

V.E.7 Accelerated Testing Validation

Rangachary Mukundan¹ (Primary Contact),
Rod Borup¹, John Davey¹, Roger Lujan¹,
Dennis Torraco¹, David Langlois¹,
Fernando Garzon¹, W. Yoon², Adam Weber²,
Mike Brady³, Greg James⁴, and Steve Grot⁵

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

DOE Manager

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

Subcontractors:

- ² Lawrence Berkeley National Laboratory (LBNL),
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

Fiscal Year (FY) 2011 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.
- Coordinate 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: 1,650
- Estimated load cycles: 1,200,000

Stationary Durability: 40,000 hours

- Survivability: Stationary -35°C to 40°C

Cost (\$25/kWe)

FY 2011 Accomplishments

- Performed all four DOE Fuel Cell Tech Team recommended ASTs on two different Ballard membrane electrode assemblies (MEAs) that were used in bus stacks.
- Failure analysis of MEAs and correlation between AST and real world data initiated.
- Initial breakdown analysis of two different types of bus stacks completed by Ballard.
- Modeling of voltage loss breakdown completed by LBNL.
- LANL validates the performance of Ion Power MEAs using different Tanaka catalysts and DuPont XL membranes.



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 hours (~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).

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 microporous layers (MPLs), 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 proposal. 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

The DOE Fuel Cell Technical Team recommended ASTs [6] were performed on two different MEA types (viz. P5 and HD6); that were used in buses operated in Hamburg (Germany), and in a bus module operated in the laboratory on an Orange Country Transit Authority cycle, respectively. The results from the potential cycling and high potential hold ASTs are illustrated in Figure 1a and b, respectively.

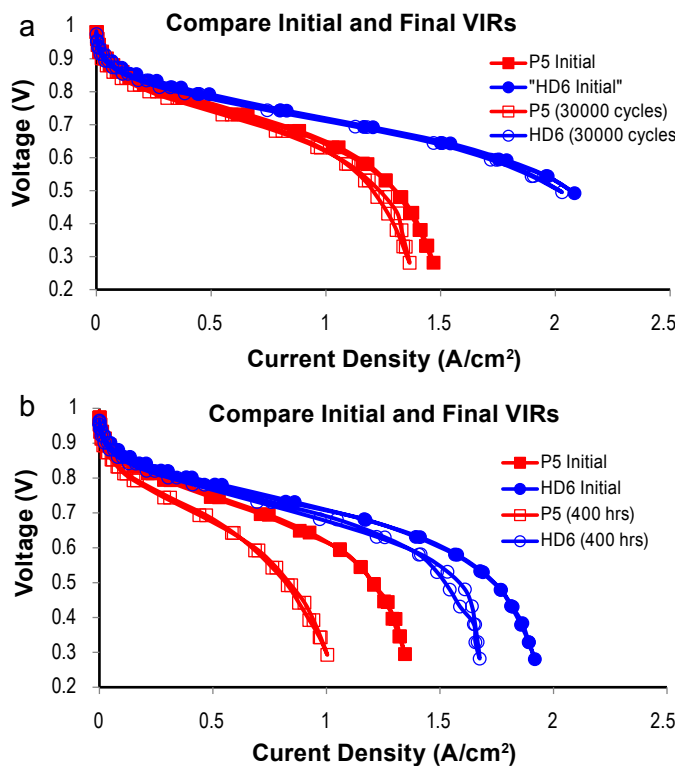


FIGURE 1. Performance of P5 and HD6 MEAs: a) before and after potential cycling and b) before and after high potential hold.

It is seen that the performance of the HD6 (circa 2007) MEA is significantly better than the performance of the P5 (circa 2002) MEA, especially in the mass transport region. Both these MEAs showed excellent durability of the Pt electrocatalyst as illustrated in Figure 1a by little performance loss after 30,000 potential cycles from 0.6 V to 1 V. Both MEAs met all performance targets including electrochemical surface area (ECSA) (<40% loss), mass activity (<40% loss) and voltage loss @ 0.8 A/cm² (<30 mV loss). On the other hand, the high potential hold AST resulted in significant degradation due to carbon corrosion especially in the P5 MEA (Figure 1b). While the P5 MEA failed to meet any of the DOE targets, the HD6 MEA met both the ECSA (<40% loss) and mass activity (<60% loss) targets, but failed to meet the voltage loss (@ 1.5 A/cm²) target (30 mV loss occurs at 175 hours while the target is 400 hours). This illustrates the fact that carbon corrosion leads to significant mass transport losses in addition to kinetic losses, and the voltage loss target is more relevant than the ECSA and mass activity targets for this particular AST.

The voltage loss breakdown in these cells as a function of ageing time was extracted by using a simple one-dimensional model to fit the polarization curves and impedance response of the single cells. This is illustrated in Figures 2a and b, for the potential cycling AST and high potential hold AST, respectively. During the potential cycling AST (Figure 2a) there is a small (<15 mV) increase in the voltage loss in the kinetic region while the

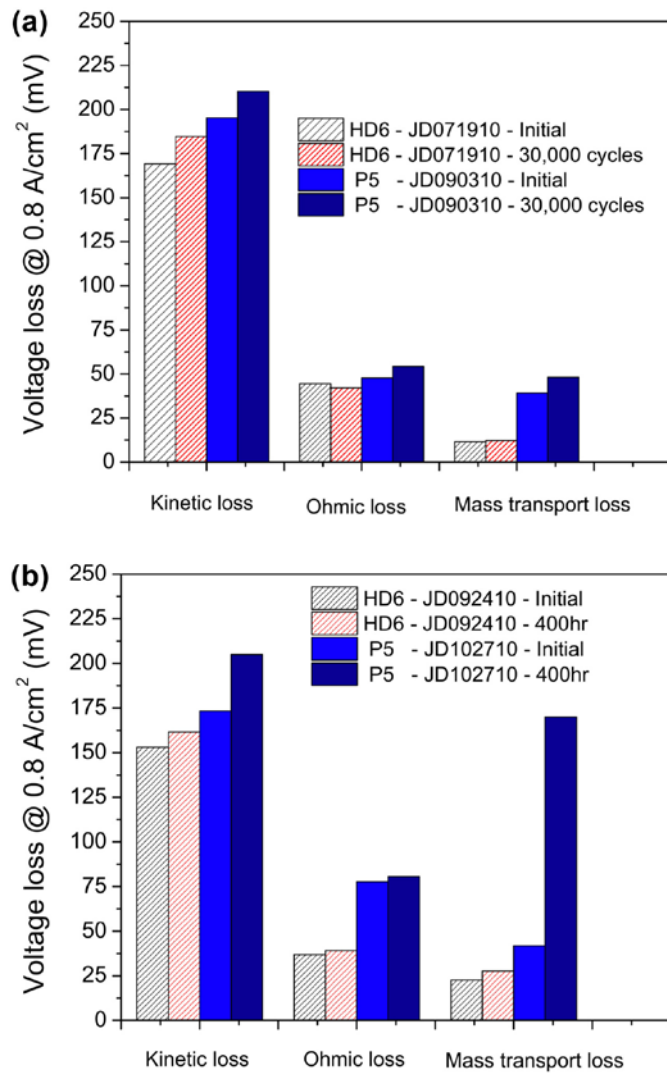


FIGURE 2. Voltage loss breakdown of the P5 and HD6 cells at 0.8 A/cm² obtained using a one-dimensional model: a) before and after potential cycling and b) before and after high potential hold.

ohmic and mass transport contributions remain virtually unchanged. This is consistent with the approx. 30% loss in ECSA observed for the two cells. During the 400 hours of high potential hold AST (Figure 2b) there is a much greater increase in both the kinetic (>25 mV loss) and mass transport losses (>125 mV loss) of the P5 cell when compared to the HD6 cell (<20 mV) at a constant current density of 0.8 A/cm². This is consistent with the more corrosion-resistant carbon used in the HD6 MEA. Failure analysis of these MEAs has been initiated and the Pt particle sizes and catalyst layer thicknesses will be measured and used to validate these ASTs with real world data from the bus fleets.

The performance of three P5 bus stacks operated in Hamburg (Germany) is illustrated in Figure 3a where all three stacks show a degradation rate of ≈30 μV/cell/hour. This is despite the fact that these stacks were exposed to

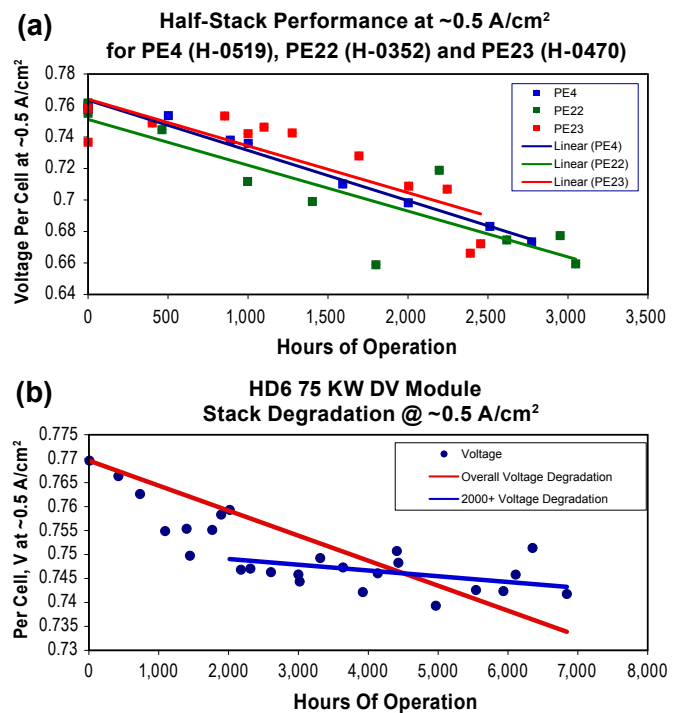


FIGURE 3. Voltage degradation observed in a) three P5 bus stacks operated in the field and b) one HD6 module operated under the Orange County Transit Authority drive cycle.

different stressors including temperature, relative humidity, voltages and air/air starts. The only tangible difference in the stressors was the lower number of air/air starts (263) in the PE23 stack which was associated with the lowest voltage degradation rate of 26.3 μV/cell/hour. The HD6 stack was operated in a laboratory under drive cycle conditions and showed an average degradation rate of 5.2 μV/cell/hour (Figure 3b). The data quality from this stack is better than the field data and clearly shows two different degradation rates with the 2,000 to 7,000 hour data showing only a degradation rate of 1.2 μV/cell/hour. The failure analysis from these stacks will be utilized to compare the field data with the AST data.

The open circuit voltage and fluorine emission rate in the effluent water during the membrane chemical degradation AST [6] test of the P5 and HD6 MEAs is shown in Figure 4a. Although the P5 MEA was 50 μm thick while the HD6 MEA was only 25 μm thick, the OCV of the P5 MEA degraded slightly faster than that of the HD6 MEA. It is also seen that the P5 MEA has a much larger fluorine emission rate than the HD6 cell, which is consistent with its worse performance in the field. This is illustrated in Figure 4b where the three P5 stacks all failed due to transfer leaks in <3,400 hours while the HD6 showed an increase in transfer leak rates only after 5,500 hours. The results of the AST test and field data will be modeling in the future and will be validated with the failure analysis from both the AST and bus stack MEAs.

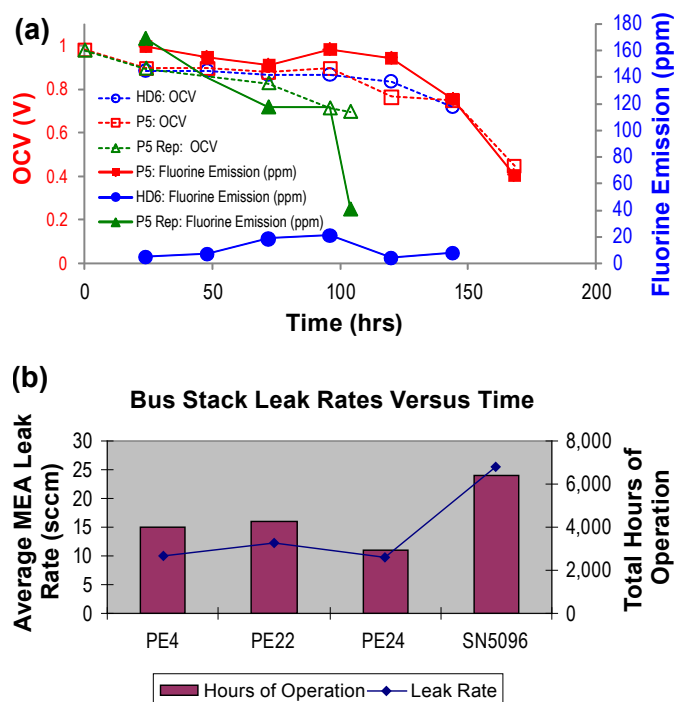


FIGURE 4. a) Fluorine content of the outlet water during an OCV AST test and b) transfer leak rates observed in P5 and HD6 stacks operated in buses.

Conclusions and Future Directions

The results from the P5 and HD6 AST tests are consistent with their performance observed in the field. While the potential cycling AST and relative humidity cycling ASTs showed little difference between the P5 and HD6 samples, the high potential and OCV hold ASTs highlighted the better performance of the HD6 MEAs. This will be correlated with the better performance in the field; both lower voltage degradation rates and delayed membrane transfer leaks. The field data is noisy due to recoverable performance losses and highly varying current demand imposed by the bus drive cycle. Moreover the effect of various stressors including temperature, voltage, relative humidity and air/air cycling complicates interpretation of field data. Failure analysis and voltage loss modeling work have been initiated and are expected to help correlate the AST data with the field data. The following specific 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 materials with differing durability supplied by Ion Power.
- Develop ASTs for ORNL-supplied bipolar plate materials and SGL-supplied GDLs/MPLs.

“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.

Characterization of Materials

- 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

- Statistical correlation of performance degradation with physical properties in both AST and “real-world” data.

FY 2011 Publications/Presentations

1. R.L. Borup and R. Mukundan, PEM Fuel Cell Degradation, *ECS Trans.* 33 (1), 17 (2010).
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3. R. Mukundan, G. James, J. Davey, D. Langlois, D. Torracco, W. Yoon, A. Weber, and R. Borup, Accelerated Testing Validation, Abstract accepted, 220th ECS meeting, Boston, MA.

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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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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.