V.H.5 Accelerated Testing Validation

Rangachary Mukundan[1] (Primary Contact),
Rod Borup [1], John Davey[1], Roger Lujan[1],
Dennis Torraco[1], David Langlois[1],
Fernando Garzon[1], Adam Weber[2], Mike Brady[3],
Greg James[4], and Steve Grot[5]

[1]Los Alamos National Laboratory (LANL)
MS D429, P.O. Box 1663
Los Alamos, NM 87545
Phone: (505) 665-8523
E-mail: Mukundan@lanl.gov

DOE Technology Development Manager:
Nancy Garland

Phone: (202) 586-5673
E-mail: Nancy.Garland@ee.doe.gov

Subcontractors:

[2] Lawrence Berkeley National Laboratory, Berkeley, CA
[3] Oak Ridge National Laboratory (ORNL),
    Oak Ridge TN
[4] Ballard Power Systems, Burnaby, BC, Canada
[5] Ion Power, New Castle, DE

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Project End Date: 2013

Objectives

- Correlation of the component lifetimes measured in an accelerated stress test (AST) to "real-world" behavior of that component.
- Validation of existing component specific ASTs for electrocatalysts, catalyst supports and membranes (mechanical and chemical degradation).
- Development of new ASTs for gas diffusion layers (GDLs) and bipolar plates.
- Co-ordinate effort with Fuel Cell Tech Team, Durability Working Group and US Fuel Cell Council (USFCC) Taskforce on Durability.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section (3.4) of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

(A) Durability

(B) Cost

Technical Targets

Cost and durability are the major challenges to fuel cell commercialization. ASTs enable the rapid screening of fuel cell materials and are critical in meeting the long life times required for stationary and automotive environments. Moreover these ASTs can also help predict the lifetime of the various components in "real-world" applications.

- Transportation Durability: 5,000 hours (with cycling)
  – Estimated Start/Stop cycles: 17,000
  – Estimated Frozen cycles: 1650
  – Estimated Load cycles: 1,200,000

- Stationary Durability: 40,000 hours
  – Survivability: Stationary -35°C to 40°C

- Cost ($25/kWe)

Accomplishments

- Performed all four DOE Fuel Cell Tech Team recommended ASTs on baseline GORE™ membrane electrode assemblies (MEAs) at two different loadings and on two different membrane types
- Ballard manufactured and supplied LANL the MEAs that went into the P5 and HD6 bus stacks.
- ORNL manufactured and supplied metal nitrided bipolar pate materials for AST testing.
- Characterized Pt particle size in the catalyst layer before and after ASTs using X-ray diffraction.

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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 [1]. Commercial viability depends on improving the durability of fuel cell components to increase the system reliability and to reduce system lifetime costs by reducing the stack replacement frequency. The need for ASTs can be quickly understood given the target lives for fuel cell systems: 5,000 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 loading) and performance (e.g. thinner membrane or a GDL with better water management properties).

DOE has suggested AST protocols for use in evaluating materials, but only for the catalyst layer (electrocatalyst and support), and for the membrane [2,3]. The USFCC has also suggested AST protocols for the same materials [4]. While these protocols have concentrated on the catalyst, catalyst support and membrane materials, to date, no accelerated degradation protocols have been suggested for GDL materials or MPL layers, bipolar plates or seals. In spite of recent advances in AST development, a main portion, which is deficient, is the quantitative correlation between the results of a given fuel cell AST, and the degradation rate or life in an operating fuel cell.

Approach

A main desired outcome of this task is the correlation of the component lifetimes measured in an AST to in situ behavior of that component in "real-world" situations. This requires testing of components via ASTs and in operating fuel cells, and delineating the various component contributions to the overall cell degradation. This will primarily be performed by using a simplified one-dimensional model that takes into account the different component contributions like membrane ionic conductivity, cathode catalyst layer kinetic losses and mass transport losses (catalyst layer and GDL) to the overall losses observed in operating cells [5]. This project will then attempt to correlate the performance losses observed due to a particular component in "real-world" situations with the degradation in AST metrics of that component. The correlation between AST and life data if state-of-the art materials are used, in essence gives one data point. Thus, for a reasonable correlation to be made, materials with different life spans will be utilized. This relies on the expertise of the suppliers as partners in the project. This work is also being coordinated with other funded projects examining durability through a DOE Durability Working Group, and through a USFCC task force on durability.

Results

GORE™ Primea® MEAs sandwiched between two SGL Sigracet™ 24BC GDLs were used as the baseline MEAs for AST testing in a single serpentine flow field. The testing was performed in accordance

with the published Fuel Cell Tech Team protocols [6]. The results from the potential cycling AST are illustrated in Figure 1, which shows the degradation in electrochemical surface area (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 2 illustrates the impedance of an MEA before and after the potential cycling test. The Nyquist plot clearly 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. It is seen that the potential cycling not only introduces a significant increase in the charge transfer resistance, but it 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.

Performance degradation due to catalyst support corrosion during a 1.2 V constant potential hold is
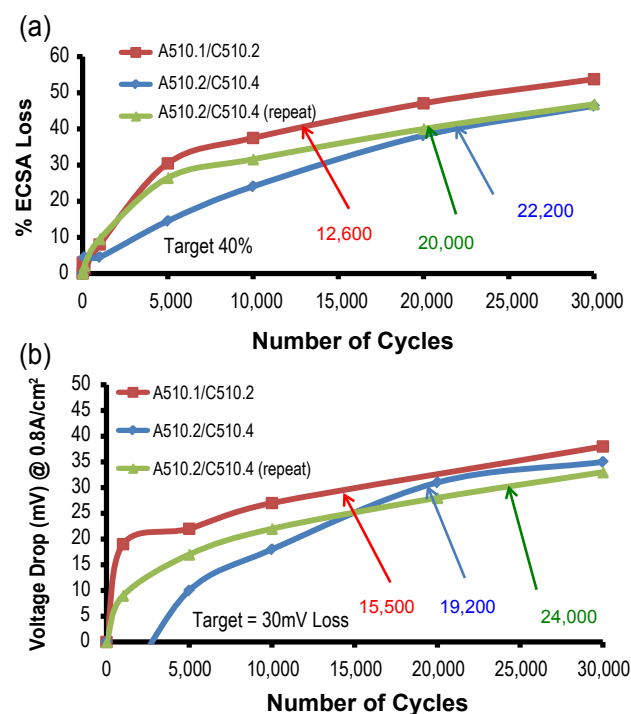

FIGURE 1. AST performance metrics of GORE™ Primea® MEAs during potential cycling (according to reference 6) with two different cathode Pt loadings (0.2 and 0.4 mg-Pt/cm^2) (a) % ECSA loss and (b) mV loss at 0.8 A/cm^2. The number of cycles for the AST metrics to reach their target degradation rate is indicated in the figures.
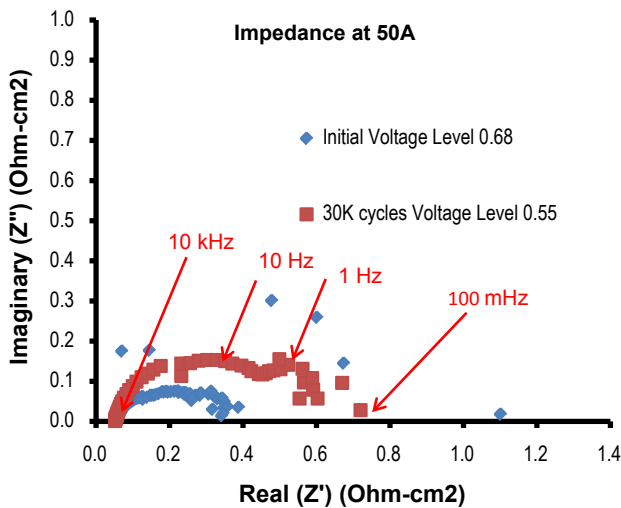
FIGURE 2. The impedance curves obtained at a current density of 1A/cm^2 in H$_2$/Air at 80°C and 100% inlet relative humidities, for a GORE™ Primea® MEA, before and after 30,000 potential cycles from 0.6 V to 1.0 V (according to reference 6).
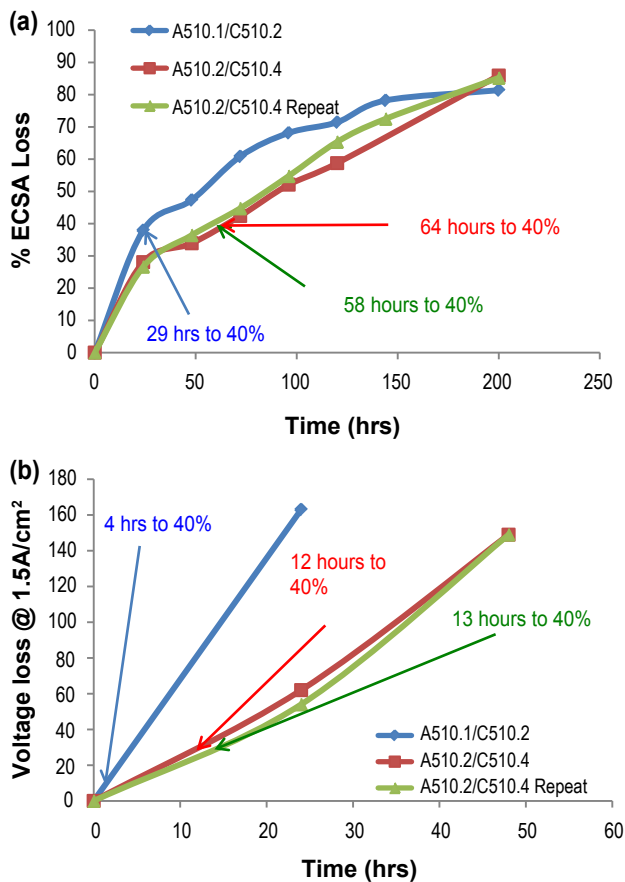

FIGURE 3. AST performance metrics of GORE™ Primea® MEAs during constant potential hold (according to reference 6) with two different cathode Pt loadings (0.2 and 0.4 mg-Pt/cm^2) (a) % ECSA loss and (b) mV loss at 1.5 A/cm^2. The number of hours for the AST metrics to reach their target degradation rate is indicated in the figures.

illustrated in Figure 3. It is seen that two identical MEAs showed very similar performance losses indicating the excellent reproducibility of the tests. Figure 3a 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. Figure 3b 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.

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 transmission electron microscopy and X-ray diffraction (XRD) has been most widely used to determine the particle size growth. As shown in Figure 4, comparing mass activity (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 two 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 and Future Directions

The ASTs performed on baseline GORE™ materials showed excellent repeatability for both the catalyst layer
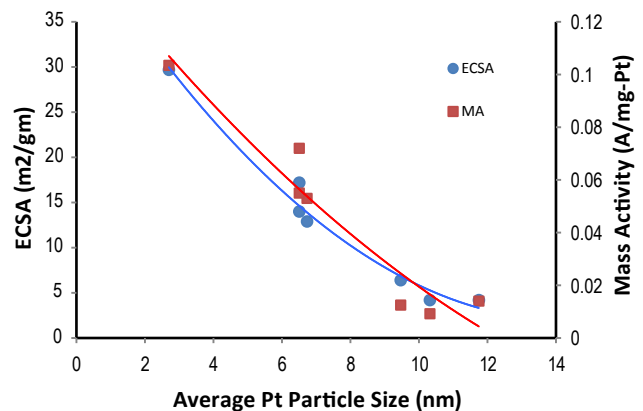

FIGURE 4. The ECSA and MA of GORE™ Primea® MEAs as a function of the average Pt catalyst particle size. Different particle sizes were obtained by subjecting the MEAs to the potential cycling and potential hold ASTs (according to reference 6).

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. The GORE^{TM} 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. The GORE-SELECT^{TM} 720 and N212 membranes had excellent mechanical stability and met the DOE AST targets. The following work will be carried out in the coming years of this project in order to validate existing ASTs and recommend new ASTs.

- AST Testing
  - Perform ASTs on the Ballard-supplied materials.
  - Perform ASTs on materials with differing durability supplied by Ion Power.
  - Develop ASTs for ORNL supplied bipolar plate materials.
  - Develop ASTs for GDLs/microporous layers.
- "Real-World" Testing
  - Perform simulated automotive drive cycle testing on selected materials with differing durability.
  - Study effect of operating conditions (stressors) like temperature, pressure and relative humidity on drive cycle testing.
  - Analyze the performance data from two different Ballard bus stacks.
- Characterization of Materials
  - In situ characterization of catalyst activity, membrane crossover and shorting resistance, and mass transport limitations as a function of AST and "real-world" testing.

- Ex situ characterization of catalyst particle size distribution, layer thickness, membrane thickness, and GDL hydrophobicity as a function of AST and "real-world" testing.
- Correlation of AST to "Real-World" Data
  - Modeling of fuel cell performance data to provide component specific degradation rates.
  - Statistical correlation of performance degradation with physical properties in both AST and "Real-world" data.

FY 2010 Publications/Presentations

1. Rodney L. Borup and Rangachary Mukundan, **PEM Fuel Cell Degradation**, submitted to 2010 ECS Transactions.

2. Joseph Fairweather, Bo Li, Rangachary Mukundan, James Fenton, and Rodney Borup, ***In Situ*** and *Ex Situ* **Characterization of Carbon Corrosion in PEMFCs**, submitted to 2010 ECS Transactions.

References

1. R. Borup, J. Meyers, B. Pivovar, et al., *Chemical Reviews*; **107(10)**, 3904 (2007).

2. T.G. Benjamin, Abstracts of the International Workshop On Degradation Issues in Fuel Cells, Hersonessos, Crete, Greece, (2007).

3. N.L. Garland, T.G. Benjamin, J.P. Kopasz, *ECS Trans.*, **V. 11 No. 1**, 923 (2007).

4. S. Knight, G. Escobedo, *Meeting Abstracts of 2006 Fuel Cell Seminar*, Honolulu, HI (2006).

5. A.Z. Weber, J. Newman, "Modeling Transport in Polymer-Electrolyte Fuel cells" *Chemical Reviews*, **V. 104**, 4679-4726 (2004).

6. DOE Cell Component AST Protocols for PEM Fuel Cells (Electrocatalysts, Supports, Membranes and MEAs), Revised October 15, 2008.