

## V.E.2 Accelerated Testing Validation

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Project Start Date: October 2009

Project End Date: September 2014

### 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
- Co-ordinate effort with Fuel Cell Tech Team (FCTT) and Durability Working Group

### Fiscal Year (FY) 2014 Objectives

- Compare the United States Driving Research and Innovation for Vehicle efficiency and Energy sustainability (U.S. DRIVE) FCTT’s new AST for carbon corrosion (1- to 1.5-V cycle) with the U.S. DRIVE FCTT’s old AST for carbon corrosion (1.2-V hold)
- Development of a new membrane AST that is representative of membrane degradation observed in the field and during the U.S. DRIVE FCTT “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 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
  - 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 2014 Accomplishments

- Completed the U.S. DRIVE FCTT 1- to 1.5-V cycling AST on membrane electrode assemblies (MEAs) utilizing three different carbon types
- Determined that 1- to 1.5-V cycling results in 1 order of magnitude greater carbon corrosion than the 1.2-V hold
- Determined that 1- to 1.5-V cycling results in approximately 100 times faster Pt growth rate and voltage decay rate than the 1.2-V hold

- Determined that 1- to 1.5-V cycling has the ability to clearly distinguish various carbon types with different degrees of graphitization
- Initiated development of a new membrane AST that has the ability to reproduce degradation mechanisms observed in the field and during simulated durability tests using the U.S. DRIVE FCTT “Protocol for Determining Cell/Stack Durability”
- Developed a GDL degradation AST that results in similar degradation to that observed during durability tests using the U.S. DRIVE FCTT “protocol for determining cell/stack durability”
- GDL fingerprinting, mercury intrusion porosimetry (MIP), and contact angle measurements utilized to quantify GDL degradation



## INTRODUCTION

The durability of polymer electrolyte membrane 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 polymer electrolyte membrane 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 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 United States 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 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

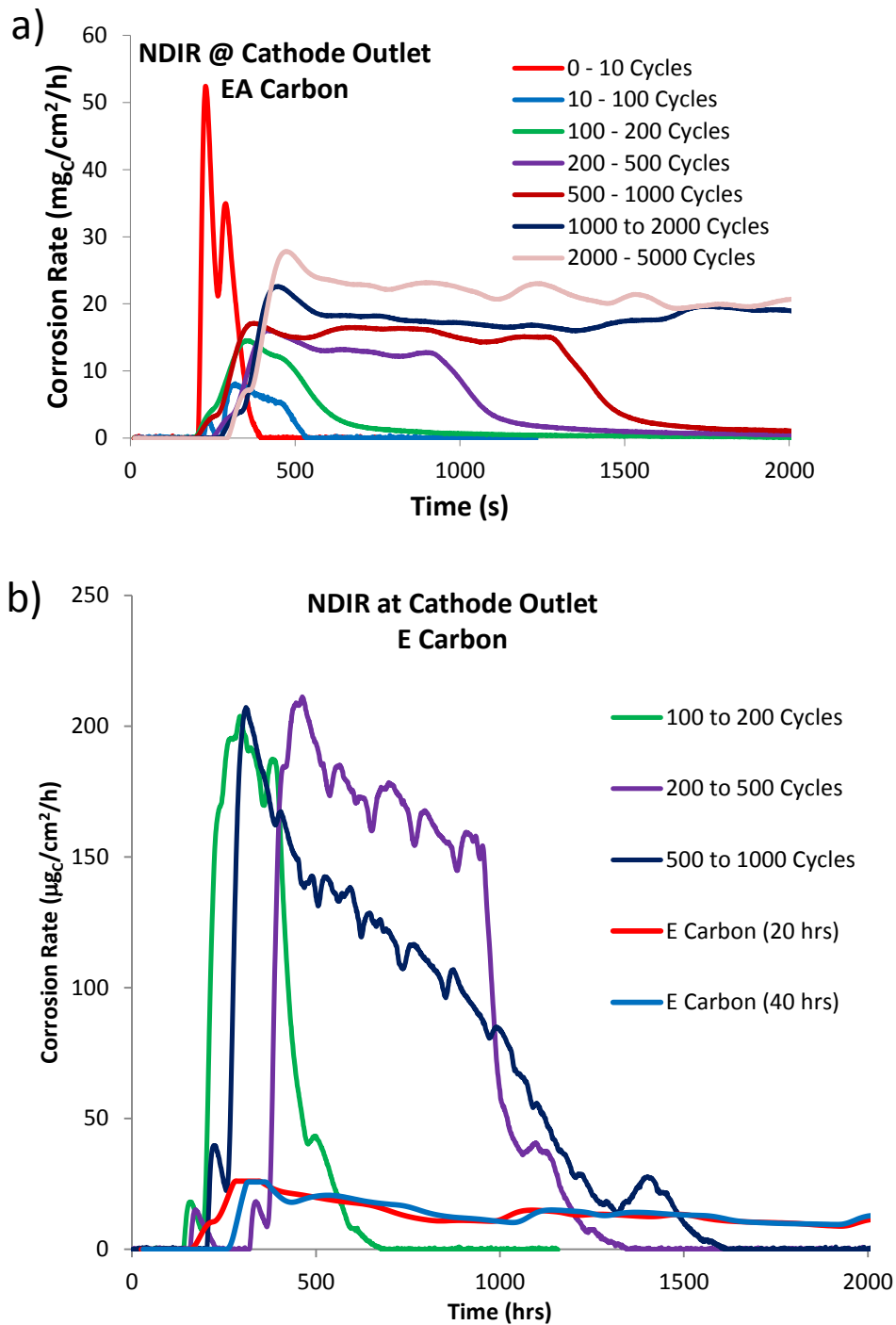
A main desired outcome of this project is the correlation of the component lifetimes measured in an AST to in situ behavior of that component in “real-world” situations. This requires testing of components via ASTs and in operating fuel cells, and delineating the various component contributions to the 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. The “real-world” data utilized in this project include field data from bus fleets provided by Ballard Power Systems and simulated drive cycle data obtained at LANL utilizing the U.S. DRIVE FCTT “Protocol for Determining Cell/Stack Durability” [6]. This work is also being coordinated with other funded projects examining durability through a DOE Durability Working Group.

## RESULTS

The U.S. DRIVE FCTT recommended ASTs and “Protocol for Determining Cell/Stack Durability” [6] was performed on various MEA/GDLs using 50-cm<sup>2</sup> single- or quad-serpentine hardware purchased from Fuel Cell Technologies Inc. Polarization curves, electrochemically active surface area, mass activity, cross-over, shorting resistance and impedance measurements were performed at regular intervals to monitor the degradation rate. For carbon corrosion testing a California Analytical Instruments Inc. non-dispersive infrared (NDIR) instrument was attached to the outlet N<sub>2</sub> from the cathode side (after condensing the water) to monitor total amount of CO<sub>2</sub> evolved.

### Catalyst Degradation

The U.S. DRIVE FCTT recommended 1- to 1.5-V cycle was performed on MEAs utilizing three different carbon types, viz: E carbon (high surface area), V carbon (VULCAN<sup>®</sup>) and EA carbon (graphitized low surface area). The NDIR analysis of the nitrogen at the cathode outlet clearly showed CO<sub>2</sub> corresponding to the corrosion of the carbon support in the cathode catalyst layer. Figure 1a) illustrates the CO<sub>2</sub> evolved from the MEA using the



**FIGURE 1.** Carbon corrosion rate measured by the  $\text{CO}_2$  concentration at the  $\text{N}_2$  cathode (using non-dispersive infrared) during AST testing of MEAs utilizing Pt/C catalysts with a) low surface area graphitized carbon (EA-Carbon) and b) high surface area E-carbon.

EA-carbon support in the cathode catalyst layer. The  $\text{CO}_2$  evolution steadily decreases over time as the number of cycles is increased. However, after characterization and resumption in testing an increased  $\text{CO}_2$  evolution rate is observed. This is consistent with the formation of a passivation layer over time that can be reduced when the

voltage is lowered below 1.0 V. NDIR results from the MEA utilizing the E-carbon (Figure 1b) show that the corrosion rate from the high surface area carbon is almost an order of magnitude larger than the corrosion from the graphitized carbon. Moreover the E-carbon also shows a dramatic lowering in the  $\text{CO}_2$  evolution rate after 500 cycles,

consistent with the low amount of residual carbon in the catalyst layer (decreased catalyst layer thickness). This is also confirmed by large increases in mass transport losses in the MEA associated with catalyst layer compaction and loss in porosity. Figure 1b also shows a comparison of the CO<sub>2</sub> emission from the 1.2-V hold AST showing about an order of magnitude greater CO<sub>2</sub> emission from the 1- to 1.5-V cycling.

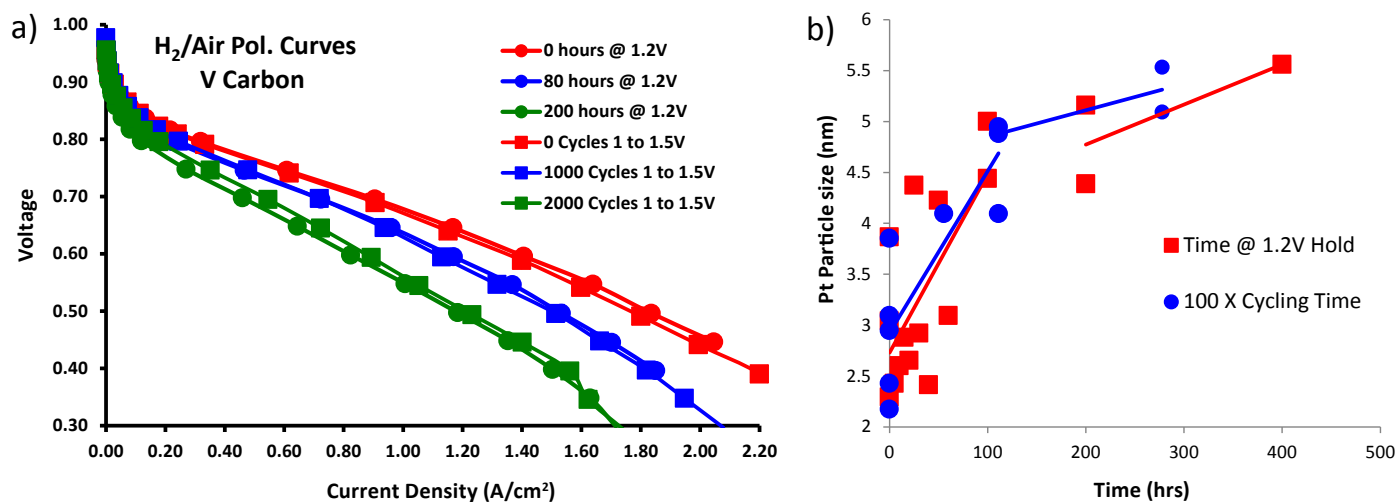
The MEA performance degradation observed during the 1.2-V hold and the 1- to 1.5-V cycling is compared in Figure 2a. The performance degradation rate during the 1- to 1.5-V cycling is at least 2 orders of magnitude greater ( $\approx 150\times$ ) than the degradation rate during the 1.2-V hold. For example the polarization curves for the MEA using the V-carbon are similar after 80 hours (200 hours) of 1.2-V hold and 1,000 cycles (2,000 cycles) from 1.0 to 1.5 V corresponding to a cycling time of 0.56 hours (1.11 hours). Similar behavior was also observed for the MEA with the E-carbon electrode where the performance after 32 hours and 96 hours of 1.2-V hold are similar to performance after 500 and 1,000 cycles from 1.0 to 1.5 V, respectively. Figure 2b shows the Pt particle size measured by X-ray diffraction (post testing) after various times of either the 1.2-V hold or 1- to 1.5-V cycling ASTs. The time of the 1- to 1.5-V cycling has been multiplied by 100 times, clearly showing the 100 times acceleration factor of Pt growth in the 1- to 1.5-V cycling AST. Both ASTs also show a lowering of the degradation rate with increasing time, consistent with the lower growth rate of the larger Pt particles [7].

### Membrane Degradation

Membrane degradation (increase in membrane cross-over) could be observed during durability testing using the U.S. DRIVE “Protocol for Determining Cell/Stack Durability.” While un-stabilized (both chemically and

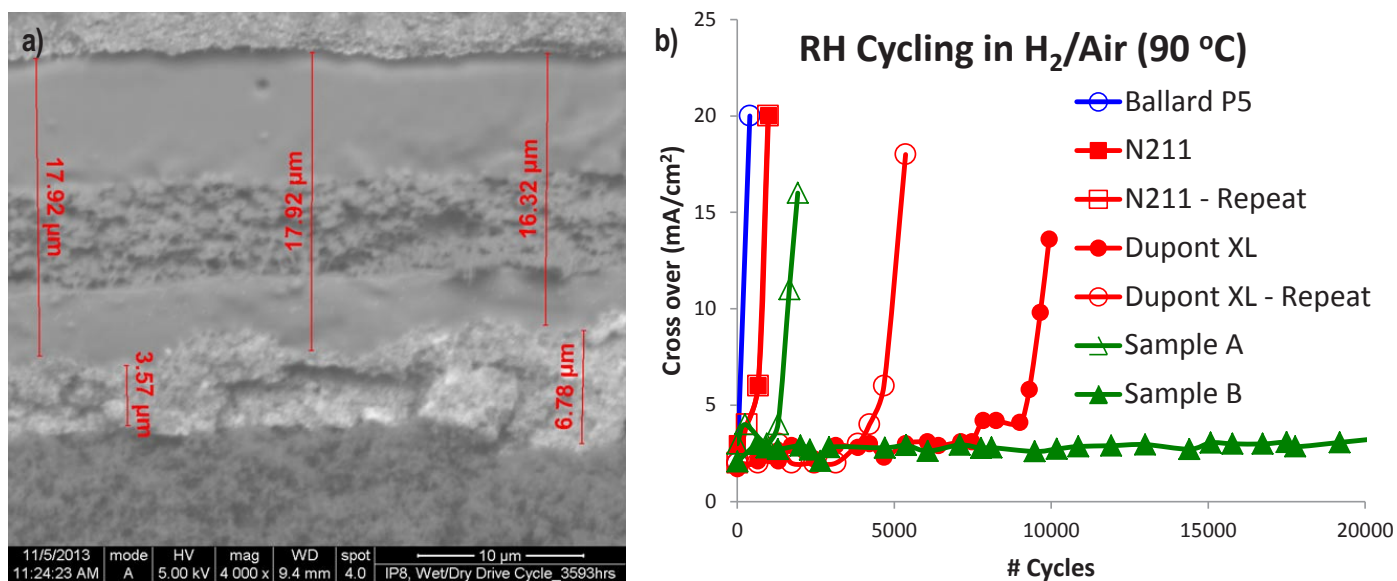
mechanically) membranes failed in <1,000 hours of this drive cycle testing, stabilized membranes showed excellent durability. For example the DuPont XL<sup>®</sup> membrane after 3,800 hours of this drive cycle showed only a 30% decrease in membrane thickness, but failed at the edges due to the absence of a sub-gasket. Figure 3a is a back-scattered scanning electron micrograph of the DuPont XL<sup>®</sup> membrane after 3,800 hours of durability testing showing thinning (originally 25  $\mu\text{m}$ ) on the cathode (bottom) side of the reinforcement. A stabilized membrane from another supplier also lasted >2,000 hours with no change in membrane thickness but the test was aborted due to test stand issues. Further testing with sub-gasketing of both these stabilized membranes is under progress to evaluate their lifetime during drive-cycle testing and should be close to the required 5,000-hour durability target. The testing of un-stabilized membranes revealed both chemical and mechanical degradation, as evidenced by global thinning and local tearing respectively. All membranes tested under this drive cycle failed due to mechanical degradation either at the edges (for stabilized membranes) or at the inlets/outlets (for un-stabilized membranes).

The current membrane ASTs fail to capture this failure mode and therefore a new relative humidity (RH) cycling test in H<sub>2</sub>/air was developed to accelerate/simulate this membrane failure mechanism. The H<sub>2</sub>/air RH cycling was performed initially at a cell temperature of 80°C with dry gases for 2 minutes and super saturated gases (dew point = 90°C) for 2 minutes and resulted in failure of unstabilized membranes in less than 300 hours (<5,000 cycles). However, stabilized membranes hardly showed any degradation under this testing with no thinning or increase in crossover observed even after 20,000 cycles ( $\approx 55$  days). In order to further accelerate this test, the cell temperature was increased to 90°C with



**FIGURE 2.** Comparison of a) polarization curves measured after various times and b) Pt particle size evolution over time, during two different U.S. DRIVE FCTT recommended carbon corrosion ASTs (1.2-V hold and 1.0- to 1.5-V cycling).





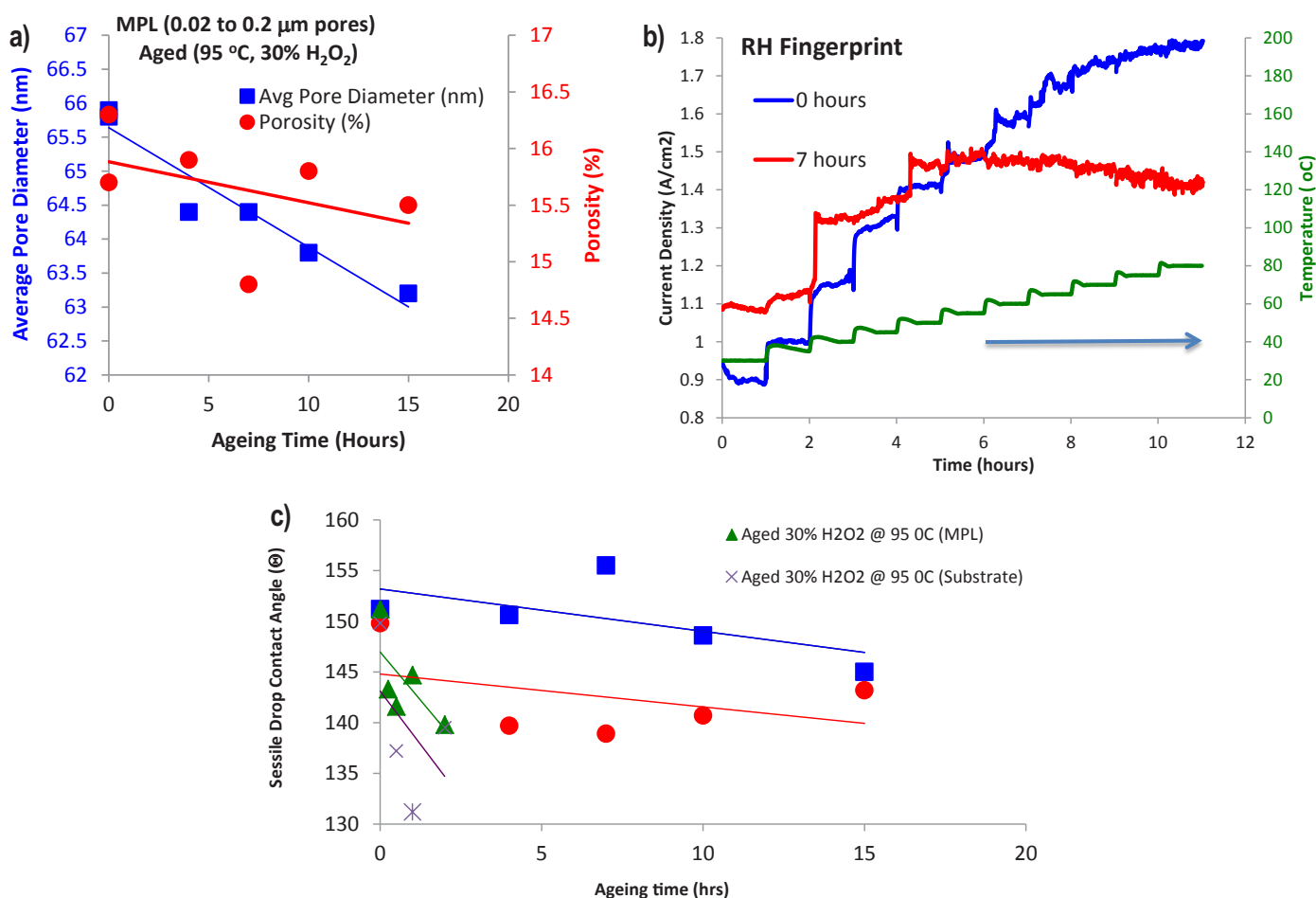
**FIGURE 3.** a) Backscattered scanning electron micrograph of DuPont XL<sup>®</sup> membrane after 3,800 hours of drive cycle testing, b) cross-over evolution of various membranes during RH cycling test in H<sub>2</sub>/air at a cell temperature of 90°C.

2 minutes of dry and 2 minutes of super-saturated (dew point = 92°C) gases. The crossover of various stabilized and unstabilized membranes subjected to this test is presented in Figure 3b. The N211 membrane failed this test within 33 hours (1,000 cycles) and exhibited both global thinning (40% reduction in thickness) and local tearing (several pinholes/cracks in membrane). However, the stabilized DuPont XL<sup>®</sup> membrane showed no global thinning even after 600 hours of this testing ( $\approx 10,000$  cycles) and showed increased crossover due to edge failure. Another stabilized membrane with a sub gasket also lasted  $>20,000$  cycles with little increase in crossover, indicating that further acceleration is required in order to evaluate state-of-the-art membranes. This AST is being refined further in order to increase chemical degradation with respect to mechanical degradation by decreasing the time during the wet part of the RH cycle.

### GDL Degradation

GDL degradation has been observed during drive cycle testing of fuel cells and an ex situ AST for GDL durability was reported last year. The ex situ aging of GDLs was achieved by submerging them in a boiling solution of 30% hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) at 95°C for prolonged intervals up to 15 hours (this protocol was first reported by SGL as their part of the DECODE project). This test resulted in qualitatively similar degradation to that observed during drive-cycle testing, i.e. increase in mass transport resistance of MEAs using aged GDLs. This year we have developed tests to quantify this degradation both in terms of fuel cell performance and materials property changes in the

GDL. MIP was used to monitor the changing average pore diameter and porosity of the GDL as a function of aging time (see Figure 4a). The decreasing porosity and average pore diameter can be used to quantify GDL degradation and are consistent with the observed mass transport increases in MEAs utilizing aged GDLs. A RH fingerprint test as first reported by D. L. Wood et al. [8] was utilized to quantify the performance changes observed due to GDL ageing. The performance of an MEA utilizing fresh and aged GDLs was monitored at a fixed voltage (selected to yield a current density of  $\approx 1.5$  A/cm<sup>2</sup>) while varying the inlet dew point of the anode and cathode gases. The cell temperature was kept constant at 80°C while the inlet dew points of H<sub>2</sub>/air were increased at 5°C intervals from 30°C to 80°C. The performance of MEAs using fresh and 7-hour aged GDLs during this test is illustrated in Figure 4b). While the fresh GDL shows increasing performance with increasing RH, the aged GDL shows improved performance at low inlet RHs and a loss in performance at high inlet RHs. These results are consistent with improved high-frequency resistance (HFR) and better membrane hydration with the aged GDLs and improved mass transport with the fresh GDLs. The contact angles measured as a function of ageing time at 95°C and 80°C are plotted in Figure 4c and illustrate the increasing hydrophilicity of the GDL with ageing. The oxidation of the carbon in the GDL material results in the formation of hydrophilic surface oxide groups which in turn result in improved performance under drier conditions (improved membrane HFR) and degraded performance under wetter conditions (increased mass transport resistance). These tests will be utilized to quantitatively correlate in situ GDL degradation in MEAs with ex situ AST degradation of



**FIGURE 4.** a) Decreasing porosity and average pore diameter of the GDL (measured using MIP) as a function of aging time, b) GDL RH fingerprint: performance (current at 0.55 V) of MEAs using fresh and 7-hour aged GDLs, as a function of cathode/anode inlet RHs, c) Sessile drop contact angles of substrate and GDL as a function of AST aging time.

GDLs. The ex situ aging time, temperature and peroxide composition will be varied to optimize this AST and correlate it to GDL ageing during drive cycle testing

## CONCLUSIONS AND FUTURE DIRECTIONS

The electro-catalyst AST (0.6-V to 1.0-V cycling) was found to accurately capture the Pt electrochemically active surface area loss occurring during wet/dry drive cycle testing. However, this test needs further acceleration that can be achieved by increasing the voltage ramp rate. The U.S. DRIVE FCTT recommended new AST (1.0- to 1.5-V cycling) for carbon corrosion results in ten times greater carbon corrosion than the older 1.2-V hold AST. The new AST results in  $\approx 100$  times acceleration of the Pt growth rate and the observed voltage decay rate. A new  $\text{H}_2$ /air RH cycling AST, which better simulates membrane degradation observed in the field and during drive cycle operation was developed. However, this AST requires further acceleration of chemical degradation with respect to mechanical degradation which

will be achieved by decreasing the duration of the wet portion of the RH cycle with respect to the dry portion. Ex situ GDL ageing in peroxide solutions was found to degrade GDLs similar to those observed during drive cycle operation. GDL fingerprint test was found to be effective in characterizing GDL degradation and will be utilized to refine the GDL AST and to define accelerating factors with respect to drive cycle testing.

- AST Testing
  - Further accelerate the catalyst cycling AST by speeding up the cycling rates from the current 50 mV/s. Perform an AST using a trapezoid wave with 0.5 s rise time from 0.6 V to 0.95 V, 2.5 s hold at 0.95 V, 0.5 s from 0.95 to 0.6 V, and 2.5 s hold at 0.6 V
  - Refine membrane AST to better simulate membrane degradation observed during durability testing using the U.S. DRIVE “Protocol for Determining Cell/ Stack Durability”

- “Real-World” Testing
  - Perform simulated start/stop tests on MEAs utilizing three different carbon types
  - Perform the U.S. DRIVE “Protocol for determining Cell/Stack durability” on MEAs using different membrane and catalyst layer types
- Characterization of Materials
  - Perform ex situ characterization of catalyst particle size distribution, layer thickness, membrane thickness, and GDL hydrophobicity as a function of drive cycle and/or AST test time
- Correlation of AST to “Real-World” Data
  - Determine acceleration factors of the membrane AST with respect to the U.S. DRIVE “Protocol for Determining Cell/Stack Durability”
  - Determine acceleration factors of the 1- to 1.5-V cycling AST with respect to the simulated start/stop cycles

## FY 2014 PUBLICATIONS/PRESENTATIONS

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