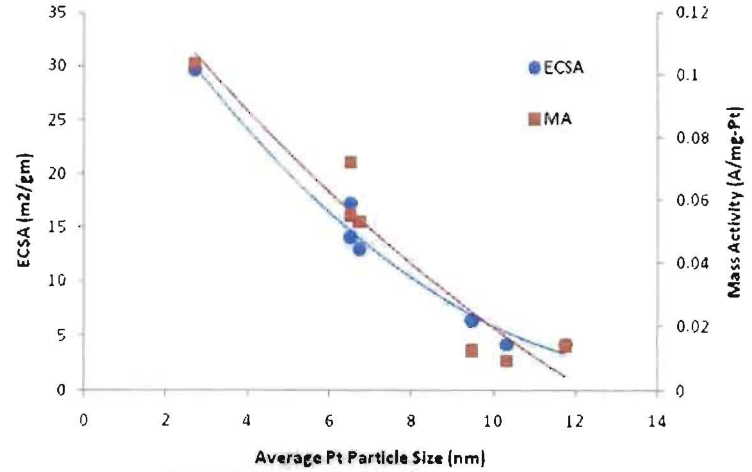

Figure 7. The ECSA and MA of Gore® Primea^{TM} MEAs as a function of the average Pt catalyst particle size. Different particle sizes were obtained by subjecting the MEAs to the potential cycling and potential hold ASTs.

Examples of this are tests to examine losses due to catalyst degradation and kinetics losses and also lead to losses in mass transport.

The ASTs performed on baseline materials show excellent repeatability for both the catalyst layer and membrane. Potential cycling led to an increase in the Pt particle size at the cathode that correlated well with catalyst MA and ECSA loss. The catalyst cycling was however found to cause some mass transport losses that may be associated with carbon corrosion. Constant potential holds led to a dramatic increase in catalyst particle size and an associated thinning of the catalyst layer that were consistent with both mass transport and kinetic losses observed in fuel cell performance. Gore® 510 catalyst layer had reasonably good Pt catalyst stability but poor carbon corrosion resistance. The durability of the catalyst and the support increased with increasing loading.

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