V.E.4 Improved Accelerated Stress Tests Based on Fuel Cell Vehicle Data

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Fiscal Year (FY) 2012 Objectives

Validate the use of post test fatigue cycling in a dynamic mechanical analyzer (DMA) as a method to estimate "remaining life" of a tested membrane.

Technical Barriers

- >5,000 hours stack durability (including cycling and all materials, e.g. membrane, seals).
- <10% overall performance decay (including start/stop and transient operation).
- Current DOE accelerated stress tests (ASTs) not calibrated with real-world degradation.

FY 2012 Accomplishments

- Accelerated life test (ALT) complete.
- Validation of post-test fatigue tool for predicting remaining life of membrane complete.

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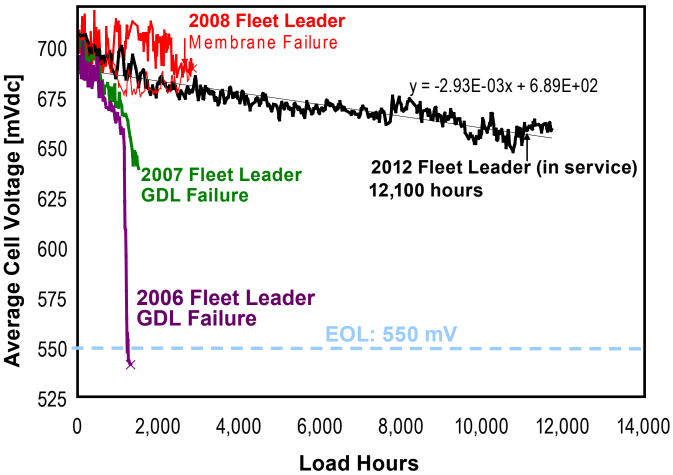
Approach

UTC lead a top-tier team of industry and national laboratory participants to update and improve DOE's ASTs for hydrogen fuel cells. This in-depth investigation focused on critical fuel cell components (e.g. membrane electrode assemblies [MEAs]) whose durability represents barriers for widespread commercialization of hydrogen fuel cell technology. UTC has access to MEA materials that have accrued significant load time under real-world conditions in PureMotion® 120 power plant used in transit buses. These materials are referred to as end-of-life (EOL) components in the rest of this document. Advanced characterization techniques were used to evaluate degradation mode progress using these critical cell components extracted from both bus power plants and corresponding materials tested using the DOE ASTs. These techniques were also applied to samples at beginning of life (BOL) to serve as a baseline. These comparisons will advise the progress of the various failure modes that these critical components are subjected to, such as membrane degradation, catalyst support corrosion, platinum group metal dissolution, and others. Gaps in the existing ASTs to predict the degradation observed in the field in terms of these modes were outlined. Using these gaps, new ASTs were recommended and tested to better reflect the degradation modes seen in field operation. Also, BOL components were degraded in a test vehicle at UTC designed to accelerate the bus field operation.

Results

An update on the durability progression of the UTC bus fleet is shown in Figure 1. The UTC fleet leader has achieved over 12,000 hours operation in the field. This corresponds to over four years in service. Three previous models had failed in the field prior to 12,000 hours. All of the failures have been verified using ASTs. These results have been reported previously, but a summary is provided here. The 2006 and 2007 fleet leaders failed due to oxidation of the carbon in the cathode microporous layer. The failure mechanism was replicated using the carbon corrosion AST. The microporous layer used in the 2008 fleet leader and beyond was determined to be 2-3 times more durable. This was borne out in the improvement of the UTC fleet from ~1,000 hours to over 2,800 hours. The 2008 fleet leader failed due to failure of the membrane at the air inlet caused in turn by hydration/dehydration cycling. A more durable membrane was implemented in the 2012 fleet leader. Both membranes were tested in a combined membrane mechanical-chemical AST. The 2012 fleet leader membrane lasted over 15 times longer than the 2008 fleet leader in the AST. Based on AST testing, the membrane in the 2012 fleet leader is expected to last longer than 30,000 hours.



GDL - gas diffusion layer

FIGURE 1. UTC Power fleet data

For FY 2012, one of the remaining tasks was to validate the use of post test fatigue cycling in a DMA as a method to estimate "remaining life" of a tested membrane. One of the advantages of this tool would be that degradation of a membrane can be detected prior to failure, reducing time consuming and expensive testing. Another advantage would be that areas with highly localized degradation could be identified, such as different areas within a cell or different cells within a cell stack assembly. This gives fuel cell developers early insight about the durability of materials in a realistic operating environment as well as the impact of cell design on durability. This is becoming more important as some market requirements, such as the bus, range from 35,000 to 50,000 hours.

In order to verify the tool, an MEA was run to failure using the combined membrane mechanical-chemical degradation AST, described in Table 1. The MEA was removed from test after 218 hours after it had failed. A second MEA was subjected to same AST protocol, but was intentionally removed from test before failure had occurred, at 70 hours. A third sample was an as-received MEA. The open-circuit voltage (OCV) voltage response to fuel pressure sweep of both test samples is shown in Figure 2.

After test, small dog-bone shaped samples were excised from the used MEAs and subjected to fatigue cycling in a DMA. The fatigue cycling was performed in an environmental chamber to control the temperature and humidity. The stress was cycled from maximum stress of 5 MPa to minimum stress of 1 MPa. A minimum stress of 20% maximum stress was used to prevent buckling of the sample. The fatigue cycling frequency was 10 Hz. The parameters for the fatigue cycling are summarized in Table 2.

Figure 3 shows the normal probability distribution function, which was fit to the fatigue test data of each MEA. (To interpret Figure 3, each line represents the frequency at

TABLE 1. Membrane Flow/Load Cycling AST Protocol

Coolant temperature	80°C	
Cycle	Square wave galvanostatic	
	20 sec	0.015 A/cm^2
	15 sec	1.5 A/cm^2
Anode	H_2; 80% utilization(S.R. = 1.25)	
Cathode	Air; 60% utilization(S.R. = 1.66)	

S.R. – stoichiomentry ratio

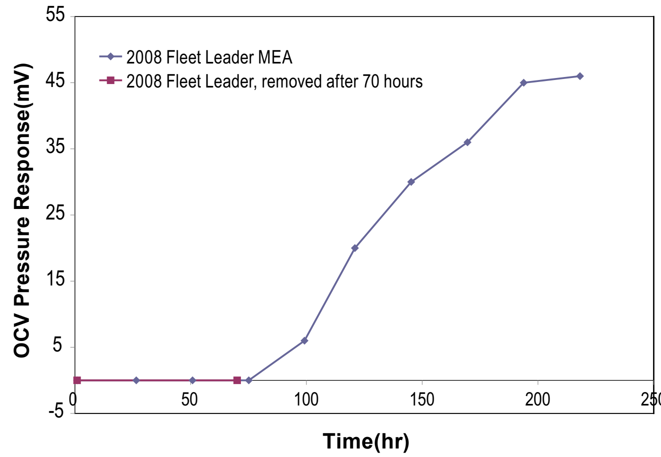


FIGURE 2. OCV pressure response during membrane combined chemical-mechanical AST

TABLE 2. Parameters used in Fatigue Cycling

Sample temperature	50°C	
Sample relative humidity	50%	
Stress	Minimum	1 MPa
	Maximum	5 MPa
Frequency	10 Hz	

which the MEA failed at a given number of fatigue cycles.) Figure 4 shows the same data in a slightly different way. The cumulative normal distribution function is shown for each MEA, along with the raw data. Also shown is the 90% confidence interval for each MEA (To interpret Figure 4, the line represents the fraction of the distribution that has failed at or before a given number of fatigue cycles. The confidence interval represents the uncertainty in the data.) For the as-received MEA, the average cycles to failure (CTF) was 193,000 cycles. The standard deviation was 13,000 cycles. For the MEA tested to 218 hours, the mean CTF decreased to 83,000 cycles, which is a 57% reduction in CTF from the as-received MEA. The standard deviation also increased to 29,000 cycles. This indicates that the membrane degradation is highly localized. For the MEA which was intentionally removed from test before failure at 70 hours, the mean

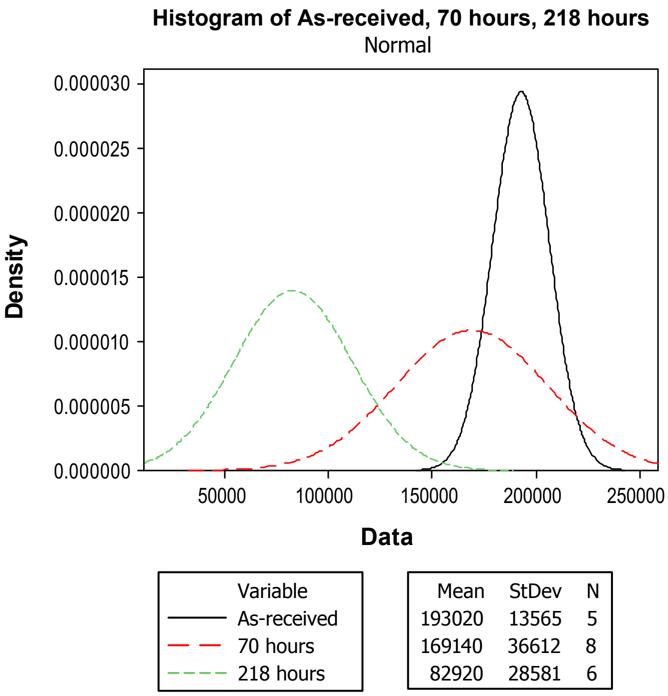


FIGURE 3. Probability distribution of cycles to failure (as-received MEA; cell run for 70 hours in membrane combined chemical-mechanical AST, and cell run for 218 hours in membrane combined chemical-mechanical AST)

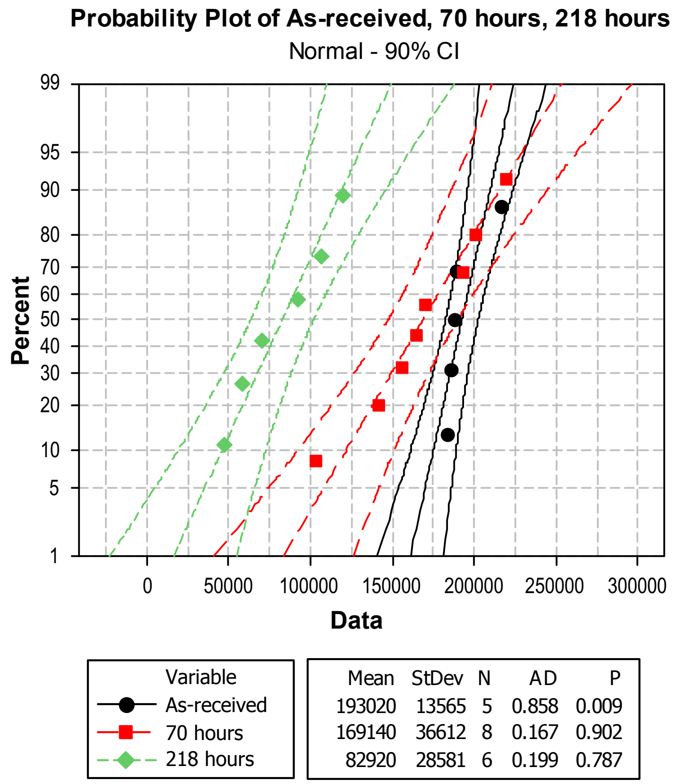


FIGURE 4. Comparison of cumulative probability distribution of the cycles to failure (as-received MEA; cell run for 70 hours in membrane combined chemical-mechanical AST, and cell run for 218 hours in membrane combined chemical-mechanical AST)

time to failure decreased to 163,000 cycles, which is only 16% reduction compared to the as-received MEA. There was a large increase in the variability of CTF, as indicated by the increase in the standard deviation to 36,000 cycles, which is almost three times the variability compared to the as-received sample. A difference between the as-received sample and a sample that had not yet exhibited any sign of failure in cell testing was detected using this method. This indicates that the technique is useful for detecting localized degradation much earlier than any other method. Further work would need to be completed to investigate the limits of the sensitivity of this method.

UTC has facilitated the development of a test vehicle for accelerated evaluation of stack components under this program. The main motivation for this exercise results from the relatively slow rate of load-hour accrual for buses in the field. Because UTC Power is currently targeting >18,000 hours stack durability for bus fleet applications, a more rapid test vehicle is necessary to increase product maturity on new stack configurations. The test vehicle for accelerated stack component evaluation is termed the accelerated life test (ALT). This small power plant has the identical piping and instrumentation configuration as the bus power plant, but operates on a 5-kW short stack. The key operating modes of the bus that have been linked to stack component degradation have been reflected in the protocol. The 2008 fleet leader MEA was tested in the ALT rig and run until membrane failure was observed. Failure was observed after 1,400 load hours, which is 50% faster than observed in the fleet (due to higher operating temperature). Just as important, the ALT rig was run 90% of the time, whereas the fleet typically operates at 34-66% of the time. Therefore, time to failure can be achieved in less than 17-34% of the time, on a calendar basis.

A summary of the ASTs for each failure mode is shown in Table 3. The table shows the time to failure in the AST and in the fleet, as well as an AST acceleration factor, for each failure mode. In some cases, an improved component was also tested in the AST. In these cases, an "AST improvement factor", which is the ratio of time to failure of a component with improved durability to the time to failure of a baseline component, is shown. Finally, where an improved component was also tested in the fleet, a "fleet improvement factor" is shown. There is good agreement for the GDL. For other failure modes, there is not yet enough fleet data to make comparisons.

Conclusions and Future Directions

- Fleet/Real-World: UTC fleet performance and operating cycle analyses have been completed and reported. Teardown analyses of the real-world degraded components have been completed and reported.

TABLE 3. Summary of ASTs for each of the Four Failure Modes

Mechanism	AST	Baseline		Acceleration Factor	Improved Component		AST Improvement Factor	Fleet Improvement Factor
		AST	Fleet		AST	Fleet		
GDL carbon corrosion	Air-air cycling	150	1,250	8X	>550	>12,000	>3.6X	>9.6 X
Catalyst layer carbon corrosion	DOE Carbon Corrosion AST	10	>12,000	>1,200X	20	TBD	2X	TBD
Membrane chemical/ mechanical failure	80°C flow/load cycling	140	2,800	20X	2,500	>12,000	18X	>4.3
Platinum loss	PGM AST	7 mV in 200 hours	15 mV in 2,800 hours	6.5X	-	-	N/A	N/A

TBD – to be determined; PGM – platinum-grade metal

- Lab-World: ASTs for platinum group metal decay, carbon support corrosion, membrane mechanical decay, and membrane chemical decay have been completed. Teardown analyses of the lab-world degraded components have been completed and reported.
- Acceleration factors for each AST have been determined. Wherever available, an "AST improvement factor" and "Fleet improvement factor" has been calculated and compared.
- ALT: Testing has been completed. A reduction in test time, on a calendar basis, of 17-34% has been demonstrated for the 2008 fleet leader.
- DMA has been used to determine remaining life of a membrane that was removed from test prior to any evidence of failure. Differences were observed between samples that were tested to 70 hours and 220 hours. Further investigation is recommended to determine limits of the sensitivity of the method.

FY 2012 Publications/Presentations

1. "Use of Mechanical Tests to Predict PEMFC Membrane Durability under Humidity Cycling", Journal of Power Sources, 196 (2011) 3851–3854.

2. "Improved AST's based on FCV data" presentation to Freedom CAR & Fuel Partnership, Fuel Cell Tech Team Review January 13, 2011.

3. "Improved AST's based on FCV data" presentation to DOE Annual Merit Review meeting May 12, 2011.

4. "A model of membrane mechanical stress in PEMFC during load cycling", to be submitted.