

## V.H.6 Development of Micro-Structural Mitigation Strategies for PEM Fuel Cells: Morphological Simulations and Experimental Approaches

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Project End Date: March 31, 2013

### Objectives

- Identify/verify catalyst degradation mechanisms:
  - Pt dissolution, transport/plating.
  - Carbon-support oxidation and corrosion.
  - Ionomeric thinning and conductivity loss.
  - Mechanism coupling, feedback, and acceleration.
- Correlate catalyst performance/catalyst structural change as a function of:
  - Unit cell operational conditions.
  - Catalyst layer morphology and composition.
  - Gas diffusion layer (GDL) properties.

- Develop kinetic and material models for catalyst layer aging:
  - Macro-level unit cell degradation model.
  - Micro-scale catalyst layer degradation model.
  - Molecular dynamics degradation model of the platinum/carbon/ionomer interface.
- Develop mitigation strategies for catalyst degradation through modification of:
  - Operational conditions.
  - Component structural morphologies/compositions.

### Technical Barriers

This project addresses the following technical barriers of the DOE Fuel Cell Technologies Program Multi-year Research, Development, and Demonstration Plan. This plan can be accessed at <http://www.eere.energy.gov/hydrogenandfuelcells/mypp/>.

#### (A) Durability

Pt catalyst and Pt catalyst layers degradation:

- Effect of structure and composition
- Effect of operational conditions

#### (B) Performance:

- Effect of cathode catalyst structure and composition

#### (C) Cost (indirectly)

### Technical Targets

This project is conducting fundamental studies of Pt/carbon catalyst degradation mechanisms and degradation rates which will be correlated with unit cell operational conditions and catalyst layer structure and composition. Furthermore, forward predictive micro- and macro- models for cathode performance and degradation will be developed. Design curves that will be generated both through model simulations and experimental work will enable membrane electrode assembly (MEA) designers to optimize performance, durability, and indirectly cost towards the 2015 stack targets for fuel cell commercialization [1]:

- Durability: 5,000/40,000 hrs (2015 transportation/2011 stationary application target)
  - Electrocatalyst support loss <30 mV after 100 hrs @ 1.2 V
  - Electrochemically active surface area (ECSA) loss <40%

- Cost: \$15/kW<sub>e</sub>
  - Platinum group metal total loading: 0.2 mg



## Approach

A dual path approach is taken in this project:

1. Development of models at the molecular, micro-structural, and macro homogeneous scales that include the degradation effects related to platinum dissolution/transport/plating, carbon surface oxidation/corrosion, and ionomer thinning/conductivity loss. These models will provide the ability to study the effects of composition, the morphological design, and the operational window on catalyst degradation via simulated accelerated stress testing (AST). The design curves generated in each scale of the modeling work will enable the development of mitigation strategies through trade-off analysis.
2. Development of key operational and catalyst/catalyst layer structural degradation design curves through AST coupled with ‘state-of-the-art’ in situ/ex situ characterizations techniques. This allows the correlation of performance loss with structural changes measured within the MEA. The experimentally collected design curves will enable the identification of mitigation strategies through MEA property trade-off analysis; as well it will provide validation data for the various levels of degradation models described above.

## Accomplishments

The following was accomplished during the first two quarters:

- The Discrete Macro-model was further developed to include a description of catalyst layer composition and structure (Agglomerate Model) with inputs for platinum loading, the catalyst compositional weight ratios, platinum particle size, utilization (or ECSA), material densities, and layer thickness. A comparison of Discrete and Agglomerate Model simulations showed that predicted performance is very sensitive to the choice of the catalyst model. The Agglomerate Model, which at the present time does not include liquid water, is able to capture mass transport losses at high current density suggesting that both the presence of liquid water and the catalyst structure have an effect on mass transport losses (Figure 1).
- Simulated design curves of the effect of performance on ionomer cathode loading reveals optimal

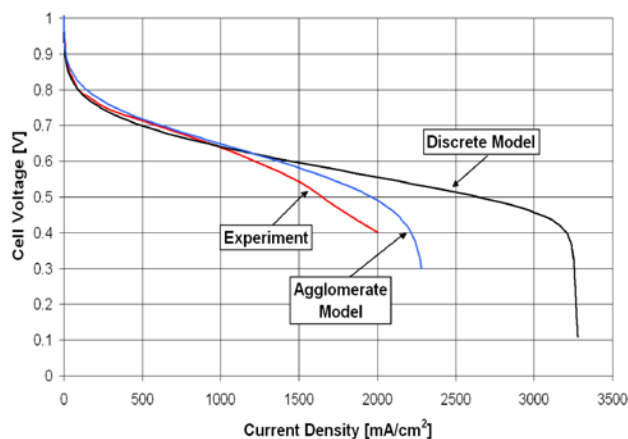


FIGURE 1. Macro Model Catalyst Effect: Comparison of Discrete Model and Agglomerate Model Simulations with Experimental Results

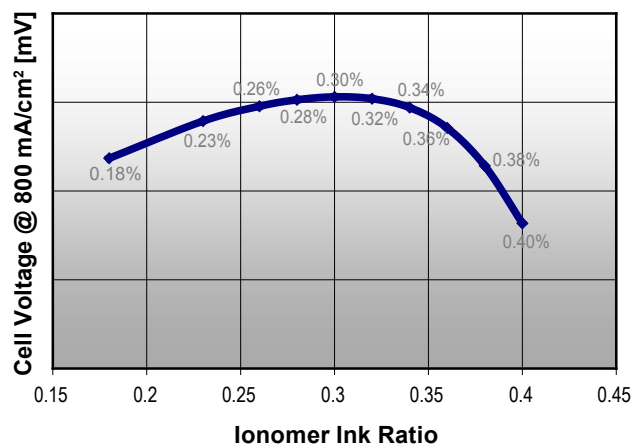


FIGURE 2. Agglomerate Model Simulation of the Effect of Cathode Ionomer Loading on Performance (Ionomer Content Design Curve)

performance at ~30% for the baseline MEA in agreement with experimental results (Figure 2).

- The methodology and diagnostic techniques for MEA characterization have been down-selected in order to establish an efficient and extensive characterization protocol.
- Key operational and structural stressors have been identified and prioritized for AST based on their effect on the degradation rates.
- The DOE catalyst AST and the Ballard Standard AST protocols were evaluated using a reference MEA in order to understand and compare their impact on catalyst layer degradation. The major differences between the two protocols are the cathode environment, cycle profile and frequency, and the upper potential voltage limit shown in Table 1. The performance losses from the two different protocols at the end of the test (Figures 3 and 4) are very similar and consistent with

predominately kinetic changes for both ASTs as shown by the voltage loss, EPSA and mass activity changes. At high current density the performance losses increase indicating some contribution of non-kinetic related losses that is somewhat larger for the BPS AST. The post-mortem analysis revealed that both the membrane and cathode thicknesses did not change under both protocols, while differences were observed in the average Pt crystallite size and Pt migration into the membrane. A larger average Pt crystallite size was observed in the MEA subjected to the DOE protocol due to re-deposition of Pt at the catalyst layer/membrane interface under N<sub>2</sub> conditions at the cathode. Under a simulated air cathode environment, a Pt band was observed in the membrane which does not form when N<sub>2</sub> is used.

TABLE 1. AST Protocols

Attributes	DOE AST Adapted for BPS Hardware	Ballard AST
Cycle Profile	Triangular Wave	Square Wave
	0.6 V to 1.0 V, 50 mV/s	0.6 V (30 s) to 1.2 V (60 s)
Time/Cycle	16 s	90 s
Number of Cycles	30,000	5,000
Total Cycling Time	133 hours	125 hours
Temperature	80°C	80°C
RH Anode/Cathode	100% /100%	100% /100%
Fuel/Oxidant	H <sub>2</sub> 4,450 sccm N <sub>2</sub> 9,000 sccm	H <sub>2</sub> 4,450 sccm 21% O <sub>2</sub> /N <sub>2</sub> 9,000 sccm
Pressure	5 psig	5 psig

RH = relative humidity

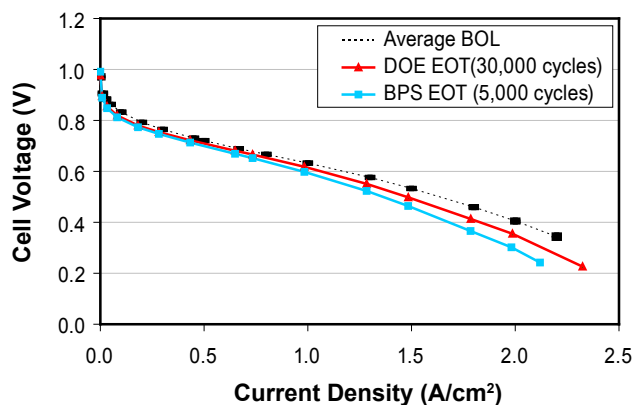


FIGURE 3. Performance Comparison of Reference MEA Tested under the DOE Catalyst AST and the BPS AST Protocols (as per Table 1)

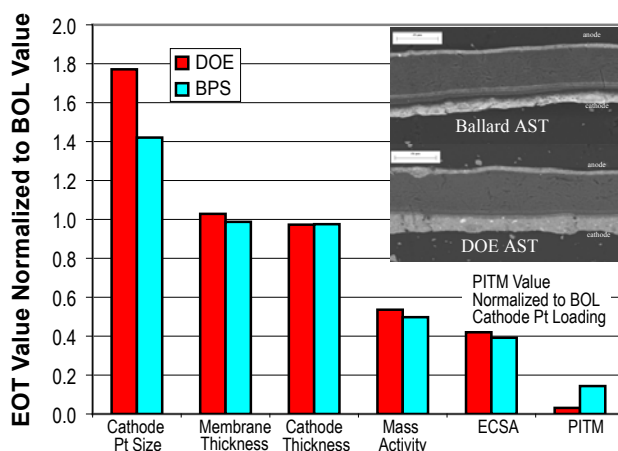


FIGURE 4. Comparison of the Effects of the AST Protocols on MEA Characteristics at the End of Test

### Future Directions

The 2010/2011 anticipated work and accomplishments are expected to be:

- Expanded macro-level model that captures the compositional-based effects with an extended range of the validation data (both operationally and compositionally).
- Modeled molecular features/characteristics of the Pt/C/ionomer interface.
- Expanded Micro-structural and Macro-homogenous Models that include a liquid water description.
- Measured performance degradation rates for different carbon supports, ionomer content, and Pt/C ratios.
- Measured performance degradation rates as a function of upper potential limit for Pt supported on a mid-range and low surface area carbon black.

### FY 2010 Publications/Presentations

1. 2009 New Fuel Cells Project Meeting, Washington, October 1, 2009.
2. Presentation to the Fuel Cell Tech Team (January 13, 2010).
3. 2010 Annual Merit Review Poster Presentation (June 8, 2010).
4. ECS Transaction Paper, Issue: Polymer Electrolyte Fuel Cells 10 (submitted): “Structural and Morphological Properties of Carbon Supports: Effect on Catalyst Degradation” Author(s): Anant Patel, Kateryna Artyushkova, Plamen Atanassov, Alan Young, Monica Dutta, Zaid Ahmad, Vesna Colbow, Silvia Wessel, and Siyu Ye.

## References

1. Hydrogen, Fuel Cells & Infrastructure Technologies Program: Multi-Year Research, Development and Demonstration Plan, U.S. Department of Energy, Energy Efficiency and Renewable Energy, October 2007 revision.