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

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- Oak Ridge National Laboratory (ORNL), Oak Ridge, TN

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Objectives

- Correlate real-world operating conditions to cell degradation.
- Correlate existing DOE accelerated stress tests (ASTs) to degradation.
- Assess degradation modes between real-world operating conditions and existing DOE ASTs.
- Recommend modified ASTs that more accurately gauge in situ component behavior.
- Identify life-limiting mechanisms not addressed by current DOE ASTs and recommend new ASTs.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

(A) Durability

(C) Performance

Accomplishments

- Fleet performance and operating cycle analyses complete.
- Correlation of platinum decay in real-world operation and lab AST complete.
- Lab ASTs for platinum degradation complete.
- Lab ASTs for carbon support corrosion complete.
- Lab ASTs for membrane mechanical degradation complete.

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Project Approach

UTC will 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 will focus 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 a PureMotion® 120 power plant used in transit buses. These materials are referred to as end-of-life (EOL) components. Advanced characterization techniques are 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 will also be 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 will be outlined. Using these gaps, new ASTs will be recommended and tested to better reflect the degradation modes seen in field operation. Also, BOL components will be degraded in a test vehicle at UTC designed to accelerate the bus field operation.

Results

Fleet Durability Growth

Before reviewing the progress on each of the individual tasks, some perspective on the role of the

DOE program in improving proton exchange membrane fuel cell durability is helpful. UTC's approach to achieve the durability targets consists of three aspects. First, UTC is analyzing its fleet operation cycle for critical factors that accelerate performance decay and materials degradation. Second, sub-scale ASTs are performed at LANL using DOE protocols. Third, UTC is implementing its accelerated life test (ALT) article to simulate real-world degradation with selected accelerated conditions identified from the data analysis. Data collected from detailed teardown analyses of aged components from these three elements are incorporated in physics-based numerical models for materials and performance decay.

Task 1.1 - Fleet Data Analysis

The first aspect of this analysis is to characterize the performance decay among the various buses in the field. Figure 1 shows the stack performance decay observed in the various bus vehicles. The 2010 fleet leaders are currently still in service with over 6,000-7,000 hours of operation. The 2008 fleet leader failed after ~2,850 hours of field service as a result of hydrogen cross-over and exhibited an overall decay of ~5-6 μV/hr. The second aspect of the fleet data analysis is to identify the key components of the field operating cycle that can be correlated to the degradation of key components (e.g. MEAs). Figure 2 shows the fleet operating cycle that is typically seen in any given hour of operation. Such a cycle imposes ~100 load cycles per hour with about ~30% time spent at an idle condition. As seen in Figure 2, the required power draw (green trace) is instantly manifested in the fuel cell voltage response (blue trace). At a high level, this indicates that the fuel cell is exposed to the bus power draw directly, and that the hybridizing batteries on-board mainly serve to recover energy during braking. Thus, the imposed cycle on the fuel cell is aggressive and represents very realistic conditions from both a fleet and light-duty vehicle perspective.

Task 1.2 – EOL Stack Diagnostic Testing

For the current DOE project, since the 2010 fleet leaders are currently still in service and not yet available, the stacks from the 2008 fleet leader were chosen for detailed diagnostics and post-mortem analyses. Cells were extracted from the stack for comparison between BOL and EOL. Although characteristics associated with all four DOE ASTs with targeted mechanisms (namely, catalyst decay, carbon corrosion, membrane mechanical and membrane chemical decay) have been investigated, only the result pertinent to platinum group metal (PGM) decay is reported here. Results associated with other

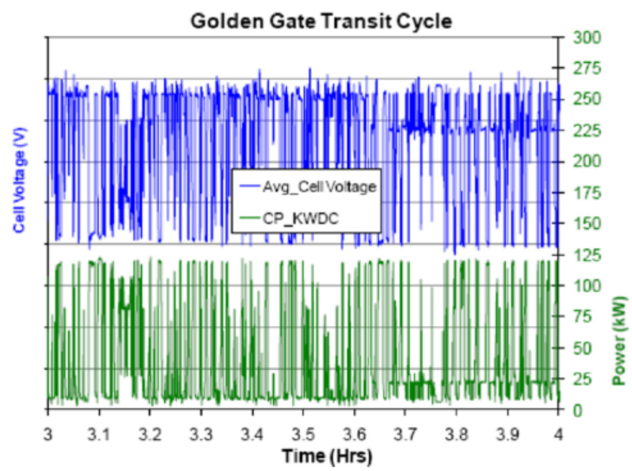

FIGURE 2. Typical drive cycle experienced by buses at Alameda-Contra Costa Transit (AC Transit) expressed in power draw (green trace) and individual cell voltage from the fuel cell stack.

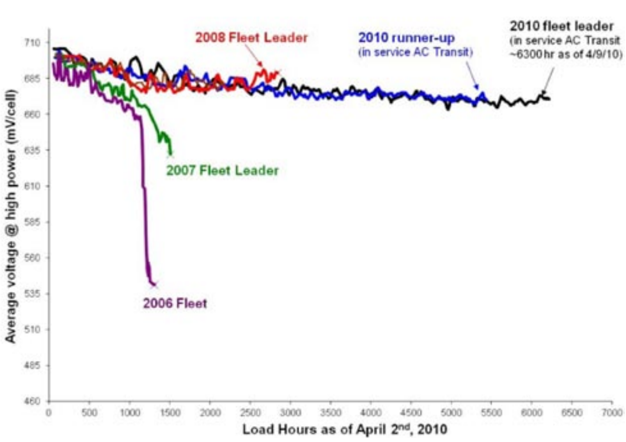

FIGURE 1. Comparison of Performance Loss at High Power for Various Generations of PM120 Bus Power Plants

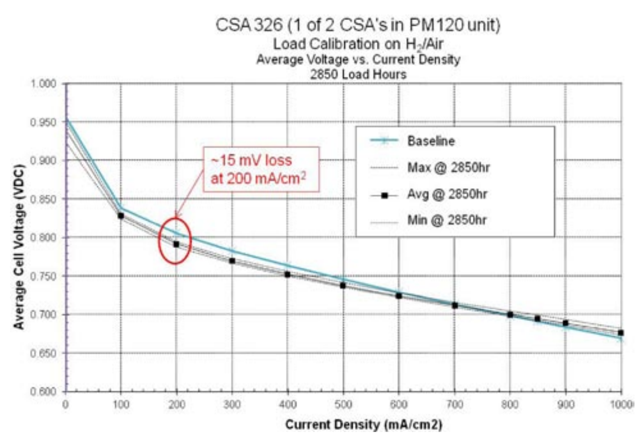

FIGURE 3. Characterization of stack performance (expressed per cell) at BOL (baseline) and following membrane failure in the field. Max/min represents +/- 1 σ substack voltages.

mechanisms will be reported in future reports. Figure 3 shows performance decay of cells from the 2008 fleet leader stack. It can be seen that after ~2,850 hrs of field operation, the voltage decay is ~15 mV at 0.2 A/cm^2.

Task 1.3 – EOL Stack Teardown Analysis

The stacks were torn down and cells extracted for detailed analysis. Four areas of the cell (air inlet and outlet, fuel inlet and outlet) were subjected to detailed analysis using a variety of ex situ techniques that include cyclic voltammetry to study Pt electrochemical surface area (ECA), X-ray diffraction (XRD) and transmission electron microscopy (TEM) techniques for Pt particle size and distribution. ECA results obtained from the 2008 fleet leader cell using cyclic voltammetry (2,850 hrs) are shown in Figure 4, which also include baseline (BOL) ECA data. At BOL, both anode and cathode catalysts had ECA of ~80 m^2/g. After 2,850 h, the average ECAs of anode and cathode are ~50 m^2/g and ~28 m^2/g, respectively. Assuming that only ~70% of Pt surface area is ionically contacted by cyclic voltammetry, the Pt particle sizes can be estimated based on Pt theoretical density which are also shown in Figure 4 (in red).

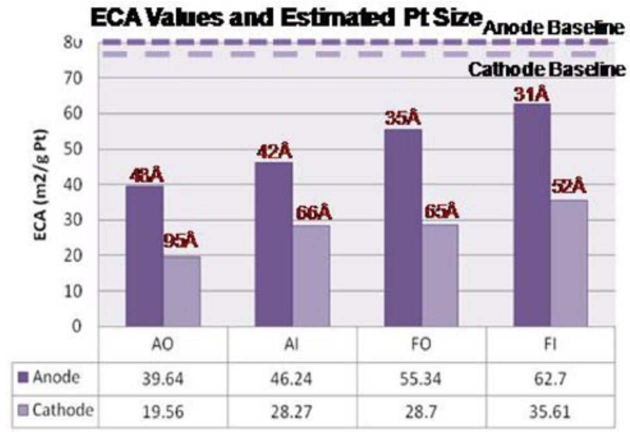

FIGURE 4. ECA data obtained from a 2,850 h cell using cyclic voltammetry. Baseline values are averages from unused samples. Pt particle sizes estimated from XRD are given at the top of the bars (from 2010 DOE Annual Merit Review FC015 – June 8th 2010).

Task 1.4 – High-Resolution TEM Analysis

PGM catalyst decay was also investigated using TEM techniques. Analysis on BOL and EOL MEAs were performed at ORNL. Images obtained from baseline and 2008 fleet leader samples are shown in Figure 5. It

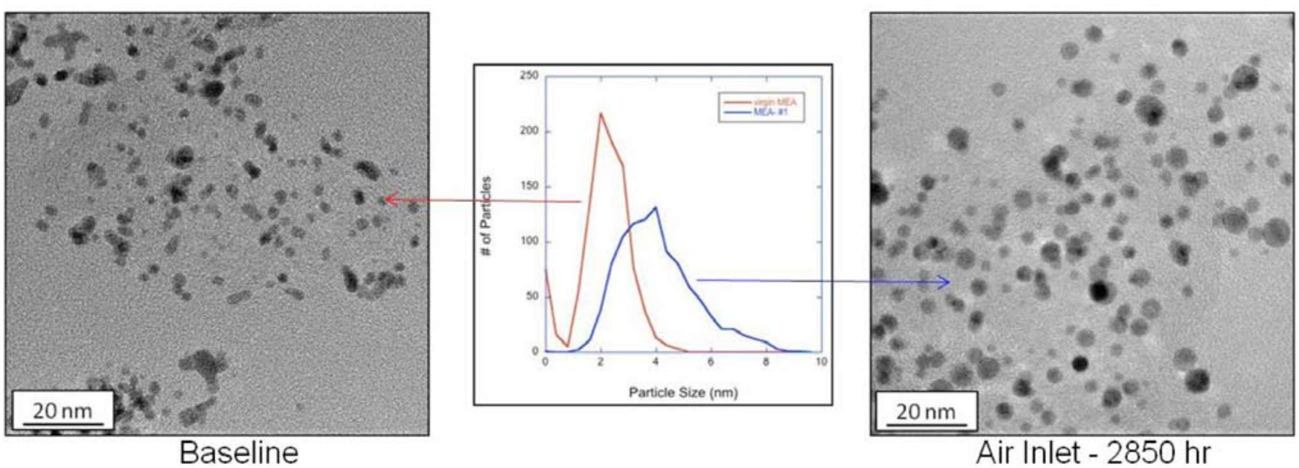

FIGURE 5. TEM Cathode Catalyst Images for Baseline and 2,850 h Catalyst Samples from Air Inlet Region

TABLE 1. Status of all AST Testing (Performed by LANL)

Component	Decay Mechanism	DOE AST Protocol	Status
Catalyst	Pt dissolution-sintering (PGM decay)	0.6 –1.0 V cycle in H_2/N_2	- Completed - Post-test analyses in progress
	Support corrosion	1.2 V hold in H_2/N_2	- Completed, data under review
Membrane	Mechanical degradation	Relative humidity cycling (0% to 90°C dew point) in air/air	- Completed - Post-mortem in progress
	Chemical degradation	Open circuit voltage hold in H_2/air	- In progress

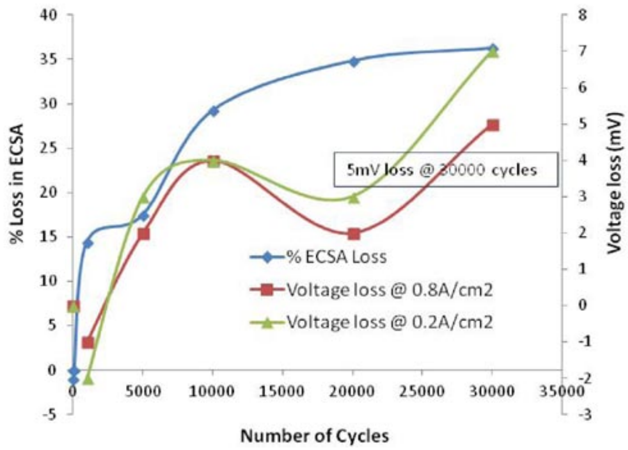

FIGURE 6. Diagnostics Results from PGM Decay AST

is clear from these images that Pt particle coarsening has occurred. ECA measurements and TEM analysis of the catalyst at the air inlet are in qualitative agreement.

Task 2 - Lab-World Degradation - DOE ASTs

All lab DOE ASTs are performed at LANL on a BOL MEA used in a UTC 2008 fleet leader. Table 1 summarizes the status of all sub-scale AST testing.

PGM Decay AST

Catalyst AST testing has been completed on the BOL MEA. The ECA and voltage loss are shown in Figure 6. It has been concluded that surface area, voltage and mass activity loss after 30,000 cycles at 0.6-1.0 V is ~37%, ~5 mV and ~20%, respectively. Comparison between these results and the DOE 2012 targets for catalyst is shown in Table 2. Post-mortem analyses on the AST-degraded electrodes are ongoing.

TABLE 2. Comparison of Observed Platinum Degradation and DOE Target at 30,000 Cycles

Observed at 30,000 Cycles	DOE Target at 30,000 Cycles
~37% ECA loss	<40% loss of initial area
~5 mV loss @ 0.8 A/cm^2	<30 mV loss @ 0.8 A/cm^2
~20% loss of mass activity	<40% loss of activity

Membrane Mechanical Degradation AST

Lab DOE AST for membrane mechanical degradation has also been performed on the BOL MEA used in a UTC 2008 fleet leader. Tested under the DOE relative humidity cycling protocol, the membrane endured ~5,500 cycles before significant cross-over was observed. Cross-over current, shorting resistance, and teardown analysis on the degraded MEA are currently underway and will be reported in the future.

Catalyst Support Degradation AST

Lab DOE AST for catalyst support corrosion has also been completed on the BOL MEA used in a UTC 2008 fleet leader. Data are currently under review.

ALT Breadboard Vehicle

UTC has facilitated the development of a test vehicle for accelerated evaluation of stack components under this project. 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 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. Accelerated testing using the BOL MEA has commenced.

TABLE 3. Summary of Tasks 1 and 2 Status

Decay Mechanism	Real world diagnostics (Tasks 1.1 & 1.2)	Real world teardown (Tasks 1.3 & 1.4)	Lab-world diagnostics (Task 2.1 & 2.4)	Lab-world teardown (Task 2.2 & 2.3)
Catalyst PGM decay	Complete Reported	Complete Reported	Complete Reported	Complete
Catalyst Support Corrosion	Complete	Ongoing	Complete	Ongoing
Membrane Mechanical Degradation	Complete	Ongoing	Ongoing	Ongoing
Membrane Chemical Degradation	Complete	Ongoing	Ongoing	Ongoing

Conclusions and Future Directions

Please refer to Table 3 for a high-level summary of the status of Tasks 1 and 2.

- Fleet/Real-World: UTC fleet performance and operating cycle analyses have been completed and reported. Teardown analyses of the real-world degraded components are near completion. Results on PGM decay have been reported.
- Lab-World: ASTs for PGM decay, carbon support corrosion and membrane mechanical decay have been completed. ASTs for membrane chemical

degradation will be performed in the third quarter in 2010.

- ALT: Test vehicle has been facilitated.
- Next Step: Correlate real-world degradation to lab tested degradation for carbon corrosion and membrane mechanical/chemical degradation. Complete testing BOL materials using ALT test vehicle.

FY 2010 Publications/Presentations

1. "IMPROVED AST's BASED ON FCV DATA" presentation to FreedomCAR & Fuel Partnership, Fuel Cell Tech Team Review Jan. 13, 2010.

2. "IMPROVED AST's BASED ON FCV DATA" presentation to DOE Annual Merit Review meeting June 8, 2010.

3. "Current Challenges in Transportation Fuel Cell Durability – Bus Fleet Applications" Keynote Presentation, ASME Fuel Cell Science, Engineering, and Technology, Brooklyn NY, June 16, 2010.