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Accelerated Testing Validation

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The DOE Fuel Cell technical team recommended ASTs were performed on 2 different MEAs (designated P5 and HD6) from Ballard Power Systems. These MEAs were also incorporated into stacks and operated in fuel cell bus modules that were either operated in the field (three P5 buses) in Hamburg, or on an Orange county transit authority drive cycle in the laboratory (HD6 bus module). Qualitative agreement was found in the degradation mechanisms and rates observed in the AST and in the field. The HD6 based MEAs exhibited lower voltage degradation rates (due to catalyst corrosion) and slower membrane degradation rates in the field as reflected by their superior performance in the high potential hold and open-circuit potential AST tests. The quantitative correlation of the degradation rates will have to take into account the various stressors in the field including temperature, relative humidity, start/stops and voltage cycles.

Introduction

The durability of PEM fuel cells is a major barrier to the commercialization of these systems for stationary and transportation power applications.[1] To rapidly evaluate materials requires relevant Accelerated Stress Tests (ASTs), the design of which relies on understanding the degradation mechanism. The need for ASTs is apparent given the target lives for fuel cell systems: 5000 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 are needed for evaluating new component durability in a reasonable turn-around time. These tests are also crucial to developers in order to quantitatively evaluate the trade-offs in cost (e.g. lower platinum group metal [PGM] loading), lifetime (eg. a lower surface area carbon with better corrosion resistance) and performance (e.g. thinner membrane or a GDL with better water management properties). Although several ASTs developed by the DOE, US Fuel Cell council (USFCC) and Japan automobile research institute (JARI) exist for PEM fuel cells[2-4], currently there are few publications that correlate AST lifetimes to actual performance in the field. In this paper we elucidate the qualitative relationship of AST lifetimes of MEAs with performance data of the same MEAs run in fuel cell bus stacks. A methodology for quantitative correlation that utilizes extensive ex-situ characterization, and voltage loss breakdown to assign losses to various degradation mechanisms is also outlined.

Experimental

Laboratory testing

ASTs were performed on two different MEAs designated P5 and HD6, that were used by Ballard Power Systems in fuel cell bus stacks starting in 2002 and 2007 respectively. While the P5 MEA was based on a 50 μm thick membrane with a total Pt loading of 1.05 mg/cm^2, the HD6 MEA had a total Pt loading of 1 mg/cm^2 on a 25 μm thick membrane. The four different ASTs recommended by the DOE - Fuel Cell Technical team[2,3] were performed on these two MEAs in 50 cm^2 single serpentine hardware. The potential cycling AST was performed at cell temperature of 80 ^oC, 100% inlet RH, atmospheric pressures with H_2 and N_2 flows at 200 sccm and 75 sccm respectively. The potential was cycled at 50 mV/sec from 0.6 to 1.0 V and the cell performance including electrochemical surface area (ECSA), polarization curves, mass activity and impedances was monitored at regular intervals. During the high potential hold AST the cell was operated at 80 ^oC in 100% saturated H_2/N_2 at 150kPa absolute pressure at 1.2V for 400 hours with characterization performed every 24 hours. The open circuit potential test was performed at 90 ^oC and 30% inlet RH in H_2(700 sccm)/Air(1667 sccm) at 250 and 200 kPa respectively. While the OCV was monitored continuously, cell characterization including cross over, high frequency resistance (HFR), cell shorting resistance in N_2/N_2 at 0.5V, and F^- release was performed every 24 hours. The RH cycling test was performed at 80 ^oC in ambient air by switching from dry to wet (dew point 90 ^oC) gases every 2 mins and monitoring the cross over and shorting resistance every 24 hours.

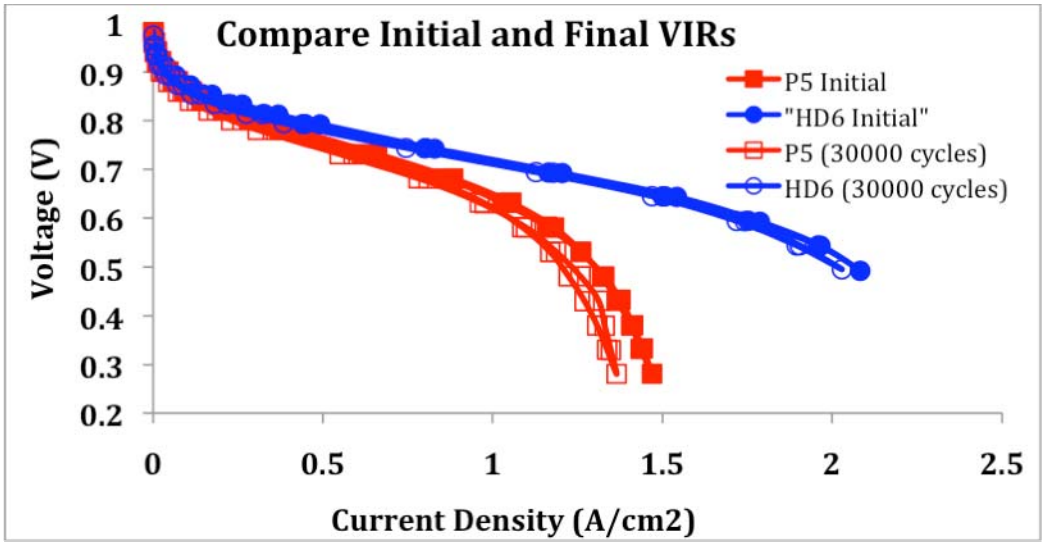
Field data

Three buses using the P5 stack, designated as PE4, PE22 and PE23 were operated in Hamburg, Germany on different routes for 2769, 3360, and 2597 hours respectively. While the voltage and current was recorded continuously, the constantly varying current

demand results in a dynamic behavior that yields data with a large scatter in current and voltage. Two hours of this data was averaged in order to produce a representative current-voltage curve for the stack. This averaging was performed at 8 to 10 different time periods during the life of the stack in order to extract degradation rates. The crossover data is not available during the lifetime of the stack and is presented only for the beginning and end of life. One HD6 module was operated in the laboratory on an Orange county transit authority (OCTA) drive cycle for 6842 hours. Polarization curve and cross over measurements of this cell was performed at regular intervals resulting in 26 data points to monitor the degradation rate and cross over during the lifetime of operation.

Results and Discussion

The results from the potential cycling and high potential hold ASTs are illustrated in Figure 1 a) and b) respectively. It is seen that the initial 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 Fig 1 a) by very little performance loss after 30,000 potential cycles from 0.6V to 1V. Both MEAs met all DOE performance targets including ECSA (< 40% loss), MA (< 40% loss) and voltage loss @ 0.8A/cm^2 (< 30mV loss). While both the cells had an ECSA loss of ≈ 30% after 30,000 potential cycles, the voltage loss and mass activity loss was greater on the P5 MEA. The P5 MEA lost 34% mass activity and 15 mV of performance at 0.2 A/cm^2 while the HD6 MEA lost 31% mass activity and 9 mV of performance at 0.2 A/cm^2.



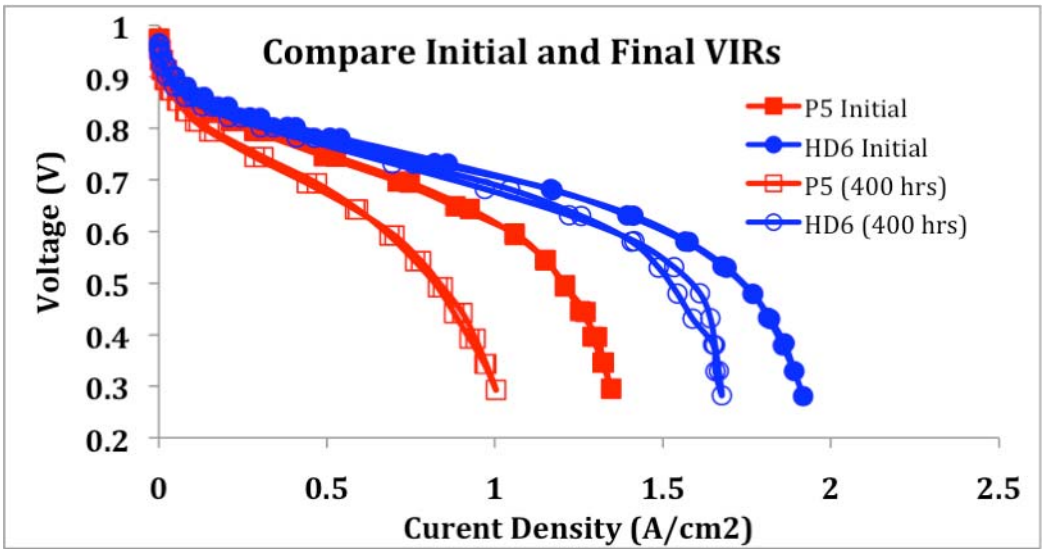


Figure 1. Performance of P5 and HD6 MEAs. a) Before and after potential cycling and b) before and after high potential hold.

The high potential hold AST resulted in significant degradation due to carbon corrosion especially in the P5 MEA (Fig. 1b). While the P5 MEA failed to meet any of the DOE targets, the HD6 MEA met both the ECSA (< 40 % loss) and MA (< 60% loss) targets, but failed to meet the voltage loss (@ 1.5A/cm^2) target (30 mv loss occurs at 400 hours). The P5 MEA lost 40% ECSA after 175 hours of testing while the HD6 MEA lost only 27% of ECSA after the 400 hours of testing. The P5 cell was unable to generate 1.5 A/cm^2 and lost 30 mV @ 0.8 A/cm^2 after ≈ 150 hours of testing. The HD6 cell lost only 17 mV of performance @ 0.8 A/cm^2 after 400 hours of testing and lost 30 mV of

performance @ 1.5 A/cm^2 after 175 hours of testing. 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 MA targets for this particular AST.

The voltage loss breakdown in these cells as a function of ageing time was extracted by using a simple 1-D model to fit the polarization curves and impedance response of the

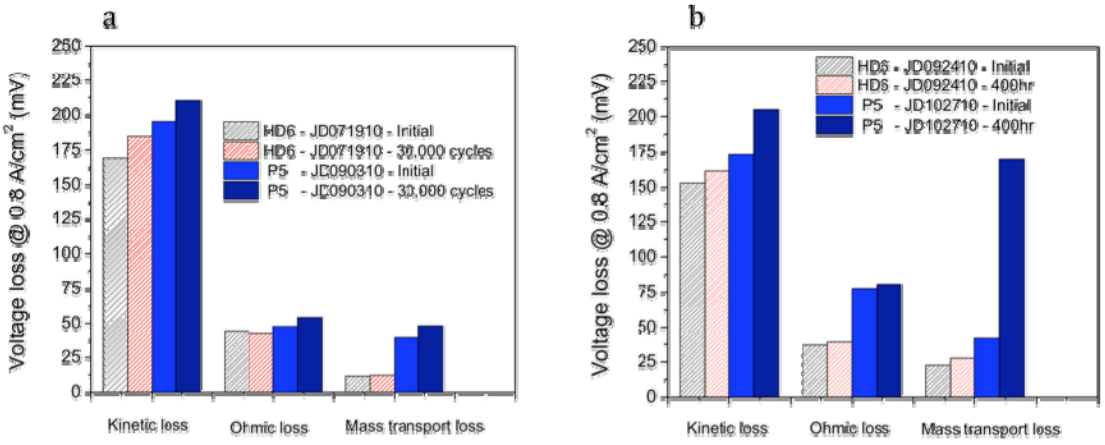


Figure 2. Voltage loss breakdown of the P5 and HD6 cells at 0.8 A/cm^2 obtained using a 1-D model. a) Before and after potential cycling and b) before and after high potential hold.

single cells[5]. The voltage loss at a fixed current density of 0.8 A/cm^2 is illustrated in Figures 2 a) and b), for the potential cycling AST and high potential hold AST respectively. During the potential cycling AST (Fig 2a) there is a small (< 15 mV) increase in the voltage loss in the kinetic region while the ohmic and mass transport contributions remain virtually unchanged. This is consistent with the loss in ECSA and the unchanged mass transport impedance observed in the two cells. During the 400 hours of high potential hold AST (Fig 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/cm^2. 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 Fig 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 different stressors including temperature, RH, voltages and air/air starts. Table 1 provides an analysis of the operational stressors

encountered in the 4 bus stacks during their lifetime of operation. The major difference in the stressors between the 3 P5 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 PE22 stack that exhibited the highest degradation rate 33.5 μV/cell/hour was

operated at a higher relative humidity and temperature indicating that these other stressors play a minor role in the degradation rate when compared to the # of air/air starts.

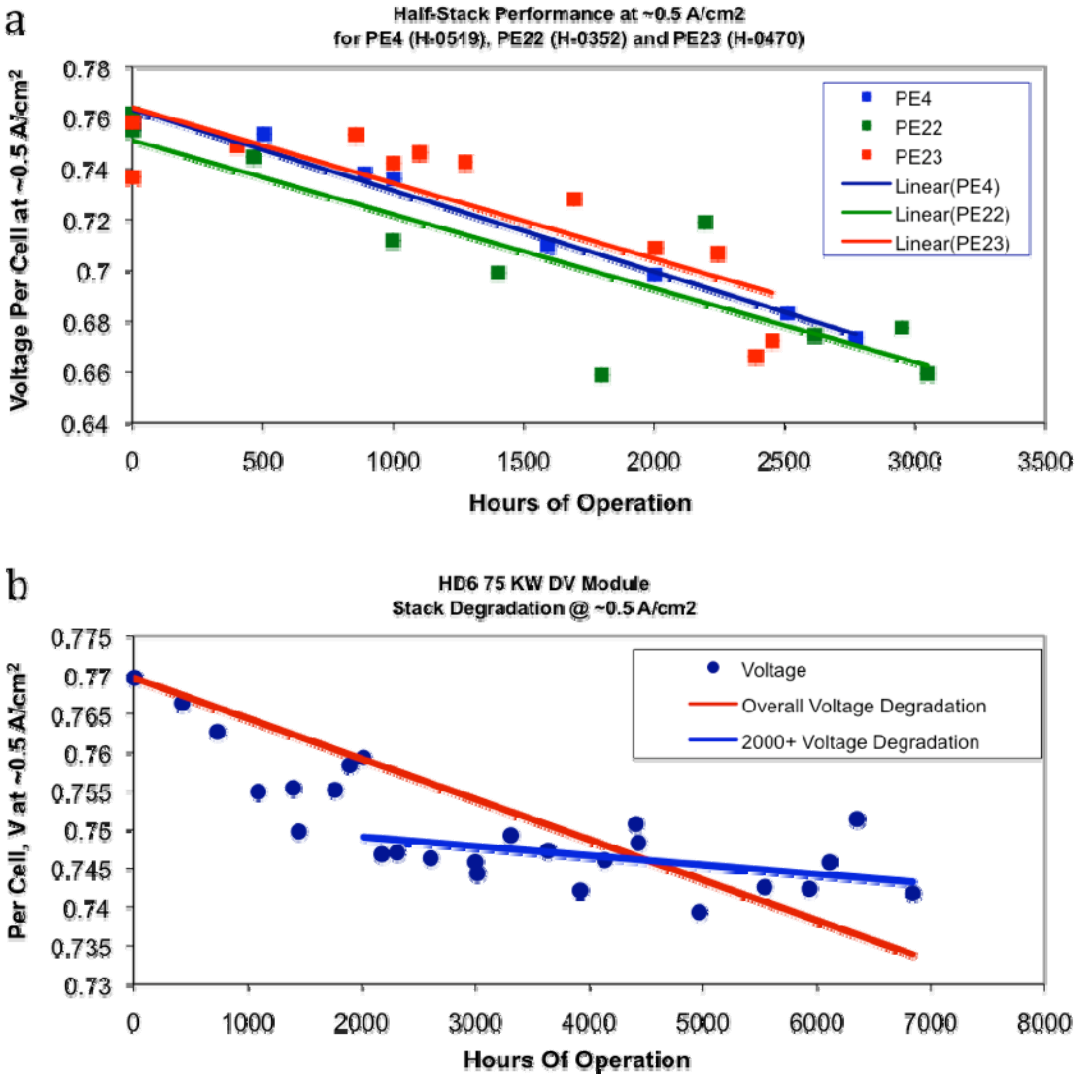


Figure 3. Voltage degradation observed in a) three P5 bus stacks operated in the field and b) one HD6 module operated under OCTA drive cycle.

Operational Stressor	PE4 (H-0519)	PE22 (H-0352)	PE23 (H-0470)	HD6 DV Module
Voltage (%cycle >0.8V/cell)	52	48	53	57
Temperature (%cycle >70C)	54.8	76.3	66.1	12.5
# Air/air starts per Hour	0.130	0.124	0.101	<0.015
Total # of Air/Air Starts	361	417	263	<100
Humidity (%cycle in RH range)	55 b/w 84-92%RH	50 b/w 90-98%RH	55 b/w 86-94%RH	100% >95%RH
Hours of Operation	2769	3360	2597	6842
Degradation Rate (BOL to EOL) at ~0.5 A/cm2 (uV/cell/hr)	**31.4**	**33.5**	**26.3**	**5.2**
mV/cell lost over life (@ ~0.5 A/cm2)	87	113	68	20
Transfer Leak Rate	15ccm/cell @2.7k Hrs	16ccm/cell @3.3k Hrs	11ccm/cell @2.6k Hrs	24ccm/cell @6.8k Hrs

Table 1. Average operational stressors encountered by the stack during field testing.

The HD6 stack was operated in a laboratory under drive cycle conditions and showed an average degradation rate of 5.2 µV/cell/hour (Fig. 3b). The data quality from this stack is

better than the field data and clearly shows two different degradation rates with the 2000 to 7000 hour data showing only a degradation rate of 1.2 μV/cell/hour. This low degradation rate is a combination of the lower total number of air/air starts in this module in addition to the better performance of the HD6 catalyst under the high potential hold test. The failure analysis from these stacks will be utilized along with the voltage loss data to compare the normalized field data with the AST data.

The Open circuit voltage (OCV) and fluorine release rate in the effluent water during the membrane chemical degradation AST[2,3] test of the P5 and HD6 MEAs is shown in Fig

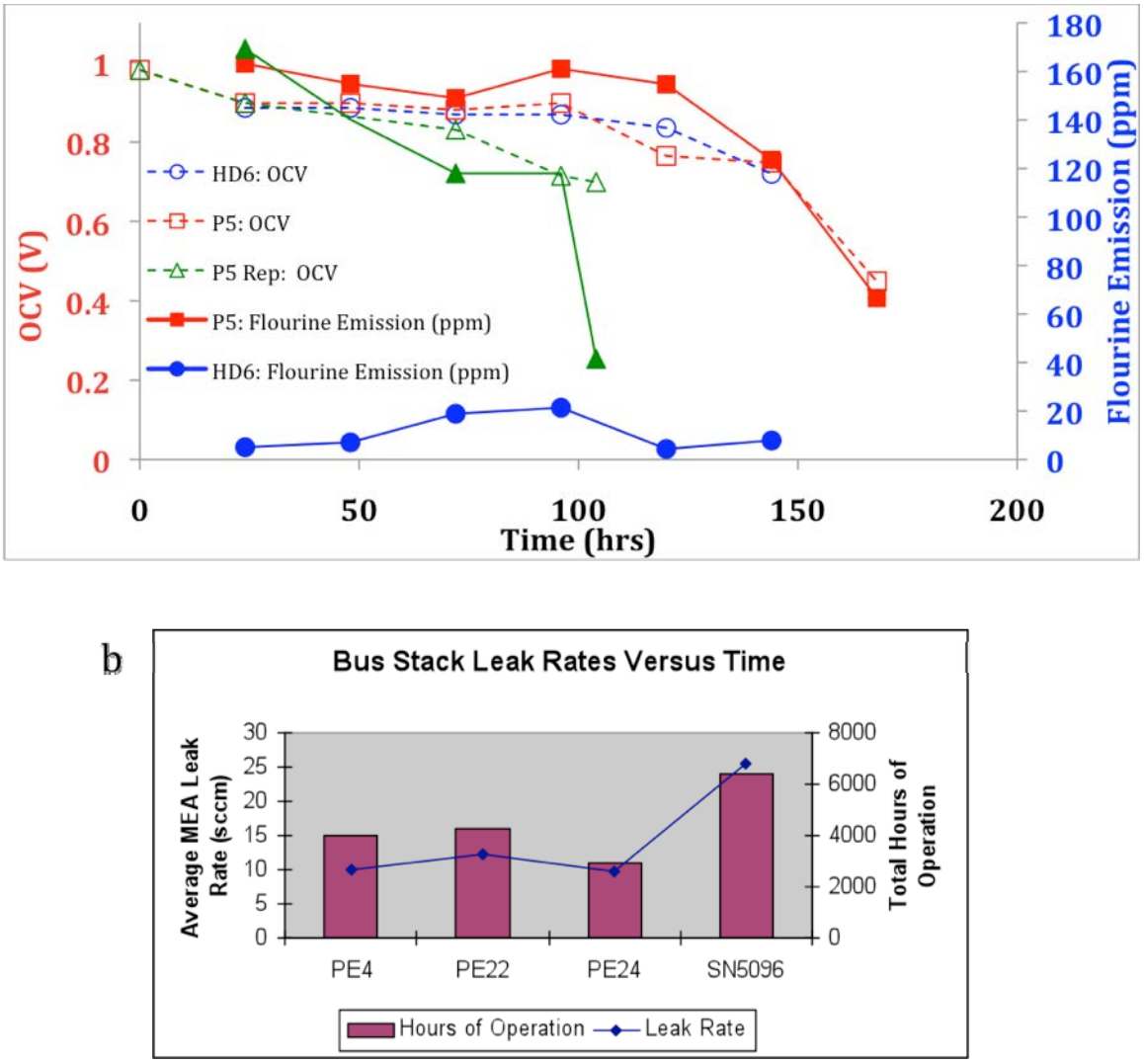


Figure 4. a) Fluorine content of the outlet water during an OCV AST test and b) transfer leak rates observed in P5 and HD6 stacks operated in buses.

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 release rate than the HD6 cell, which is consistent with its worse performance in the field. This is illustrated in Fig 4b) where the three P5 stacks all failed due to transfer leaks in < 3400 hours while the HD6 showed an increase in transfer leak rate only after 5500 hours (not shown). The HD6 MEA was operated under more humid conditions at a lower temperature when compared to the P5 MEAs. Therefore the quantitative correlation of the lifetimes will have to take into account the effect of temperature and RH. Controlled laboratory drive cycle tests have been initiated to study the effect of these stressors and will be utilized in the future. The RH cycling AST showed that both the HD6 and P5 MEAs were able to operate the entire 20,000 RH cycles without any loss in performance. This result is not surprising since that test was designed for thin automotive MEAs and these thick MEAs (25 and 50 μm for the HD6 and P5 respectively) are expected to be stable during this test. 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.

Conclusions

The DOE – Fuel cell technical team recommended ASTs were performed on two different MEAs designated P5 and HD6 that were utilized in buses built by Ballard in circa. 2002 and 2007 respectively. The HD6 MEA performed significantly better in the high potential hold and OCV tests indicating its better carbon corrosion and membrane chemical degradation resistance respectively. The field data from these two MEAs was

consistent with this result but quantitative correlation between the field data and the AST needs to take into account the various stressors like temperature, RH, air/air starts and potential cycles. Controlled laboratory tests to evaluate the effect of these stressors has been initiated and will be incorporated with the failure analysis data in the future to better elucidate this quantitative correlation.

Acknowledgments

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