

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

Dr. Silvia Wessel (Primary Contact), David Harvey,
Dr. Vesna Colbow

Ballard Power Systems
9000 Glenlyon Parkway
Burnaby, B.C. V5J 5J8
Phone: (604) 453-3668
Email: silvia.wessel@ballard.com

DOE Managers

HQ: Kathi Epping Martin
Phone: (202) 586-7425
Email: Kathi.Epping@ee.doe.gov

GO: David Peterson
Phone: (720) 356-1747
Email: David.Peterson@go.doe.gov

Technical Advisor

John Kopasz
Phone: (630) 252-7531
Email: kopasz@anl.gov

Contract Number: DE-EE0000466

Subcontractors:

- Georgia Institute of Technology, Atlanta, GA (Dr. S.S. Yang)
- Los Alamos National Laboratory, Los Alamos, NM (Dr. R. Borup)
- Michigan Technological University, Houghton, MI (Dr. J. Allen)
- Queen's University, Kingston, Ontario (Drs. K. Karan, J. Pharoah)
- University of New Mexico, Albuquerque, NM (Dr. P. Atanassov)

Project Start Date: January 1, 2010

Project End Date: March 31, 2013

Fiscal Year (FY) 2012 Objectives

- Completion of the molecular dynamics model of the catalyst 3-phase interface.
- Implementation of 2-phase flow in the micro-structural catalyst model and simulation of effective properties and performance with liquid water.
- Validation of the one-dimensional (1D)-statistical membrane electrode assembly (MEA) model as a function of catalyst layer composition and operational conditions, including an investigation of low loaded

catalyst layers using both the 1D-statistical MEA model and micro-structural catalyst model.

- Evaluation of the effect of cathode catalyst layer composition (Pt loading, Pt/C ratio, ionomer equivalent weight) and operational conditions (relative humidity [RH], dwell time at 1.4 V upper potential limit) on degradation mechanisms, performance degradation, and structural changes of the cathode catalyst layer.

Technical Barriers

This project addresses the following technical barriers of the Fuel Cells section of the Fuel Cell Technologies Program Multi-Year Research, Development, and Demonstration Plan [1].

- (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 (in-direct)

Technical Targets

In this project fundamental studies of the Pt/carbon catalyst degradation mechanisms and degradation rates are conducted and 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, generated both through model simulations and experimental work, will enable MEA designers to optimize performance, durability, and cost towards the 2020 targets for fuel cell commercialization [1]:

- System Durability (10% performance loss)
 - Transportation applications: 5,000 hours
 - Stationary applications (1-10 kW_e): 60,000 hours
- Electrocatalyst (transportation applications)
 - Support Stability: <10% mass activity loss after 400 hrs @ 1.2 V in H₂/N₂
 - Electrochemically active catalyst surface area (ECSA) loss <40%
 - Precious group metal (PGM) total loading: 0.125 mg/cm²

FY 2012 Accomplishments

- Completed the molecular dynamics-based description of the carbon supported-Pt and ionomer system and evaluated the platinum surface coverage of a variety of moieties.
- Extended validation of the 1D-statistical Unit Cell Performance model over the compositional ranges of interest.
- Model predictions suggest higher water content in low-loaded catalyst layers as a partial cause of low performance and increased oxygen sensitivity.
- Correlated the cathode catalyst layer structure and composition (Pt/C ratio, Pt loading) and operational conditions (RH, temperature) with durability.
- Developed a semi-empirical carbon corrosion model.



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 [2,4,5,6]. 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 operating 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 quantification of the cathode catalyst layer degradation mechanisms and rates and correlation of materials properties to key operational and structural parameters.

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 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.

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

Model Development

During this year the modeling efforts continued to focus on advancing capabilities on each of the three length scales. For the molecular dynamics, the focus was on completion of the Pt/ionomer/carbon interface model, with species interactions and estimates of the Pt surface coverage by a variety of moieties. On the micro-structural scale, attention was directed to completing a refinement of the performance solvers with water saturation and the prediction of a capillary pressure relationship for the catalyst morphologies. The unit cell performance model was expanded to transient operation, with the inclusion of a multi-step oxygen reduction reaction description, and integration of a profilometry-based contact resistance model (gas diffusion layer [GDL]/catalyst, GDL/plate).

Molecular dynamics simulations investigated interactions between a bare and oxygen covered Pt particle anchored at graphene sheet dislocations and H_2O , H_3O^+ , O_2 , RSO_3 , and polymer species. The simulations were run at different time scales to probe the state of relaxation of the interface structure. Figure 1A shows the oxygen covered Pt particle and coverage by the various species. An estimation of the concentration of these surface moieties reveals that O_2 molecules appear to prefer the ionomer phase over water and that RSO_3 species interact strongly with the Pt/PtO surface. The interaction and occupation of the various species at the Pt and PtO surfaces (Figure 1B) are important factors in fundamentally understanding the mechanism of Pt dissolution.

The 1D-MEA model which allows for statistical variation of the structural, operational, and physico-chemical parameters was used to study the effect of cathode platinum loadings from 0.05 to 0.5 mg/cm^2 on beginning of test (BOT) performance. The catalyst layer thickness varied linearly from 2.5 μm to 18 μm and ECSA values ranged from 25 to 250; the ECSA values indicated that utilization

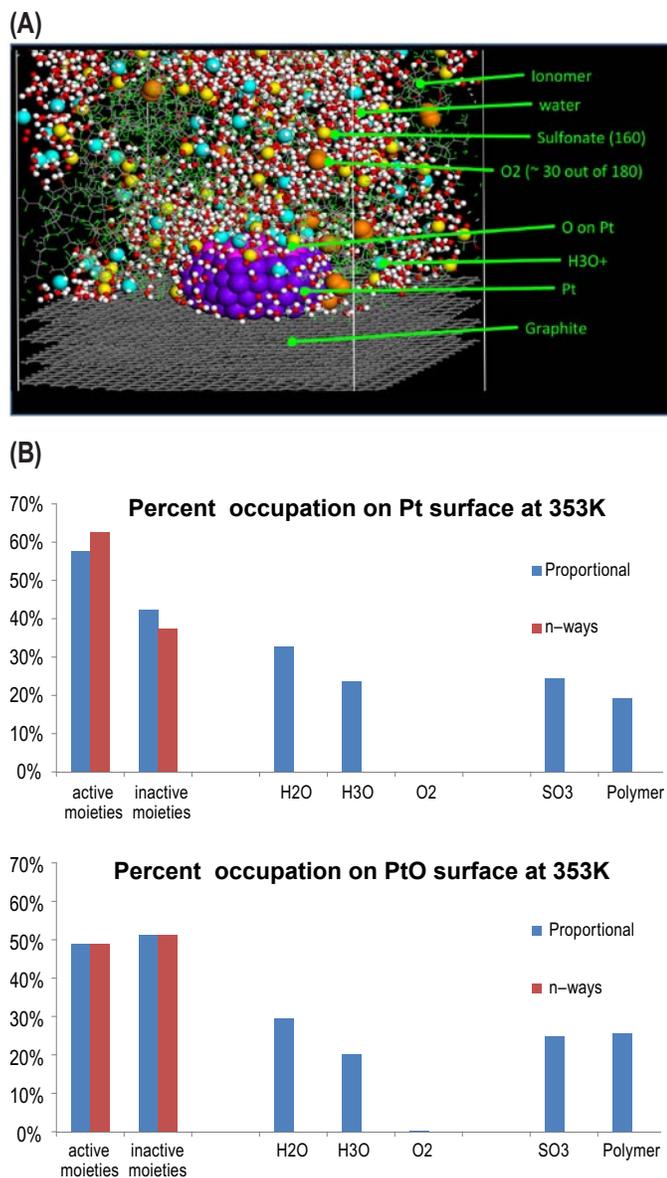


FIGURE 1. (A) Molecular Dynamics Model simulation of PtO anchored on graphene sheets interacting with H_2O , H_3O^+ , O_2 , SO_3 , and polymer species, (B) % occupation of Pt and PtO sites by the moieties.

was nearly constant for the beginning of life (BOL) MEAs across the loading range. As shown in Figure 2A, the model demonstrates the ability to capture the changes in performance between a high and low platinum-loaded cathode under various O_2 partial pressures; specifically the model captures the effect of changes in surface area and reaction penetration within the catalyst layer as a result of proton penetration, oxygen transport, liquid water content. The model results shown in Figure 2B suggest that the increased sensitivity to lower oxygen partial pressures for low loaded catalyst structures was, at least in part, due to higher liquid water saturation levels within the MEA, particularly within the electrode itself.

Experimental Parametric Studies

Efforts within this FY were focused on correlating the cathode catalyst layer structure and composition for a range of platinum loadings and Pt/C ratios with the AST degradation rates. Further, the effect of ionic equivalent weight was studied in order to identify its role on the degradation mechanisms (platinum dissolution and carbon corrosion). A semi-empirical carbon oxidation/corrosion model was developed to assist in understanding and enabling the separation of the effects of oxidation and corrosion as a function of several key variables (operation/structural). The in-house MEAs (low surface area carbon supported Pt catalyst coated on Nafion[®] 211 membrane and sandwiched between Ballard Materials Product GDLs) were subjected to AST cycling using a square wave cycle (30 s at 0.6 V to 60 s at 1.2 V) under baseline operational conditions (air/ H_2 , 80°C, 100% RH). The MEAs used a catalyst with a Pt/C ratio of 50 wt% and a anode/cathode Pt loading of 0.1/0.4 mg/cm² unless stated otherwise. Cell characterization was performed at 0 (BOT), 50, 700, 1,400, 2,100, and 4,700 (end of test [EOT]) cycles with a post mortem failure analysis performed at EOT.

The effect of Pt loading on BOT performance and degradation is shown in Figure 3. For loadings larger than 0.3 mg/cm² (ECSA >75), the performance at 1 A/cm² is relatively constant; however, for low loadings <0.2 mg/cm² (ECSA <50), the BOT performance is severely impacted. As discussed above; this is believed to be due, at least in part, to the increased water content in thin catalyst layers. Figure 3A shows that the performance correlates well with ECSA with the relationship holding as the structure changes and the ECSA is reduced due to Pt dissolution and agglomeration. Moreover, the degradation rate and ECSA loss follow the same trend with Pt loading, as seen in Figure 3B. There is an ~8-fold increase in voltage degradation rate when the Pt loading is reduced from 0.3 to 0.1 mg/cm².

The effect of the Pt/C ratio on the catalyst layer structure (BOT) was primarily through a change in the catalyst layer thickness which ranged from 9 μ m to 31 μ m and the ECSA which varied from ~100 to 200 for Pt/C ratios from 60 to 30 wt%. It was observed that the porosity of the catalyst layer effectively remained unchanged at ~70%; further, the higher Pt/C ratios demonstrated low ECSA primarily due to the presence of substantially larger Pt crystallites. The BOL performance was found to be very similar for all Pt/C ratios while the larger crystallites seen at higher Pt/C ratios were observed to affect the Pt dissolution and agglomeration rates. At EOT (4,700 cycles at 1.2 V upper potential limit [UPL]) the catalyst layer containing 60% Pt/C showed the lowest degradation and the 30% Pt/C showing the highest. ECSA results revealed an ECSA loss at EOL of ~50% independent of the Pt/C ratio. Voltage loss analysis showed that the voltage degradation was predominantly a result of catalyst layer ionic

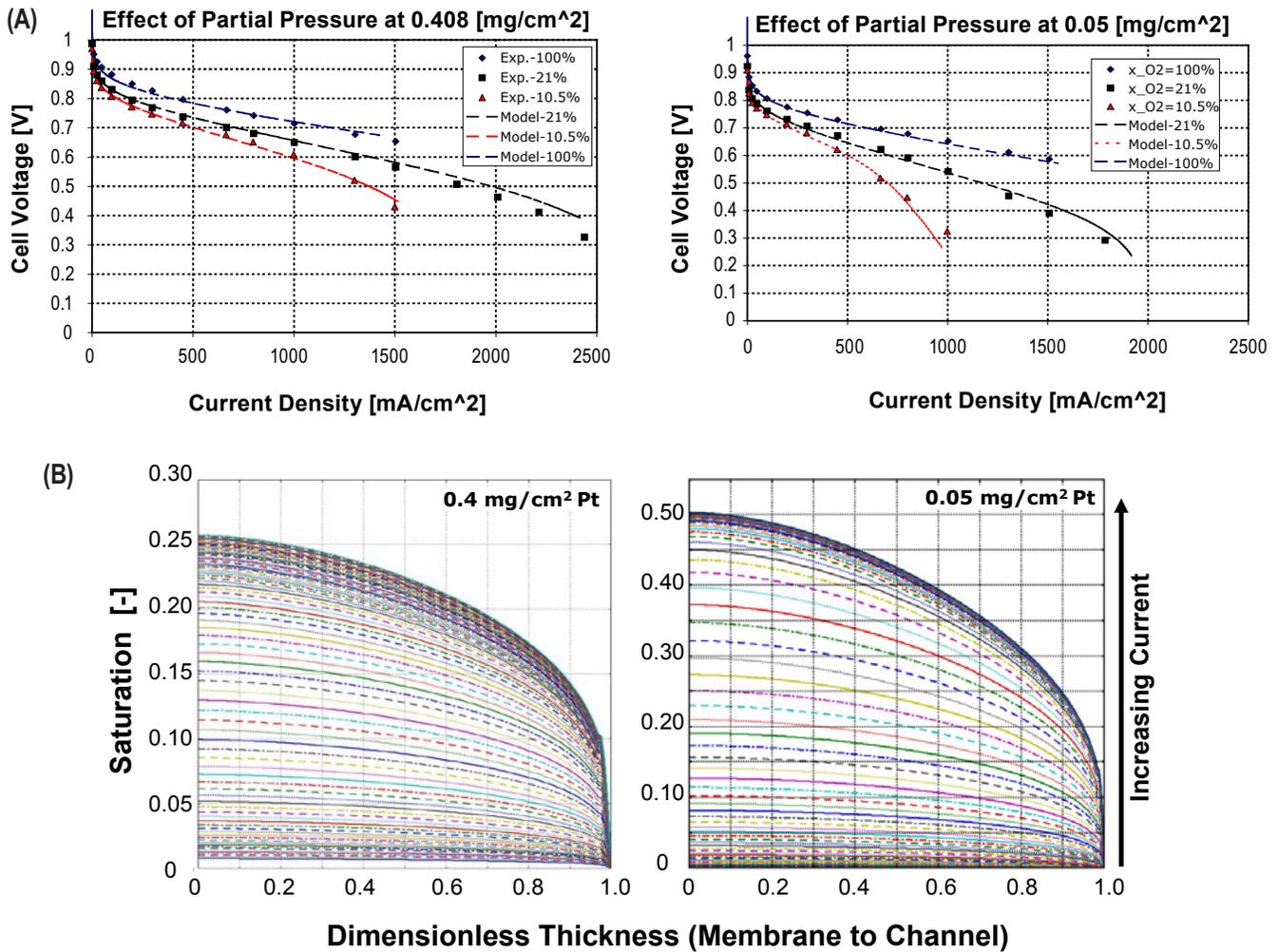


FIGURE 2. (A) 1D-statistical Unit Cell Model BOT performance simulations of 0.4 and 0.05 mg/cm² Pt loaded catalyst layers at different O₂ concentrations, (B) Modeled water saturation characteristics of the 0.4 and 0.05 mg/cm² Pt loaded catalyst layers.

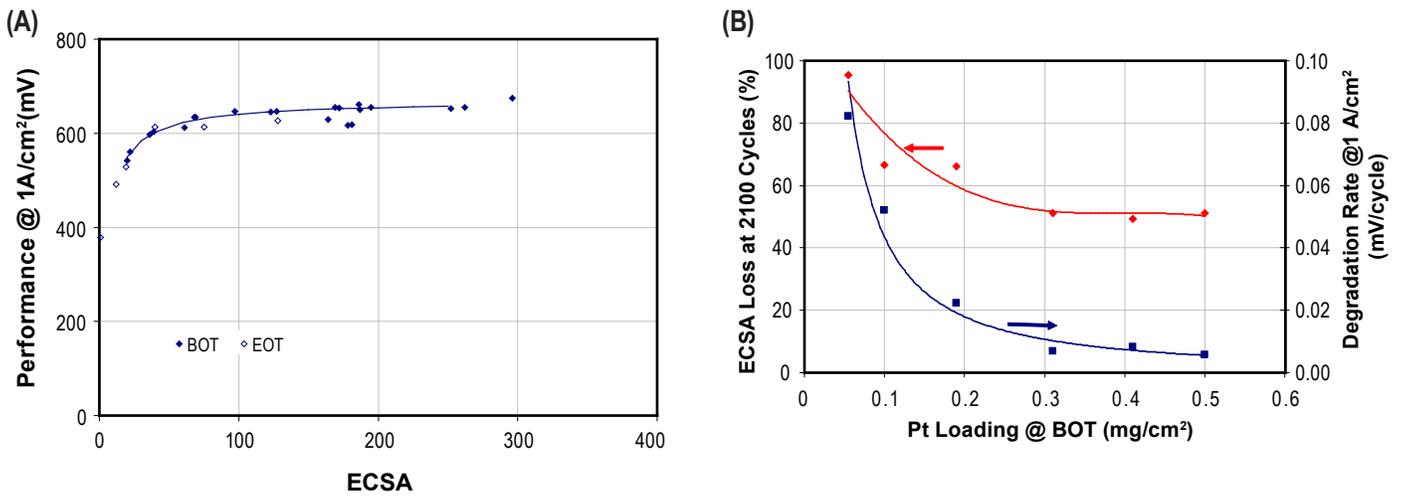


FIGURE 3. (A) BOT and EOT performance characteristics as a function of ECSA, (B) ECSA loss and degradation rate behaviour as a function of cathode catalyst layer loading.

resistance changes due to the reaction penetration pushing further into the catalyst layer as a result of the low ECSA.

Semi-Empirical Carbon Corrosion Model

In order to understand carbon catalyst support degradation, the performance of MEAs subjected to AST cycling at an upper potential limit ranging from 0.9 to 1.4 V was analyzed for changes in double layer capacitance (Cdl). Carbon support corrosion can be separated into two reaction steps: (1) oxidation of the carbon surface forming surface oxide species and (2) corrosion of the carbon sites causing evolution of carbon dioxide/monoxide. The carbon surface oxidation and carbon corrosion reactions have opposing effects on Cdl which enables separation of the two reaction rate constants. Surface oxidation increases the Cdl due to a larger specific capacitance for a carbon surface with carbon-oxygen groups, while the corrosion reaction evolving carbon dioxide/monoxide causes a decrease in the carbon surface area and Cdl. The reaction rate constants, after accounting for the effect of changing platinum surface area due to Pt dissolution/agglomeration on the Cdl, showed a clear trend in increasing reaction rate with UPL for both steps of the corrosion mechanism. A comparison of two carbons with different corrosion resistance (low surface area carbon [LSAC] and medium surface area carbon [MSAC]) showed a distinct difference in the surface oxidation reaction, while the corrosion reaction and the specific capacitances (at BOT and EOT) were similar. Further, to understand the effects of cycling versus potential hold stress tests, i.e. transient vs. pseudo steady-state behaviour, the effect of dwell time at 1.4 V UPL was evaluated between 5 to 600 seconds; no significant differences as a result of increased dwell time were found. Figure 4A shows that the onset of corrosion (performance loss) is dependent on the total time spent at the upper potential rather than the number of AST cycles. Furthermore, as shown in Figure 4B, the onset of corrosion (observed performance loss) decreases logarithmically with increasing upper potential limit. For example, a total time of ~4 hours at a UPL of 1.4 V is equivalent to ~160 hours at a UPL of 1.2 V for the LSAC catalyst, while ~1 hour and ~80 hours were observed for the MSAC catalyst, respectively.

Conclusions and Future Directions

The interim conclusions are:

- Molecular modeling of the carbon/Pt/ionomer and interaction with different moieties showed that the RSO_3^- species of the ionomer side chain strongly interacts with Pt and/or PtO.
- 1D-statistical Unit Cell model predictions of BOT performance for a variety of different catalyst layer structures and operating conditions show good agreement with experimental results over the full range of current densities.

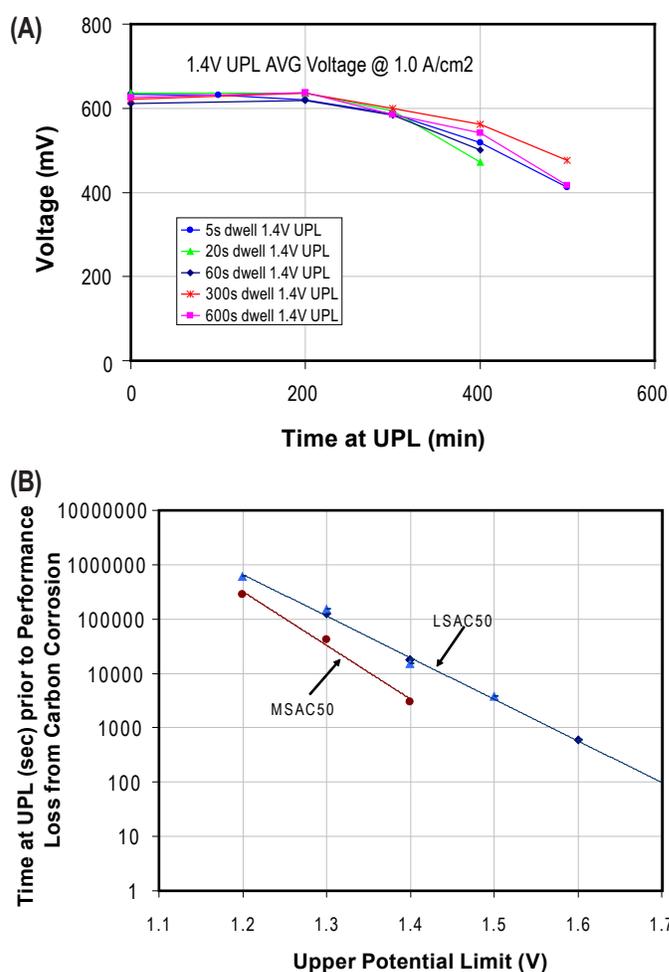


FIGURE 4. (A) Voltage characteristics as a function of dwell time at an upper potential limit of 1.4 V, (B) Onset of carbon corrosion (performance loss) as a function of upper potential limit for two different Pt catalysts (Pt catalyst supported on graphitized carbon [LSAC] and MSAC).

- Cathodes with Pt loadings $<0.2 \text{ mg/cm}^2$ (ECSA <50) exhibit BOT performance that is severely impacted due at least in part, to the increased water content in thin catalyst layers. Degraded catalyst layers that reach ECSA values <50 indicate the same performance impact.
- The catalyst Pt/C ratio (30 to 60 wt%) affects the thickness and ECSA of the catalyst layer. While the BOT performance was not impacted by the Pt/C ratio, the degradation was found to be higher for the lower Pt/C ratios.
- A semi-empirical carbon oxidation/corrosion model was used to separate the carbon oxidation and carbon corrosion reaction rates for different catalyst supports.

Future directions include:

- Complete the Pt dissolution molecular dynamics model

- Expand and refine the Micro-structural catalyst and 1D-statistical Unit Cell Degradation Models and validate with experimental AST cycle data.
- Correlate catalyst materials and structural properties with performance and degradation.

FY 2012 Publications/Presentations

1. A. Patel, K. Artyushkova, P. Atanassov, D. Harvey, M. Dutta, V. Colbow, and S. Wessel, “Effect of Graphitic Content on Carbon Supported Catalyst Performance”, presented at 220th ECS Meeting & Electrochemical Energy Summit in Boston, Massachusetts (October 9-14, 2011).
2. A. Patel, K. Artyushkova, P. Atanassov, D. Harvey, M. Dutta, V. Colbow, S. Wessel, “Effect of Graphitic Content on Carbon Supported Catalyst Performance”, ECS Transactions 41 (1), 845-852, 2011.
3. D.B. Harvey, M. Khakbazzaboli, B. Jayasankar, C.C. Chueh, C.A. Bellemare-Davis, J.G. Pharoah, and K. Karan, “Multi-scale Modelling of the PEMFC Catalyst Layer: Coupling Microstructure to Performance”, presented at 220th ECS Meeting & Electrochemical Energy Summit in Boston, Massachusetts (October 9-14, 2011).
4. J. Pharoah, H-W. Choi, C-C Chueh, D. Harvey, “Effective Transport Properties Accounting for Electrochemical Reactions of Proton-Exchange Membrane Fuel Cell Catalyst Layers”, ECS Transactions 41 (1), 221-227, 2011.
5. Silvia Wessel, David Harvey, Vesna Colbow, “Considering the Role of Component Structure on PEM Fuel Cell Durability”, Presented at Zing Hydrogen and Fuel Cells Conference 2011, Xcaret Mexico, December 1 to 5, 2011.
6. S. Wessel, V. Colbow, D. Harvey, S. Knights, “The Effect of Cathode catalyst structure on PEM Fuel cell Durability”, presented at Grove Fuel Cells Conference 2012, Berlin, April 11–12, 2012.

7. A. Patel, K. Artyushkova, P. Atanassov, V. Colbow, M. Dutta, D. Harvey, S. Wessel, “Investigating the Effects of PEMFC Conditions on Carbon Supported Platinum Electrocatalyst Composition and Performance”, J. Vac Sci & Tech, A: Vacuum, Surfaces, and Films 30 (4), 04D107 – 04D107-7, 2012.

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, 2011 revision. <http://www.eere.energy.gov/hydrogenandfuelcells/mypp/>
2. J. Wu, X.Z. Yuan, J.J. Martin, H. Wang, J. Zhang, J. Shen, S. Wu, W. Merida, A Review of PEM Fuel Cell Durability: Degradation Mechanisms and Mitigation Strategies. Journal of Power Sources 184, 104-119.
3. R. Borup, J.P. Meyers, B. Pivovar, Y.S. Kim, R. Mukundan, N. Garland, D. Myers, M. Wilson, F. Garzon, D. Wood, P. Zelenay, K. More, K. Stroh, T. Zawodinski, J. Boncella, J.E. McGarth, M. Inaba, K. Miyatake, M. Hori, K. Ota, Z. Ogumi, S. Miyata, A. Nishikata, Z. Siroma, Y. Uchimoto, K. Yasuda, K. Kimijima, N. Iwashita, Scientific Aspects of Polymer Electrolyte Fuel Cell Durability and Degradation. Chemical Reviews 2007, 107, 3904-3951.
4. Y. Shao, G. Yin, Y. Gao, Understanding and Approaches for the Durability Issues of Pt-Based Catalysts for PEM Fuel Cell. Journal of Power Sources 2007, 171, 558-566.
5. M.S. Wilson, F. Garzon, K.E. Sickafus, S. Gottesfeld, Surface Area Loss of Supported Platinum in Polymer Electrolyte Fuel Cells. Journal of the Electrochemical Society 1993, 140, 2872-2876.
6. P.J. Ferreira, G.J. Ia O', Y. Shao-Horn, D. Morgan, R. Makharia, S. Kocha, H. Gasteiger, Instability of Pt/C Electrocatalysts Membrane Fuel Cells A Mechanistic Investigation. Journal of the Electrochemical Society 2005, 152, A2256-A2271.