V.E.4 Development of Micro-Structural Mitigation Strategies for PEM Fuel Cells: Morphological Simulations and Experimental Approaches

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Fiscal Year (FY) 2011 Objectives

- Identify/verify catalyst degradation mechanisms, i.e. Pt dissolution and transport/ plating), carbon-support oxidation/corrosion, ionomeric thinning/conductivity loss, and mechanism coupling/feedback/acceleration.
- Correlate catalyst performance/catalyst structural change as a function of unit cell operational conditions, catalyst layer morphology/composition, and gas diffusion layer (GDL) properties.
- Develop kinetic and material models for catalyst layer aging, i.e. macro-level unit cell model, micro-scale catalyst layer model, and molecular dynamics model of the platinum/carbon/ionomer interface.
- Develop mitigation strategies for catalyst degradation through modification of: operational conditions and component structural morphologies/compositions.

Technical Barriers

This project addresses the following technical barriers of the DOE Fuel Cell Technology 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 cathode structure and composition
- Effect of operational conditions

(B) Performance
- Effect of cathode catalyst structure and composition

(C) Cost

Technical Targets

This project conducts fundamental studies of Pt/carbon catalyst degradation mechanisms and degradation rates which are correlated with unit cell operational conditions and catalyst layer structure and composition. Furthermore, forward predictive micro and macro models for cathode performance and degradation are being developed. Design curves will be generated, both through model simulations and experimental work, enabling membrane electrode assembly (MEA) designers to optimize performance, durability, and 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 @ 1.2V
    - Electrochemical Surface Area (ECSA) Loss <40%
- Cost: $15/kW_e
    - Precious Group Metal (PGM) total loading: 0.2 mg

FY 2011 Accomplishments

- Validated the one-dimensional (1D), 2-phase MEA model with statistical inputs for material, design, and operational deviations within the 95% variability of the experimental data (baseline MEA).
- Developed a molecular-dynamics-based description of the Pt/C/ionomer system.
- Expanded the micro-structural and 1D-MEA Model for 2-phase flow.
- Quantified Pt/C cathode catalyst layer degradation (performance loss and structural changes) as a function

of carbon catalyst support type, ionomer loading, upper potential voltage cycling in the accelerated stress test (AST), and number of AST cycles.

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Introduction

Catalyst/catalyst layer degradation has been identified as a substantial contributor to fuel cell performance degradation and this contribution will most likely increase as MEAs are driven to lower Pt loadings in order to meet the cost targets for full-scale commercialization. Over the past few years significant progress has been made in identifying catalyst degradation mechanisms [2,3] and several key parameters that greatly influence the degradation rates, including electrode potentials, potential cycling, temperature, humidity, and reactant gas composition [2,4-6]. Despite these advancements, many gaps with respect to catalyst layer degradation and an understanding of its driving mechanisms still exist. In particular, acceleration of the mechanisms under different fuel cell conditions, due to different structural compositions, and as a function of the drive to lower Pt loadings remains an area not well understood. In order to close these gaps an understanding of the effect of operating conditions and the layer structure and composition on catalyst layer degradation mechanisms and degradation rates is needed.

The project focus is to develop forward predictive models and to conduct systematic cell degradation studies that enable the quantification of the cathode catalyst layer degradation mechanisms and rates, as well as the coupling between mechanisms for key operational and structural stressors.

Approach

Models will be developed at the molecular, micro-structural, and macro-homogeneous scales that include degradation effects related to platinum dissolution, transport and plating, carbon surface oxidation and corrosion, and ionomer thinning/conductivity loss. The models will provide the ability to study the effects of composition, the morphological design, and the operational window on catalyst degradation via simulated ASTs. The design curves generated in each scale of the modeling work will enable the development of mitigation strategies through trade-off analysis.

Accelerated stress testing coupled with 'state-of-the-art' in situ/ex situ characterization techniques will be used to correlate MEA performance loss with structural changes measured within the Pt cathode, as well as to develop key operational and catalyst/catalyst layer structural degradation design curves. The experimental results will also serve to provide model validation.

Results

Under the modeling tasks, molecular modeling was used to determine the cohesive energy for the Pt clusters and its interaction with H_2O and O_2, carbon and the ionomer. The Microstructural Catalyst Model has been extended to include 2-phase flow in order to simulate the capillary transport inside the catalyst structure. Furthermore, the model has been used to extract effective properties for the low surface area catalysts used in the project, with the results currently implemented in the Macro MEA model. The Macro MEA model was re-scripted in a manner that separated relevant sections of model functionality into self-contained modules enabling the use of statistical inputs based on component to component and operational variability. Shown in Figure 1(a), the model was validated using experimental data generated with different MEAs and test-stands. The model validates within the 95% variability of the experimental data for current densities up to ~1,000 mA/cm^2. Beyond this point the experimental and model data diverge, the discrepancy is believed to be due to the formation of liquid water and its interaction statistically with the MEA structure. To improve the validation, a 2-phase flow module was implemented and a repeat of the validation shows the improved mass transport predictions over the entire polarization range, Figure 1(b), such that the model is fully validated within the 95% variability of the experimental data.

The key operational and structural stressors affecting catalyst layer durability were identified and prioritized based on literature and Ballard data. With a focus on the catalyst layer structure and composition, the impact of catalyst carbon support type, catalyst layer ionomer content, and cathode catalyst layer degradation was investigated using ASTs. In addition, selected designs were also investigated for performance degradation and catalyst layer structural changes as a function of AST upper potential and as a function of AST cycle number. The MEAs were in-house catalyst-coated Nafion® membranes with a anode and cathode loading of 0.1/0.4 mg/cm^2, respectively, and Ballard Material Products' GDLs. The AST standard conditions are: 80ºC, 100% relative humidity (RH), air/H_2, square wave cycle from 0.6 V (30 s) to 1.2 V (60 s) for 4,700 cycles. Comprehensive cell diagnostics and characterization were conducted after 50, 700, 1,400, 2,100, and 4,700 cycles and failure analysis was performed at the end of the stress test (4,700 cycles).

The effect of ionomer loading on Pt dissolution/corrosion was investigated for a range of 12 to 50 wt% Nafion® content using a Pt catalyst supported on a low surface area carbon (LSAC). The MEAs were subjected to AST testing (1.2 V upper potential limit, 4,700 cycles). The key findings were:

- ~30% ionomer loading yields optimal beginning of test (BOT) performance in agreement with literature results [7] and internal model predictions.
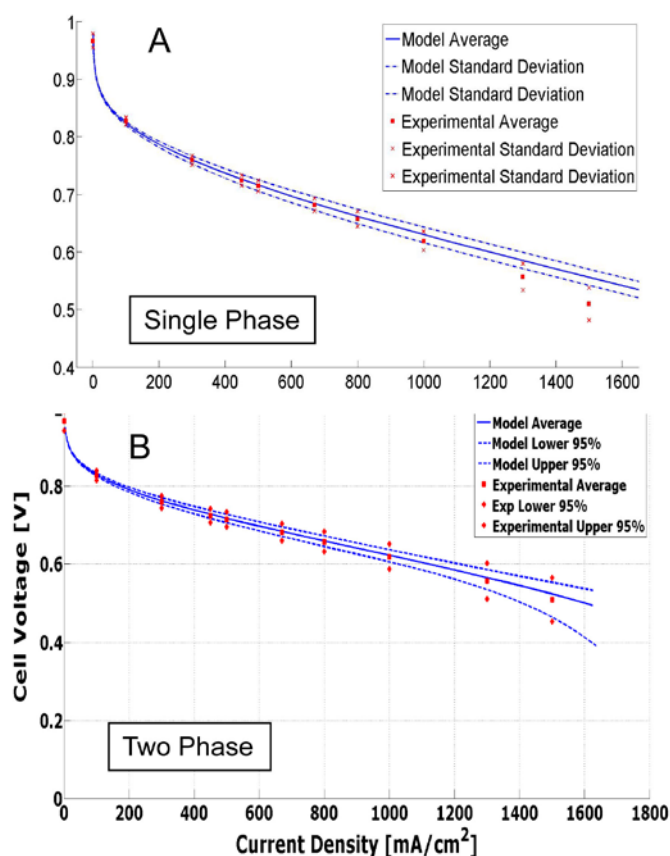
FIGURE 1. 1D MEA Model: Comparison of statistical model predictions with experimental data (a) single phase flow using input parameter uncertainty of 1 standard deviation, (b) 2-phase flow using input parameters confidence level of 95%.

- The ionomer content impacts the BOT catalyst structure: catalyst layer porosity decreases with increasing ionomer loading, Figure 2(a).
- After 4,700 AST cycles end of test (EOT) the highest ECSA loss occurs at an ionomer content of ~30 to 40%, Figure 2(b). The voltage loss is dominated by cathode catalyst layer ionic loss.

The effect of catalyst carbon support type on catalyst performance and degradation was studied using a variety of Pt catalysts supported on different carbons (surface area from <200 m^2/g to 800 m^2/g) at an upper AST potential of 1.0 and 1.2 V. The catalyst powders and carbon support materials were analyzed for surface species, morphology, and particle distribution.

Transmission electron microscope micrographs revealed a carbon aggregate structure with graphitic walls and amorphous center for the LSAC; the mid-range carbon support (MSAC) and Vulcan (V) also exhibit some graphic walls that are in general less uniform. One of the high surface area carbons (HSAC1) showed some graphitic centers throughout the aggregates; while a second one
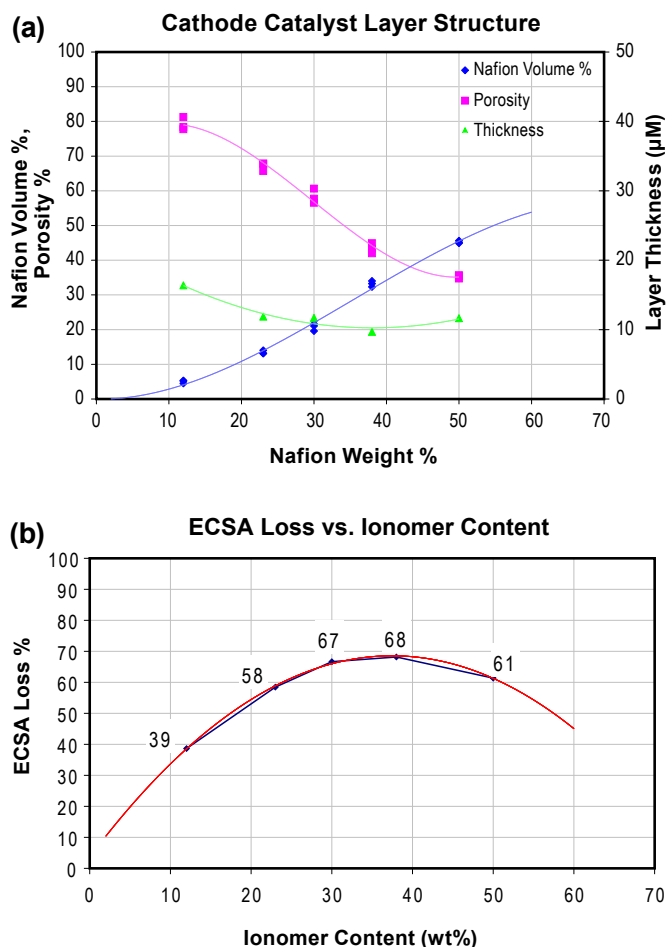

FIGURE 2. Effect of ionomer content in the cathode on (a) catalyst layer structure and (b) cathode ECSA loss after 4,700 AST cycles.

(HSAC2) showed a highly amorphous structure. It was also noticeable that the Pt distribution on the different supports becomes more dispersed with increasing surface area.

In general, Pt catalysts supported on high surface area carbon exhibited higher BOT performance due to higher ECSA; however, the carbon surface structure and surface functionality were found to also have a significant impact on the catalyst layer structure and its resistance to corrosion. The key findings were:

- The BOT performance did not show a clear trend with the carbon support surface area.
- Cycling at 1.0 V upper potential limit (UPL) exhibited similar Pt dissolution and minimal carbon oxidation for all investigated carbons.
- Cycling at 1.2 V UPL showed increased Pt dissolution, Pt agglomeration and Pt in the membrane with increasing carbon surface area due to greater catalyst ECA and Pt dispersion. As expected, greater Pt surface area and distribution enhanced the Pt catalysis of the
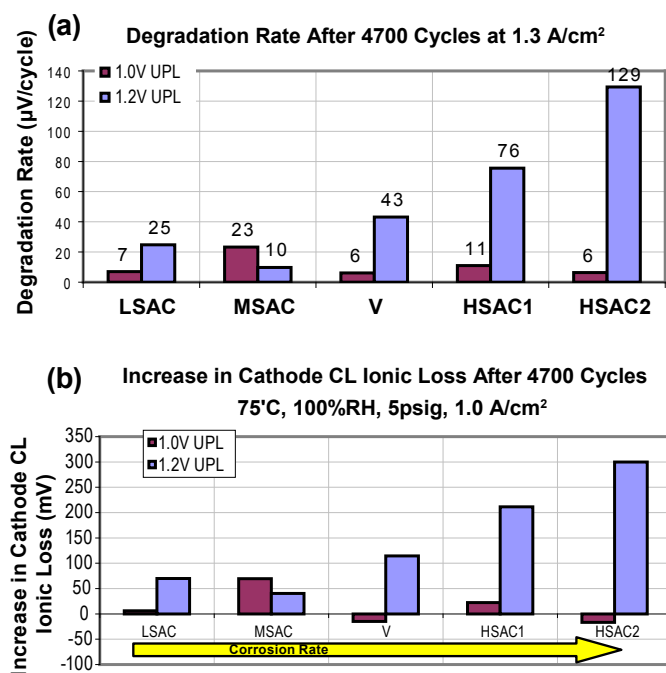
(a) Degradation Rate After 4700 Cycles at 1.3 A/cm²

(b) Increase in Cathode CL Ionic Loss After 4700 Cycles
75'C, 100%RH, 5psig, 1.0 A/cm²

FIGURE 3. (a) Voltage degradation rate and (b) cathode catalyst layer ionic resistance loss after 4,700 AST cycles at an upper potential of 1.0 and 1.2 V for a variety of carbon supports (LSAC - Low, MSAC - Medium, HSAC - High Surface Area Carbon support, V - Vulcan).

carbon support, thus catalyst layer thinning increased with increasing carbon surface area.

- The cathode catalyst layer performance and specifically the ionic resistance were impacted significantly by corrosion, most severely for high surface area carbon supports (Figure 3). The MSAC catalyst was found to be an exception to the trend, likely due to enhanced carbon surface oxidation causing increased cathode catalyst ionic conductivity and consequently higher performance.

- The carbon structure and morphology impacts catalyst layer durability. Pt dissolution (ECSA/kinetic loss) and corrosion (cathode layer ionic/thickness loss) decreased linearly with increasing graphitic content of the carbon support surface.

The effect of upper potential on catalyst layer degradation was studied by subjecting Pt catalysts on MSAC and LSAC supports to AST cycling at upper potentials from 1.0 to 1.4V. The two catalysts exhibit similar platinum dissolution and support corrosion trends with some subtle differences in degradation rates. The LSAC catalyst was found to be slightly more stable at an UPL ≤1.3 V; however, it was notably less stable than the MSAC catalyst at a UPL ≥1.3 V which may be associated with the collapse of the LSAC aggregates due to severe corrosion of the amorphous centers.
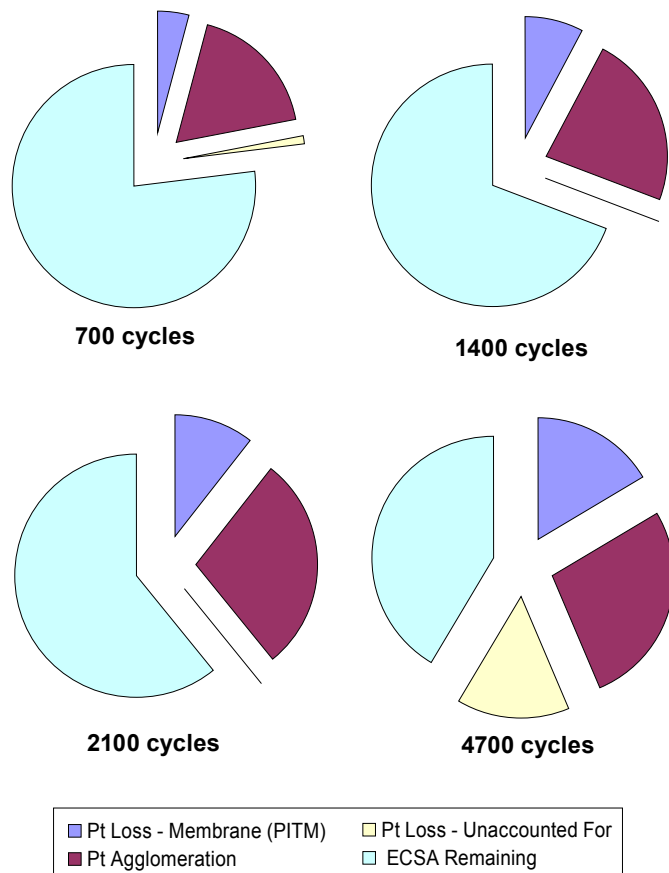

FIGURE 4. Pt loss break-down (Pt agglomeration, Pt in the membrane, and "unaccounted for Pt" at 50, 700, 1,400, 2,100, and 4,700 AST cycles with 1.2 V upper potential.

The impact of AST cycle number on catalyst layer degradation was investigated to quantify changes in degradation mechanisms for the LSAC catalyst with progressive AST cycling. MEAs using the LSAC catalyst were cycled at 1.2 V UPL to different EOT cycle numbers (50, 700, 1,400, 2,100, 4,700 cycles). A significant ECSA loss was observed after only 50 cycles; for <2,100 cycles the kinetic losses were found to dominate (Pt dissolution, agglomeration, Pt in the membrane); while at cycles ≥2,100 the catalyst layer ionic losses became dominant due to the onset of carbon corrosion (catalyst layer thinning). The Pt loss with cycle number with respect to the total initial Pt in the catalyst layer, measured as ECSA, is depicted in the pie chart in Figure 4 as follows: 1) the fraction labeled "ECSA remaining" is still active; 2) the fraction labeled "Pt agglomeration" is ECSA lost due to Pt agglomeration; 3) the fraction labeled "Pt Loss - Membrane (PITM)" is Pt ECSA lost due to dissolved Pt depositing in the membrane; 4) the fraction of initial ECSA lost that can't be accounted for by Pt agglomeration or the Pt found in the membrane is labeled "Pt loss - Unaccounted For" and is presumed to be due to support corrosion and Pt particle detachment from the support.

Conclusions

The interim conclusions are:

- The 1D MEA Model, with 2-phase flow, has been validated within the 95% variability of the experimental data for the entire current density range (up to 1.5 A/cm^2). Additionally, the model has been validated across a range of catalyst compositions and operational conditions.
- The catalyst layer ionomer content affects the catalyst layer structure (porosity). Optimal performance and lowest degradation rate were observed for 30% ionomer content (LSAC catalyst).
- The Pt catalyst carbon support surface area is not the only measure of susceptibility to catalyst support corrosion; the catalyst layer structure and carbon functionality play an important role. The graphitic content of the carbon surface correlates linearly with degradation.
- BOT performance does not show a clear trend with carbon support surface area except for kinetic losses which decrease with increasing surface area. However, catalyst degradation increases with increasing carbon surface area, i.e. higher Pt dissolution (ECSA loss, Pt agglomeration, and Pt in the membrane) and higher corrosion (ionic resistance loss, catalyst layer thickness loss).

Future Directions

- Investigate catalyst degradation rates (Pt dissolution and carbon corrosion) as a function of the Pt/carbon ratio, cathode catalyst loading, and ionomer equivalent weight.
- Correlate degradation with catalyst material properties.
- Model Pt dissolution on the molecular scale.
- Refine two-phase flow implementation and validation for both the micro-structural catalyst and 1D-MEA model (linkage of the two scales).
- Expand the micro catalyst layer and 1D MEA models to transient operation and develop/include degradation mechanisms.
- Integrate electrical contact resistance model with the 1D MEA model.

FY 2011 Publications/Presentations

1. A. Patel, K. Artyushkova, P. Atanassov, A. Young, M. Dutta, Z. Ahmad, V. Colbow, S. Wessel, S. Ye, "Structural and Morphological Properties of Carbon Supports: Effect on Catalyst Degradation", ECS Transactions Volume 33 #1 (2010) Catalysts-Durability.

2. D. Harvey, A. Bellemare-Davis, J.G. Pharoah, K. Karan: Development of a validated statistical Beginning of Life (BOL) Performance Model, Hydrogen and Fuel Cells 2011 Conference, Vancouver, B.C., 15–18 May 2011.

3. D. Harvey, J.G. Pharoah: Development of a full thickness micro structural catalyst model for estimation of effective properties and performance, Hydrogen and Fuel Cells 2011 Conference, Vancouver, B.C., 15–18 May 2011.

4. A. Patel, K. Artyushkova, P. Atanassov, D. Harvey, M. Dutta, V. Colbow, and S. Wessel, "Effect of Graphitic Content on Carbon Supported Catalyst Performance", accepted abstract, 220th ECS Meeting & Electrochemical Energy Summit in Boston, Massachusetts (October 9–14, 2011).

5. S. Knights, R. Bashyam, P. He, M. Lauritzen, C. Startek, V. Colbow, J. Kolodziej, and S. Wessel, "PEMFC MEA and System Design Considerations", accepted abstract, 220th ECS Meeting & Electrochemical Energy Summit in Boston, Massachusetts (October 9–14, 2011).

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