

V.E.5 Accelerated Testing Validation

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Fiscal Year (FY) 2012 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 the Durability Working Group.

Technical Barriers

This project addresses the following technical barriers from Fuel Cells section (3.4.5) 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 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: 1,650
 - Estimated Load cycles: 1,200,000
- Stationary Durability: 40,000 hours (2015); 60,000 hours (2020)
 - Survivability: Stationary -35°C to 40°C
- Cost: (30 \$/kW)

FY 2012 Accomplishments

- Performed the electrocatalyst and catalyst-support ASTs on three different catalyst types based on different carbon support materials.
- Performed the membrane chemical and mechanical ASTs on four different membranes and proposed a new combined mechanical/chemical membrane AST.
- Performed failure analysis of MEAs and correlation between AST and real world data.
- Modeling of voltage loss breakdown and assigning voltage losses to specific degradation mechanisms.
- Proposed GDL AST based on ex situ aging in H₂O₂ and evaluated mass transport losses after aging.



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 with a rapid 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 verify that durability is not sacrificed 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).

DOE has suggested AST protocols for use in evaluating materials, but only for the catalyst layer components (electrocatalyst and support), and for the membrane [2,3]. The US Fuel Cell Council 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 micro-porous 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 are utilized in this project. Providing the variable material durability relies on the expertise of the suppliers as partners in this project. This work is also being coordinated with other funded projects examining durability through a DOE Durability Working Group.

Results

Carbon Corrosion

The DOE Fuel Cell Technical Team-recommended AST [6] for carbon corrosion was performed on three different MEAs, each with a different catalyst supplied by Tanaka Kikinoku Kogyo K.K., and designated TEC10E20E, TEC10V40E and TEC10EA40E. The carbon supports included a high surface area carbon (E-carbon), a vulcan carbon (V-carbon) and a highly graphitized carbon (EA-carbon). The MEAs with these three carbons had nominal cathode Pt loadings of 0.15 mg-Pt/cm² (E-carbon), 0.17 mg-Pt/cm² (V-carbon), and 0.25 mg-Pt/cm² (EA-carbon). Figure 1a illustrates the performance of these three MEAs after various periods of the 1.2 V AST. The initial performance of all three MEAs is comparable while their degradation rate is distinctly different. After only 20 hours of the AST, the E-carbon shows significant loss in performance, the V-carbon a slight loss in performance, and the EA carbon a slight improvement in performance. After 400 hours of this AST, only the MEA based on the EA-carbon had reasonable fuel cell performance with a loss of <40 mV @ 1.5 A/cm². The DOE target of 30 mV loss @ 1.5 A/cm² was exceeded after 4 hours, 32.5 hours and 240 hours for the E-carbon, V-carbon and EA-carbon respectively.

The electrochemical surface area (ECSA) and mass activity (MA) obtained before and after the high potential

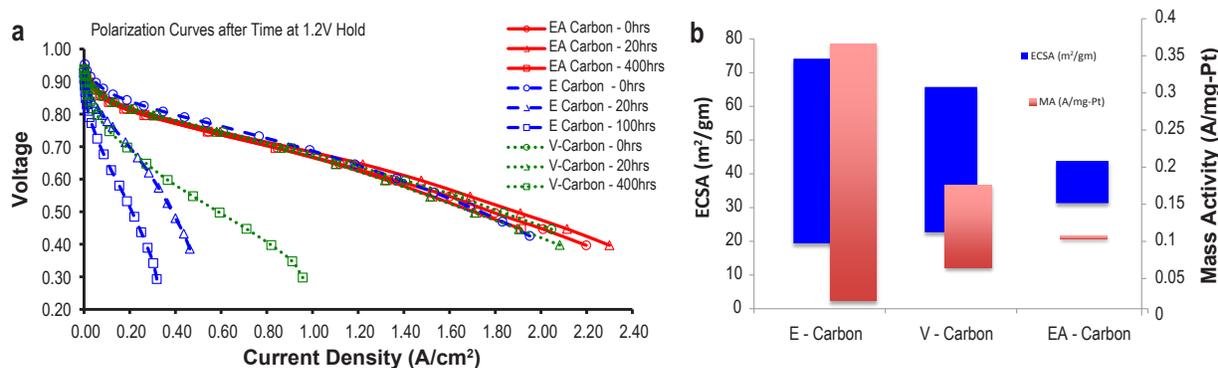


FIGURE 1. a) Polarization curves of three different catalysts using different carbon types before and after carbon corrosion AST of 1.2 V potential hold. b) Initial performance (electrochemical surface area and mass activity) characteristics of three different catalysts and degradation (bar length) using different carbon types.

hold (1.2 V) AST is illustrated in Figure 1b (the bar length represents the loss in performance). The performance characteristics of the three different carbon types used in this experiment are significantly different, with the E-carbon having the highest initial ECSA ($74 \text{ m}^2/\text{gm-Pt}$) and MA (0.37 A/mg-Pt) and the EA-carbon having the lowest initial ECSA ($44 \text{ m}^2/\text{gm-Pt}$) and MA (0.1 A/mg-Pt). However, the degradation rates of these three carbons are dependent on the degree of graphitization with the EA-carbon showing the most resistance to corrosion. As a result, after the 400-hour hold (only 100 hours for the E-carbon) the EA-carbon exhibited the best performance characteristics (ECSA = $31 \text{ m}^2/\text{gm-Pt}$; MA = 0.1 A/mg-Pt) and the E-carbon the lowest (ECSA = $19 \text{ m}^2/\text{gm-Pt}$; MA = 0.02 A/mg-Pt). Scanning electron microscopy studies revealed that the E-carbon and V-carbon corroded significantly and lost $\geq 60\%$ of their electrode thickness, in contrast to the EA-carbon that exhibited little ($<15\%$ loss in catalyst layer thickness) corrosion. Transmission electron microscopy studies showed that the catalyst based on the EA-carbon retained its structure while the E-carbon and V-carbon based electrodes exhibit significant densification and loss of porosity due to carbon becoming more amorphous.

Correlation of AST and Field Data

The AST (performed at LANL) and field data (obtained by Ballard) from two different bus module configurations were presented in our FY 2011 report. The two bus modules were labeled P5 and HD6 and operated in the field in Hamburg, Germany and on an Orange County Transportation Authority drive cycle in the laboratory respectively. In FY 2012 the ex situ analysis was completed and the correlations between the AST data and field data established.

Catalyst Degradation: The coarsening of Pt observed in the AST and field data is plotted in Figure 2 and illustrates significant Pt particle agglomeration variations in field samples from inlet to outlet. The HD6 AST showed a 58% increase in Pt crystallite size with respect to the beginning of life while the HD6 module sample showed similar Pt crystallite growth (average from inlet to outlet) at around 1,900 hours of operation (Figure 2a). The P5 AST showed a 102% increase in Pt crystallite size with respect to the beginning of life while P5 field samples at 2,600 hours showed a larger average Pt crystallite size growth of 157%. These results indicate that 30,000 AST potential cycles correspond to $\approx 2,000$ hours of field operation under high relative humidity (RH) conditions. Carbon corrosion AST samples also showed excellent agreement with field data with the HD6 catalyst layer exhibiting no thinning while the P5 data showed 60% thinning in the AST and 30–70% thinning in the field.

Membrane Degradation: The open circuit voltage (OCV-hold) AST resulted in failure of the P5 and HD6 MEAs after approximately 100 hours. This test also resulted in significant

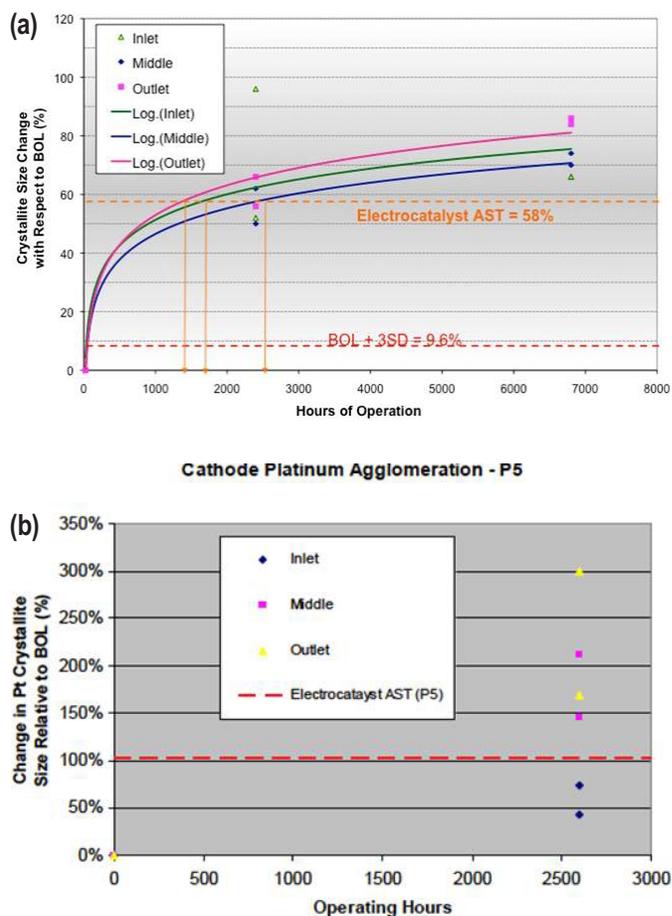


FIGURE 2. Platinum crystallite growth in AST and field samples: a) HD6 bus module operated in OCTA drive cycle, b) P5 bus modules operated in the field

thinning of the P5 and HD6 membranes before failure. The thickness change for the P5 MEA after the AST and bus operation is illustrated in Figure 3a. The P5 MEA shows no thinning after $>2,500$ hours of field operation (left 2 bars of Figure 3a) whereas the AST resulted in 28% and 48% thinning after 104 and 168 hours at OCV respectively (right two bars in Figure 3a). Similar results were obtained for the HD6 MEA (not shown) where no thinning was observed after $>6,500$ hours of operation in a bus module, while the AST resulted in 20% thinning after 144 hours. This clearly illustrates that the chemical degradation AST that has been designed for drier automotive applications is too severe and does not capture the membrane degradation occurring in the wetter bus module environment.

The RH cycling AST resulted in no observable increase in crossover in either the P5 or the HD6 MEAs over the life of the test, which was 20,000 cycles or 1,333 hours (open symbols in Figure 3b). However, this test did result in a partial tearing of the MEA near the cathode side and the formation of divots, with the catalyst layer detached from the MEA. Similar failure was observed in the field for both

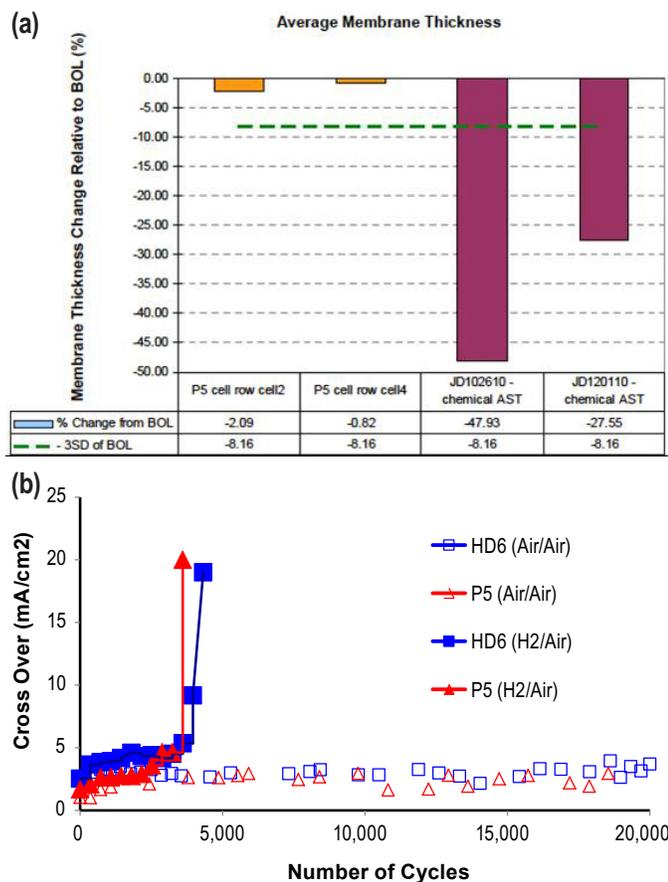


FIGURE 3. a) Change in membrane thickness of the P5 MEA after field test and after AST. Field test data from cell 2 and cell 4 are shown (orange bars) and AST data after 168 and 104 hours from two different cells are shown (maroon bars). b) Crossover of P5 and HD6 MEAs subjected to RH cycling in air/air and RH cycling in H₂/Air.

P5 and HD6 modules especially near the inlets and outlets. These results indicate that while the chemical degradation AST greatly overestimates the membrane degradation rate, the RH cycling greatly underestimates it. Therefore to better capture the failure modes observed in the field a combined chemical/mechanical AST was performed. As illustrated by the solid symbols in Figure 3b this combined chemical/mechanical AST (replacing the air on one side of the MEA in the RH cycling test with H₂) resulted in the failure of the P5 MEA after 3,500 cycles (233 hours) and the HD6 MEA after 4000 cycles (267 hours). Failure analysis of these MEAs and repeat experiments are in progress to verify the degradation mechanisms under operation during this combined membrane degradation test.

GDL AST

Different GDL materials were subjected to ex situ aging protocols in H₂O₂, and in situ tested with fresh commercial Gore MEAs to illustrate the effect of GDL aging on fuel cell performance. The simulated aging of GDLs was achieved by

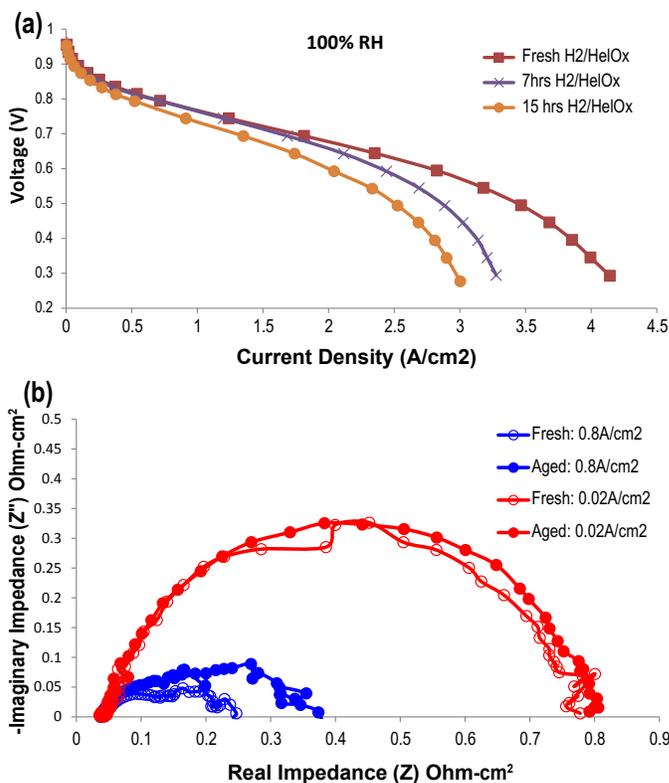


FIGURE 4. a) Performance of fresh and ex situ AST aged 25BC GDL materials and b) impedance of fresh and ex situ AST aged 25BC GDL materials

boiling them in 30% hydrogen peroxide at 95°C, contained in a reaction vessel equipped with a coil reflux condenser (based on previously developed AST by SGL). GDLs were removed periodically at different time intervals to examine rate of aging. Figure 4a illustrates the effect of aging on performance losses of an SGL Sigracet® 25BC GDL under high RH, 21% oxygen/79% helium gas mixture operation while the dry performance is identical to the fresh GDL (not shown). Figure 4b shows that both fresh and aged GDLs have identical cell resistances in the kinetic region (0.2 A/cm²), while the resistance of the aged cells in the mass transport region (low frequency arc of 0.8 A/cm²) is significantly increased. Contact angle measurements revealed that the hydrophobicity of these GDLs decreased over time consistent with in situ fuel cell GDL degradation reported previously [7].

Conclusions and Future Directions

High surface area carbon exhibited the best initial performance but also the fastest degradation rate. Highly graphitized carbon on the other hand, had the lowest initial performance while also exhibiting the slowest degradation rate. Transmission electron microscopy analysis of the MEAs after corrosion indicated Pt particle size growth in all the catalyst layers in addition to significant thinning of the high surface area carbon-based catalyst layers. While Pt sintering

due to coalescence led to performance losses up to 40 mV, the greatest performance loss (up to 360 mV) was associated with mass transport losses resulting from a compaction of the catalyst layer porosity due to the formation of amorphous oxidized carbon. The carbon corrosion and electrocatalyst ASTs were able to accurately capture the field data with 30,000 AST potential cycles corresponding to \approx 2,000 hours of bus operation. The membrane/chemical degradation AST resulted in significant membrane thinning not observed in the field. The membrane mechanical degradation AST was able to reproduce the degradation phenomenon observed in the field but had little ability to distinguish between various membranes each operating for over 1,300 hours without observable performance degradation. A combined mechanical/chemical AST was successful at accelerating the degradation rates observed in the field and failure analysis is in progress to correlate this AST to field data. A new GDL AST was designed and this AST resulted in performance losses due to hydrophobicity loss of GDL consistent with previously reported in situ fuel cell data. The following specific work will be carried out in the next year of this project in order to validate existing ASTs and recommend new ASTs.

- AST testing:
 - Develop ASTs for metal bipolar plate materials
 - Correlate degradation in newly proposed GDL AST with Fuel Cell testing
- “Real-world” testing:
 - Complete simulated automotive drive cycle testing on selected materials with differing durability
 - Continue studying effect of operating conditions (stressors) like temperature, pressure and RH on drive cycle testing
- Characterization of materials:
 - Complete ex situ characterization of catalyst particle size distribution, layer thickness, membrane thickness, and GDL hydrophobicity as a function of AST, drive cycle, and “real-world” testing
- Correlation of AST to “real-world” data:
 - Statistical correlation of performance degradation with physical properties in both AST and “real-world” data

FY 2012 Publications/Presentations

1. R. Mukundan, Invited talk, 2nd International Workshop on Degradation Issues of Fuel Cells, Thessaloniki, Greece, September 2011.
2. R. Mukundan, Invited talk, 220th ECS meeting, Boston, MA, October, 2011.
3. R. Mukundan, G. James, J. Davey, D. Langlois, D. Torrace, W. Yoon, A.Z. Weber, and R. Borup, “Accelerated Testing Validation” ECS Trans. 41 (1), 613 (2011).
4. R. Mukundan, G. James, D. Ayotte, J. Davey, D. Langlois, D. Spornkaj, D. Torrace, S. Balasubramanian, A. Weber, K. More, and R. Borup, Accelerated testing of carbon corrosion and membrane degradation in PEM fuel cells, Abstract accepted, 222th ECS meeting, Honolulu, HI.

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).
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5. A.Z. Weber, J. Newman, “Modeling Transport in Polymer-Electrolyte Fuel cells” *Chemical Reviews*, **V. 104**, 4679-4726 (2004).
6. FreedomCAR Fuel Cell Tech Team Cell Component AST and polarization curve Protocols for PEM Fuel Cells (Electrocatalysts, Supports, Membranes and MEAs), Revised December 16, 2010.
7. D. Wood, Ph.D. Thesis, “Fundamental Material Degradation Studies During Long Term Operation of Hydrogen/Air PEMFCs”, University of New Mexico, (2007).