V.D.3 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],
Dusan Spernjak[1], Joe Fairweather[1],
Sivagaminathan Balasubramanian[2], Adam Weber[2],
Mike Brady[3], Karren More[3], Greg James[4],
Dana Ayotte[4], Paul Beattie[4], Steve Grot[5],
Gaël Maranzana[6], Adrien Lamibrac[6], Jérôme Dillet[6],
Olivier Lottin[6], and Kateryna Artyushkova[7]

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

DOE Manager

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

Subcontractors:
[2] Lawrence Berkeley National Lab, Berkeley, CA
[3] Oak Ridge National Laboratory, Oak Ridge, TN
[4] Ballard Power Systems, Burnaby, BC, Canada
[5] Ion Power, New Castle, DE
[6] LEMTA, Université de Lorraine, Vandoeuvre-lès-Nancy, France
[7] University of New Mexico, Albuquerque, NM

Project Start Date: October 2009
Project End Date: 2013

Overall 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

- Coordination of effort with the Fuel Cell Technical Team and the Durability Working Group

Fiscal Year (FY) 2013 Objectives

- Correlation of the component lifetimes measured in an AST to those measured during U.S. DRIVE "Protocol for Determining Cell/Stack Durability"

- Validation of existing component-specific ASTs for catalyst and membrane degradation against U.S. DRIVE "Protocol for Determining Cell/Stack Durability"

- Development and validation of new AST for GDL materials

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section (3.4.5) of the Fuel Cell Technologies Office 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 lifetimes required for stationary and automotive environments. Moreover, these ASTs can also help predict the lifetimes 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

  - Cost (30 $/kWe)

- Stationary Durability: 40,000 hours (2015); 60,000 hours (2020)

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

- Bus Durability: 12 years/500,000 miles (2016 and ultimate)

  - Power plant lifetime: 18,000 hours (2016), 25,000 hours (ultimate)

  - Power plant cost: $450,000 (2016), $200,000 (ultimate)

  - Range: 300 miles

  - Fuel economy: 8 miles/gallon diesel equivalent

FY 2013 Accomplishments

- Completed U.S. DRIVE recommended drive cycle test on four different membrane electrode assemblies (MEAs) utilizing three different membranes and three different catalyst layers

- Completed failure analysis of MEAs and derived correlation between AST and drive cycle data

- Identified correlations between electro-catalyst AST and drive cycle operations and identified carbon corrosion during drive cycle operation

- Identified mechanical degradation as main membrane failure mode during drive cycle operation

- Identified GDL degradation during drive cycle operation at high humidities

- Identified previously proposed GDL AST as too severe to correlate with in situ fuel cell testing and initiated development of a new AST based on drive cycle degradation data

- Modeled voltage loss breakdown with assignment of voltage losses to specific degradation mechanisms

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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 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 (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 lifetime 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 the DOE Durability Working Group.

RESULTS

The U.S. DRIVE Fuel Cell Technical Team recommended protocol for determining cell/stack durability [6] was performed on various MEA/GDLs using 50-cm^2 quad-serpentine hardware purchased from Fuel Cell Technologies Inc. An example of this drive cycle is demonstrated in Figure 1a, where two cycles are shown for clarity. We have termed this drive cycle as the "Wet/Dry Drive Cycle" since it involves both current cycling and relative humidity (RH) cycling. A modified drive cycle was used in some of these tests where only the high RH portion of the test was repeated. We have termed this test the "Wet Drive Cycle," and it consists of current cycling from 0.02 A/cm^2 to 1.2 A/cm^2 for 30 seconds each at a cell temperature of 80°C with anode and cathode dew points at 83°C. MEAs were also subjected to the start/stop protocol recommended by the Durability Working Group, as illustrated in Figure 1b. Here the cell was operated at a current density of 1.2 A/cm^2 for 5 minutes and then shut down with air at the anode for 200 secs, followed by the next start-up in H_2 and operation for a further 5 minutes. To distinguish the effect of just the start-up (shut-down), the air (H_2) used during the shut-down (start-up) was replaced with N_2.
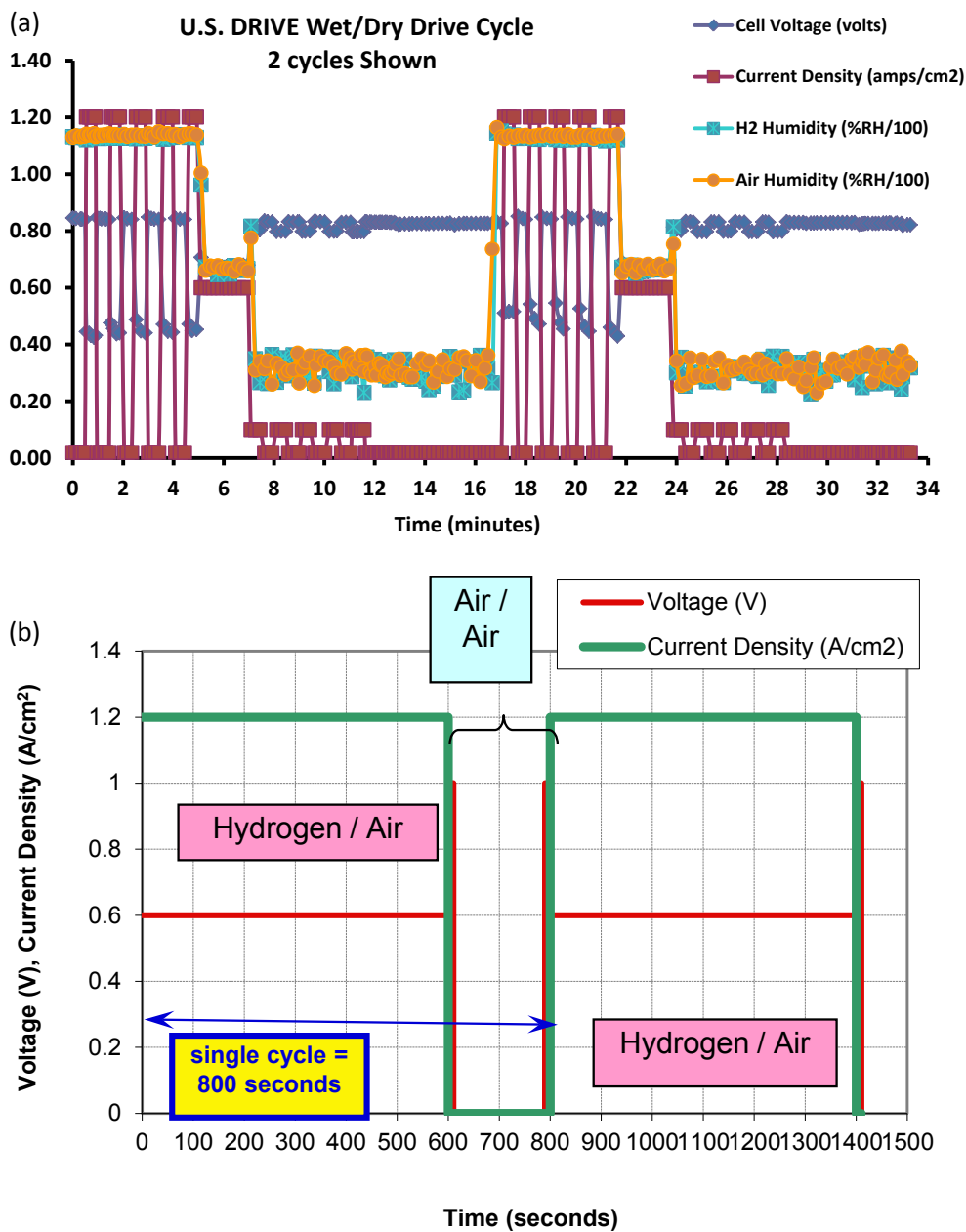
FIGURE 1. a) Voltage, current density, flow rates, and RHs as a function of time during the Wet/Dry Drive Cycle testing protocol. b) Voltage and current density as a function of time during the start/stop protocol.

Catalyst Degradation

The electro-catalyst degradation observed in the Wet/Dry Drive Cycle test showed a direct correlation with the electro-catalyst AST performed on an identical catalyst. For example, the percent electrochemical surface area (ECSA) loss observed in the Wet/Dry Drive Cycle and the 0.6 to 1.0 V cycling AST is plotted in Figure 2a and shows excellent agreement in terms of ECSA loss with potential cycles. Similar results were also obtained for the Wet Drive Cycle testing, where the ECSA loss was similar during the first

20,000 cycles. The wet cycling, however, showed increased loss in ECSA compared to the AST (at >20,000 cycles), which is probably due to the higher RH (114%) used in the Wet Drive Cycle. Post-mortem testing illustrated an increase in Pt crystallite size with decreasing ECSA consistent with field test data from buses reported in FY 2012. In addition to the Pt growth, significant electrode thinning was also observed after long-term drive cycle testing, especially in high surface area carbon (HSAC)-based MEAs. This is consistent with non-dispersive infrared measurements showing evolved CO_2
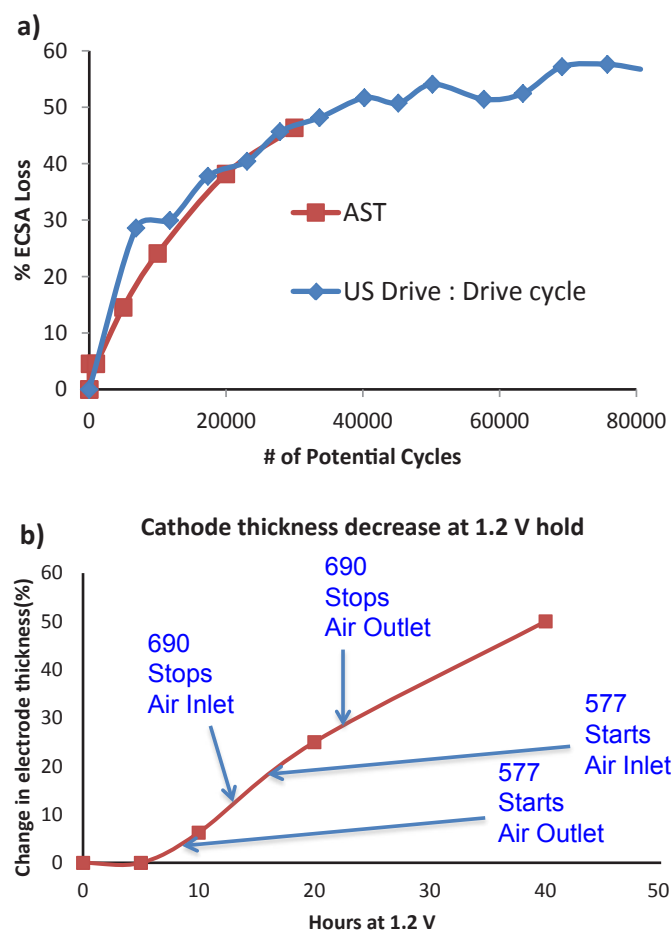
FIGURE 2. a) ECSA loss (%) of HSAC-based catalyst layer during Wet/Dry Drive Cycle testing and during 0.6 to 1.0 V cycling electro-catalyst AST. b) Change in electrode thickness (%) as a function of duration during the 1.2 V carbon corrosion AST. Data from start and stop tests of a similar MEA is also presented for comparison.

effect. Moreover, the U.S. DRIVE Fuel Cell Technical Team has recommended a new AST for carbon corrosion (cycling from 1.0 to 1.5 V), which will be evaluated in the future.

Membrane Degradation

The drive cycle results showed membrane degradation in addition to the catalyst degradation reported in the previous section. This membrane degradation resulted in increased crossover and eventual failure of the cells. This is illustrated in Figure 3a, where the crossover of various MEAs tested under both the Wet and Wet/Dry Drive Cycles is plotted. The Wet/Dry Drive Cycle resulted in faster failure than the Wet Drive Cycle, and the non-stabilized (Sample A) membrane resulted in faster failure than the chemically and mechanically stabilized membrane (Sample B). Ex situ characterization of beginning-of-life (BOL) and end-of-life (EOL) MEAs revealed little change in thickness of the membrane (Figure 3b) up to 2,500 hours of the drive cycle testing. The failure of the MEAs was due to local thinning of the membrane probably caused by membrane mechanical degradation accelerated by chemical degradation, rather than purely membrane chemical degradation. These results are consistent with the field data from buses reported in FY 2012, where no membrane thinning was observed in the field at EOL and failure was due to cracks in the membrane mainly at the inlet and outlet of cells. Thus, drive cycle testing confirms that the open-circuit voltage AST is too severe and the RH cycling AST too benign when compared to the degradation observed in real-world applications. A combined mechanical/chemical AST which involves RH cycling under open-circuit voltage at 80°C was able to reproduce the failure mode observed in the field data and will be studied further to serve as a membrane AST capable of predicting lifetimes. Further testing is ongoing and has revealed that mechanically and chemically stabilized membranes (Gore-Select® M720.18 and Dupont™ Nafion® XL) last over 3,000 hours of Wet/Dry Drive Cycle testing without any observable increase in crossover.

GDL Degradation

The durability of two different GDL materials provided by SGL Carbon was evaluated. The standard GDL material was Sigracet® 25BC with 5% poly-tetrafluoroethylene in the substrate and 23% poly-tetrafluoroethylene in the MPL. A new GDL material (25BN) that contained 25% multi-walled carbon nano-tubes in the MPL was also evaluated [7]. The cells with BC and BN cathode GDLs were subjected to either the Wet/Dry Drive Cycle or Wet Drive Cycle. Extensive in situ characterization including cyclic voltammetry, alternating current impedance, and polarization curves in air/oxygen/HelOx were performed periodically during the drive cycle ageing. Ex situ characterization including scanning electron microscope cross-sections, X-ray photoelectron spectroscopy (XPS), and transmission electron microscopy were performed on MEAs at BOL and
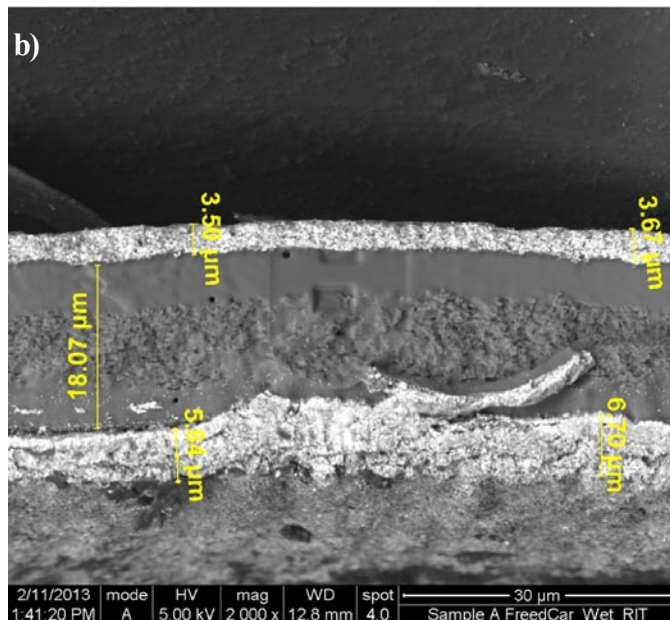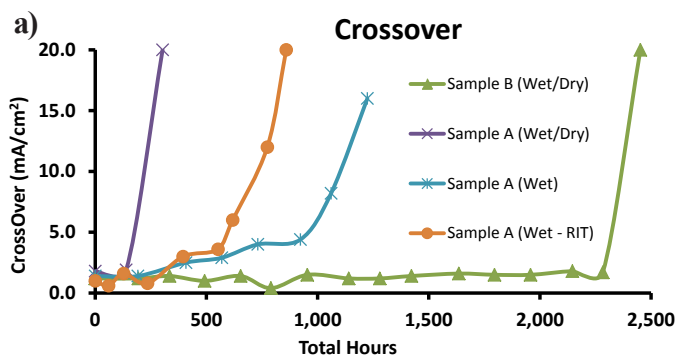
from carbon corrosion of the cathode at voltages as low as 0.9 V.

The effect of start/stops on a HSAC-based electrode was evaluated at University of Lorraine (Nancy, France) in a counter-flow configuration on a 5 parallel channel 1 cm x 30 cm segmented cell. These results indicate that start-ups are more damaging than shut-downs, and those segments exposed to air/air potentials for the longest time show the most degradation. The degradation results in both a decrease in catalyst layer thickness and an increase in the Pt particle size. These changes result in a loss in both the kinetic and mass transport performance of the MEAs. The catalyst layer thickness for an HSAC-based MEA observed during the start/stop tests is compared to that observed during the 1.2 V AST test in Figure 2b. Approximately 15 hours of the AST corresponds to ≈300 start/stop operations, implying that 400 hours of testing will correspond to ≈8,000 start/stop operations. Further experimentation is underway with higher durability carbons and longer hold-times to quantify this

a)

b)

FIGURE 3. a) Crossover of various non-stabilized membranes (Sample A) and mechanically/chemically stabilized (Sample B) during both Wet/Dry and Wet Drive Cycle testing. b) Cross section of a non-stabilized MEA subjected to 850 hours of Wet Drive Cycle testing.

a)

b)

FIGURE 4. a) Alternating current impedance at high current density of MEAs with a) in situ and b) ex situ aged GDLs.

at EOL. The GDL materials were also subjected to an ex situ AST ageing protocol and subsequently tested in situ with fresh commercial Gore® Primea® MEAs to illustrate the effect of GDL AST-ageing on fuel cell performance. The ex situ ageing of GDLs was achieved by submerging them in a boiling solution of 30% hydrogen peroxide at 95°C for prolonged intervals up to 15 hours (this protocol was first reported by SGL as their part of the DECODE project). The GDLs were removed periodically at different time intervals, and XPS and contact angle measurements were performed to quantify any changes to the GDL material as a function of ageing time.

The drive cycle testing of the MEA/GDLs resulted in voltage degradation as a function of time. The MEA with the low surface area carbon (LSAC)-based cathode-catalyst showed little change in the kinetic region and <20% ECSA loss after approximately 125 hours of ageing. However,
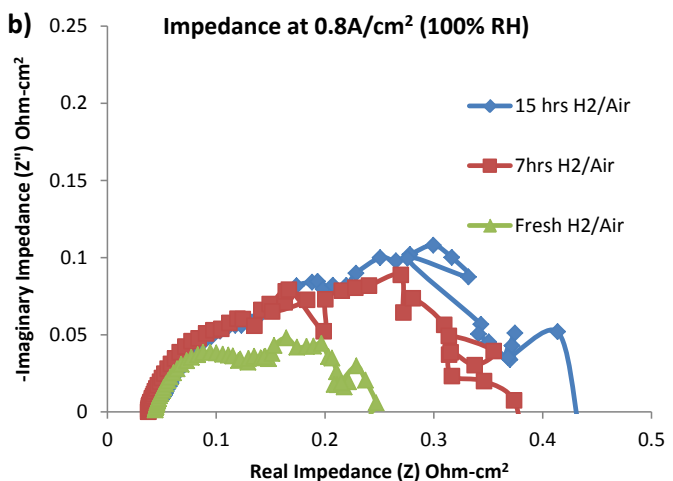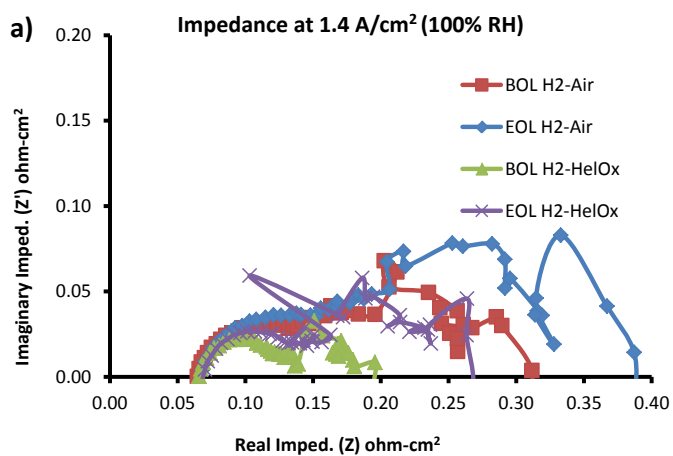
this MEA showed up to 100 mV loss at a current density of 2 A/cm^2. The catalyst layer thickness of the EOL MEAs indicates no change in the catalyst layer thickness of this TEC10EA40E catalyst-based MEA. These results indicate that while there is little catalyst degradation in the LSAC-based MEA, there is still voltage degradation at high current densities. Alternating current impedance data were obtained to delineate the voltage losses observed in the polarization curves. The impedance at high current densities for this MEA is illustrated in Figure 4a, showing an increase in the low frequency region of the impedance. Moreover, this increase in resistance was greater when measured with air at the cathode than when measured with HelOx at the cathode (Figure 4a). These results, when combined with the ex situ examination of the catalyst layer, confirm that the LSAC catalyst layer itself does not degrade much and does not contribute significantly to voltage loss while ageing. These results also indicate that the mass transport losses are probably arising from changes to other components in the system, namely the GDL. The high current impedance shown in Figure 4b clearly illustrates increase in the mass transport

resistance (low frequency arc) of the cells using the ex situ aged GDL when compared to the cell using the fresh GDL. The impedance and voltage-current-resistance characteristics obtained from the ex situ aged GDLs were similar to those observed in the in situ drive cycle-aged GDLs. This provides further evidence of GDL degradation during drive cycle operation of fuel cells and suggests that the ex situ ageing can be used as an AST for probing the durability of GDL materials. Finally, the use of the improved 25 BN GDL showed remarkable improvement in the drive cycle durability performance, further confirming GDL degradation as the major degradation mechanism in these MEAs. XPS results from the ex situ aged GDLs confirmed GDL oxidation consistent with loss of hydrophobicity and observed decreases in contact angle. The XPS and polarization results also indicate that most of the changes in the GDL happen during the first few hours of the ex situ ageing. Further tests using lower peroxide concentrations and lower temperatures are underway in order to design an improved GDL AST that can simulate in situ GDL degradation.

CONCLUSIONS AND FUTURE DIRECTIONS

The electro-catalyst AST was found to accurately capture the Pt ECSA loss occurring during Wet/Dry Drive Cycle testing. While the 1.2 V hold AST was able to simulate the carbon corrosion occurring during unmitigated start/stops, the duration of the AST was long (400 hours). The Fuel Cell Technical Team has recommended a new AST (1.0 to 1.5 V cycling) for carbon corrosion, which will be performed in FY 2014. Significant carbon corrosion was observed during drive cycle testing of a HSAC-based MEA, while negligible catalyst thinning (corrosion) was observed on a LSAC-based MEA. GDL degradation was found to be the limiting factor during the Wet/Dry Drive Cycle testing (at high current densities) of low-loaded LSAC-based MEAs. This GDL degradation can be mitigated using an advanced GDL that incorporates 25% multi-walled carbon nanotubes in the MPL. Membrane mechanical degradation was found to be the limiting factor during the Wet/Dry Drive Cycle testing of high-loaded MEAs.

AST Testing

- Conduct tests on LSAC, HSAC, and Vulcan carbon-based MEAs using the 1.0 to 1.5 V cycling carbon corrosion AST
- Develop ASTs for metal bipolar plate materials
- Refine GDL AST to better simulate GDL degradation observed during drive-cycle testing

"Real-World" Testing

- Complete Wet/Dry Drive Cycle testing (up to 5,000 hours) on chemically and mechanically stabilized membranes (Dupont™ Nafion® XL)

- Obtain "real-world" data from materials handling applications

Characterization of Materials

- Complete ex situ characterization of catalyst particle size distribution, layer thickness, membrane thickness, and GDL hydrophobicity as a function of drive cycle test time

Correlation of AST to "Real-World" Data

- Complete statistical correlation of performance degradation with physical properties in both AST and "real-world" data

FY 2013 PUBLICATIONS/PRESENTATIONS

1. S. Arisetty, X. Wang, R.K. Ahluwalia, R. Mukundan, R. Borup, J. Davey, D. Langlois, F. Gambini, O. Polevaya, S. Blanchet, "Catalyst Durability in PEM Fuel Cells with Low Platinum Loading", Journal of the Electrochemical Society (2012), 159(5), B455-B462.

2. J.D. Fairweather, D. Spernjak, A.Z. Weber, D. Harvey, S. Wessel, D.S. Hussey, D.L. Jacobson, K. Artyushkova, R. Mukundan, and R.L. Borup, "Effects of Cathode Corrosion on Through-Plane Water Transport in Proton Exchange Membrane Fuel Cells", *J. Electrochem. Soc.*, **160 (9),** p. F980-F993 (2013).

3. R. Mukundan, G. James, D. Ayotte, J. Davey, D. Langlois, D. Spernjak, D. Torraco, S. Balasubramanian, A. Weber, K. More, and R. Borup, "Accelerated testing of carbon corrosion and membrane degradation in PEM fuel cells", *ECS Trans.*, **V. 50 No. 2**, 1003-1010 (2013).

4. R. Mukundan, J. Davey, K. Rau, D. Langlois, D. Spernjak, J. Fairweather, K. Artyushkova, R. Schweiss, and R. Borup, "Degradation of Gas Diffusion Layers in PEM fuel cells during drive cycle operation", *Abstract Accepted, 224th ECS Meeting, San Franciso* (2013).

5. R. Mukundan, et. al., "Accelerated Testing Validation", FC Tech Team, Detroit, MI, February 12, 2013 (Invited Presentation).

6. R. Mukundan, et. al., "Durability of Polymer Electrolyte Membrane Fuel Cells", The 19th International Conference on Solid State Ionics, Kyoto, Japan 2013 (Invited Presentation).

7. R. Mukundan, et. al., "Durability of Polymer Electrolyte Membrane Fuel Cells", University of Lorraine, Nancy, France, June 2013 (Invited Presentation).

8. R. Mukundan, et. al., "Durability of Polymer Electrolyte Membrane Fuel Cells", CEA, Grenoble, France, June 2013 (Invited Presentation).

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. 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. R. Schweiss, M. Steeb, P. M. Wilde, and T. Schubert, *J. Power Sources*, **220**, 79-83 (2012).