V.D.5 Development of Micro-Structural Mitigation Strategies for PEM Fuel Cells: Morphological Simulations and Experimental Approaches

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Project Start Date: January 1, 2010
Project End Date: March 31, 2013

Overall Objectives

- Identify/verify catalyst degradation mechanisms
- Correlate catalyst performance/catalyst structural change as a function of unit cell operational conditions and catalyst layer morphology/composition
- Develop kinetic and material models for catalyst layer aging, i.e., macro-level unit cell degradation model, micro-scale catalyst layer degradation model, and molecular dynamics degradation model of the platinum/carbon/ionomer interface
- Develop durability windows and mitigation strategies for catalyst degradation through modification of operational conditions and component structural morphologies/compositions

Fiscal Year (FY) 2013 Objectives

- Simulate Pt dissolution and transport of Pt species in the ionomer using the developed Molecular Dynamics Model
- Complete the 2-phase flow transient micro-structural catalyst model and simulation of effective properties
- Recode the one-dimensional unit cell performance model in OpenFOAM© and include degradation
- Develop correlations linking the catalyst layer structure with membrane electrode assembly (MEA) performance and degradation
- Develop Durability Windows

Technical Barriers

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

(A) Durability (of the Pt catalyst and Pt cathode catalyst layer)

(B) Performance

(C) Cost (indirect)

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 H_2/N_2
  - Effective catalyst surface area (ECSA) loss <40%
  - Platinum-grade metal total loading: 0.125 mg/cm^2

FY 2013 Accomplishments

- Identified the preferred Pt dissolution site on a Pt crystal anchored on a carbon surface and extracted the transport/diffusion rates of Pt species in the ionomer
- Predicted the local distribution of effective properties and identified oxygen "storage" aspects of ionomeric films through transient micro-structural catalyst model simulations
- Developed a Pt dissolution model for mixed Pt oxide formation from water and air for performance and degradation prediction
- Built the Unit Cell Model in an open-source platform that allows for continued improvement of the model in the public domain.
- Developed correlations of beginning of test (BOT) and end of test (EOT) performance loss breakdown with cathode catalyst layer composition, morphology, material properties, and operational conditions
- Identified design windows and parameters which are key MEA design levers
- Identified a design flow path of interactions from materials properties and catalyst layer effective properties to performance loss breakdown for conditioned and degraded catalyst layers

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INTRODUCTION

Catalyst/catalyst layer degradation has been identified as a substantial contributor to fuel cell performance degradation and this contribution is expected to increase as MEAs are driven to lower Pt loadings in order to meet the cost targets for full-scale commercialization. Prior to the start of this project significant progress was 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 existed. 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 was an area not well understood. In order to close these gaps, this project focused on understanding of the effect of operating conditions and cathode catalyst layer structure and composition on catalyst degradation mechanisms and degradation rates.

The project objective was 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 as a function of key operational and structural parameters.

APPROACH

Models have been 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 provide the ability to study the effects of composition, the morphological design, and the operational window on catalyst degradation via simulated accelerated stress testing. The design curves generated in each scale of the modeling work 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 have been 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 also served to provide model validation.

RESULTS

Model Development

Efforts within this fiscal year were focussed on the open-source integration into OpenFOAM©, development of the graphical user interface, the completion of work on the platinum oxide model, and the investigation of the effect of platinum loading mass transport limitations in the microstructural catalyst model.

In order to simulate platinum dissolution and plating, a platinum oxide model capable of predicting the oxide coverage under air and hydrated conditions was required. As noted previously, literature models for the prediction of oxides under air and hydrated conditions were readily available, but were only validated for voltages below the equilibrium open-circuit voltage (OCV) potential of the cell. Upon investigation it was found that these models were not capable of capturing the growth of oxides on the platinum surface for potentials above the OCV. A re-derivation and modification of the existing models was undertaken such that key changes were made in the behavior of oxide growth and the description for the availability of active platinum sites. The modified and improved oxide model (Figure 1B) shows substantially better predictive capability as compared to the original (Figure 1A) model. In particular, the ability of the model to capture the oxidation peak has been dramatically improved while the reduction peak still shows some room for improvement around the location of the onset

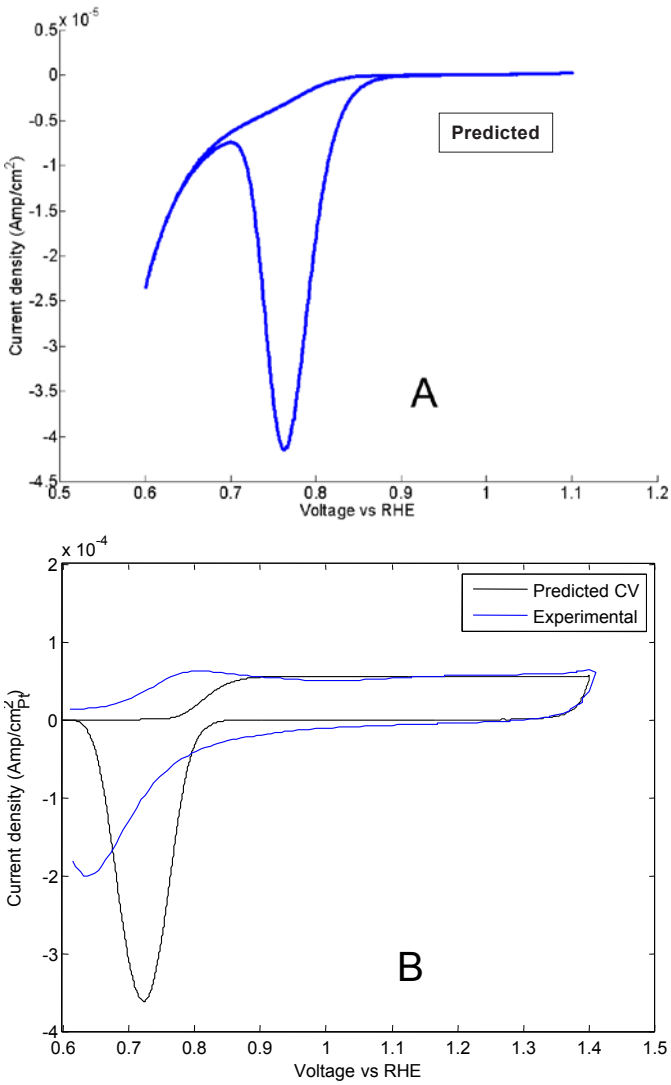

FIGURE 1. Cyclic voltammogram predictions using (A) the literature Pt-oxide model and (B) a re-derived, modified Pt-oxide model.

potential. Coupling the modified Pt oxide model to transport and oxygen reduction reaction kinetic parameters in the integrated MEA Degradation Model will properly capture the performance in the operating range of the fuel cell.

The effect of platinum loading was studied in the micro-structural model by systematically increasing the overall loading and probing the specific transport phenomena within the catalyst morphology. In each case the local Knudsen effects (Figure 2A) were accounted for, in addition to transport across and within the ionomeric films. It was found that the oxygen concentration dropped substantially as a function of the increased catalyst layer thickness (Figure 2B) such that gas phase transport worsens as the thickness increases. The effect of this thickness change is contrary to what is seen in regards to the polarization predictions (Figure 2C) in which there are additional losses related to the gas phase transport. These polarization curves show a distinct loss due to a reduction in platinum surface area, but the loss of this area also incurs a secondary effect related to the interfacial areas between ionomer and platinum. This change in the interfacial area produces an effect which can be described via a shape factor correction in the local diffusion and resulting concentration (Figure 2D). This shape factor is a predicted plot from the microstructural simulations and shows clearly that the localized species transport resistance increases significantly as the platinum loading is reduced.

The open-source model integration has been completed in OpenFOAM© and will be fully released as the FC-PEM Simulation Package. The model has been implemented in a flexible dimensional format such that one-, two-, and three-dimensional simulations are possible. Further, the package has a graphical user interface in order to manage case files, runs, and modification of various required user input data. The model uses front end mesh generators, calculation packages, and post-processing that is freely available in the open-source domain.

Experimental Parametric Studies

Efforts within this fiscal year were focused on developing (1) correlations that link MEA performance and degradation to catalyst layer composition, structure, component properties, and effective properties and (2) design windows. The overall motivation was to identify parameters which are key levers for the MEA designer, and that would allow the catalyst manufacturer to optimize catalyst parameters for enhanced MEA performance and durability. Figure 3A shows the approach taken in linking the catalyst carbon support and catalyst powder structure to the catalyst layer structure, effective properties, and performance of the MEA. This approach addresses both BOT and EOT performance; the latter being captured via changes in the catalyst layer structure and effective properties with degradation. The detailed interactions of the different measurables is shown on Figure 3B. While most of the parameters were quantified (green boxes), the yellow and pale blue colors highlight the gaps in quantification methods, and these are subsequently calculated by the Unit Cell Model.

The reaction distribution in the catalyst layer is affected through balancing of the different over-potentials in order to minimize the total polarization losses. Thus, changes to one catalyst layer property can have an affect on each of the different over-potentials that are inherent in the polarization characteristics. For example, mass transport limitations, caused by reduced diffusivity or increased catalyst layer thickness, will reduce the local oxygen concentration at the catalyst surface causing an increase in kinetic losses. This results in a shift of the reaction distribution in the catalyst layer to access more oxygen, thus causing a reduction in mass transport losses and an associated increase in catalyst layer ionic loss. Similarly, proton conductivity, intrinsic kinetic

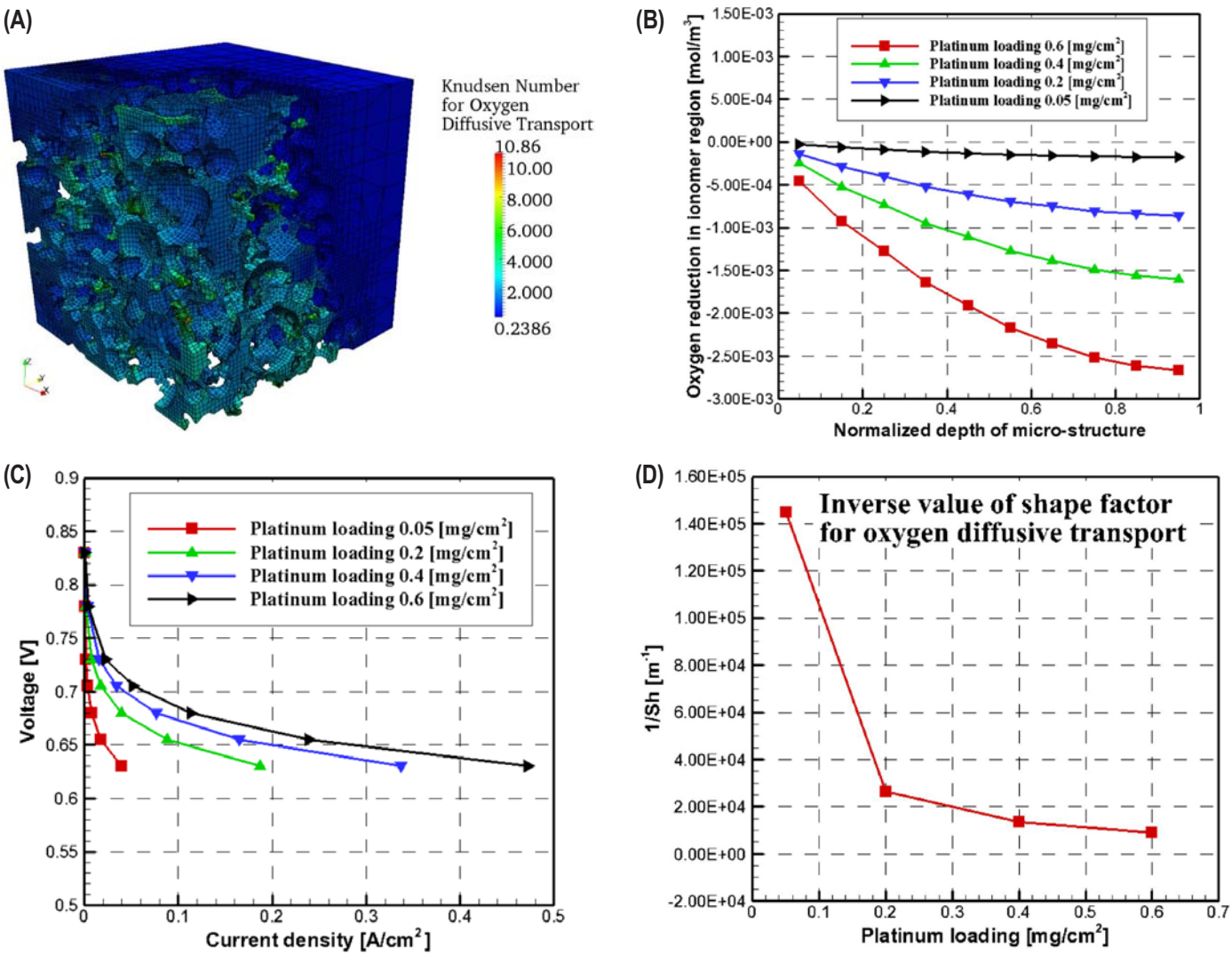

FIGURE 2. (A) Knudsen number for a catalyst morphology; platinum loading effect on (B) oxygen transport normalized depth profile, (C) catalyst polarization, and (D) the effective shape factor for oxygen transport.

activity, and catalyst surface area can also affect the reaction distribution and polarization losses. An example of the effect of catalyst layer thickness is shown in Figure 4.

While an increase in catalyst layer thickness affects mass transport losses due to oxygen depletion effects, catalyst layer ionic loss, caused by an increase in ionic resistance, was observed to be the dominant loss mechanism (Figure 4a). In this example, the Pt loading was held constant, and the thickness increase was due to a lower Pt/C ratio within the catalyst layer. For the thicker catalyst layers the current distribution is forced further into the catalyst layer to access the same amount of ECSA as the thinner catalyst layer. As a result, the thicker catalyst layer exhibits a higher ionic loss. With degradation (Figure 4A), the catalyst layer ionic loss increases due to Pt depletion at the membrane/catalyst interface (Figure 4C) which shifts the reaction penetration further into the catalyst layer. An effective thickness (Figure 4B) calculated from the catalyst layer ionic losses and the ionic resistivity shows that the increase in effective thickness (reaction penetration) agrees with the thickness of the Pt depleted region (~3 μm Pt depletion for the 9 μm layer and 6-8 μm Pt depletion for the 31 μm layer).

Durability windows were developed for both the catalyst layer structural design levers and operational conditions. Table 1 summarizes the time at the upper AST potential to reach 15% performance loss at a current density of 1.0 A/cm^2 for a variety of operational parameters. As shown before, the impact of the upper potential limit is most severe; under 100% relative humidity (RH) conditions, the operational time is increased ~34 times by reducing the upper potential limit from 1.4 V to 1.0 V. The effect of temperature is less severe and in fact at lower potentials (≤1.2 V) when Pt dissolution is the dominant degradation mechanism, the effect of temperature in the range from 60 to 90°C is

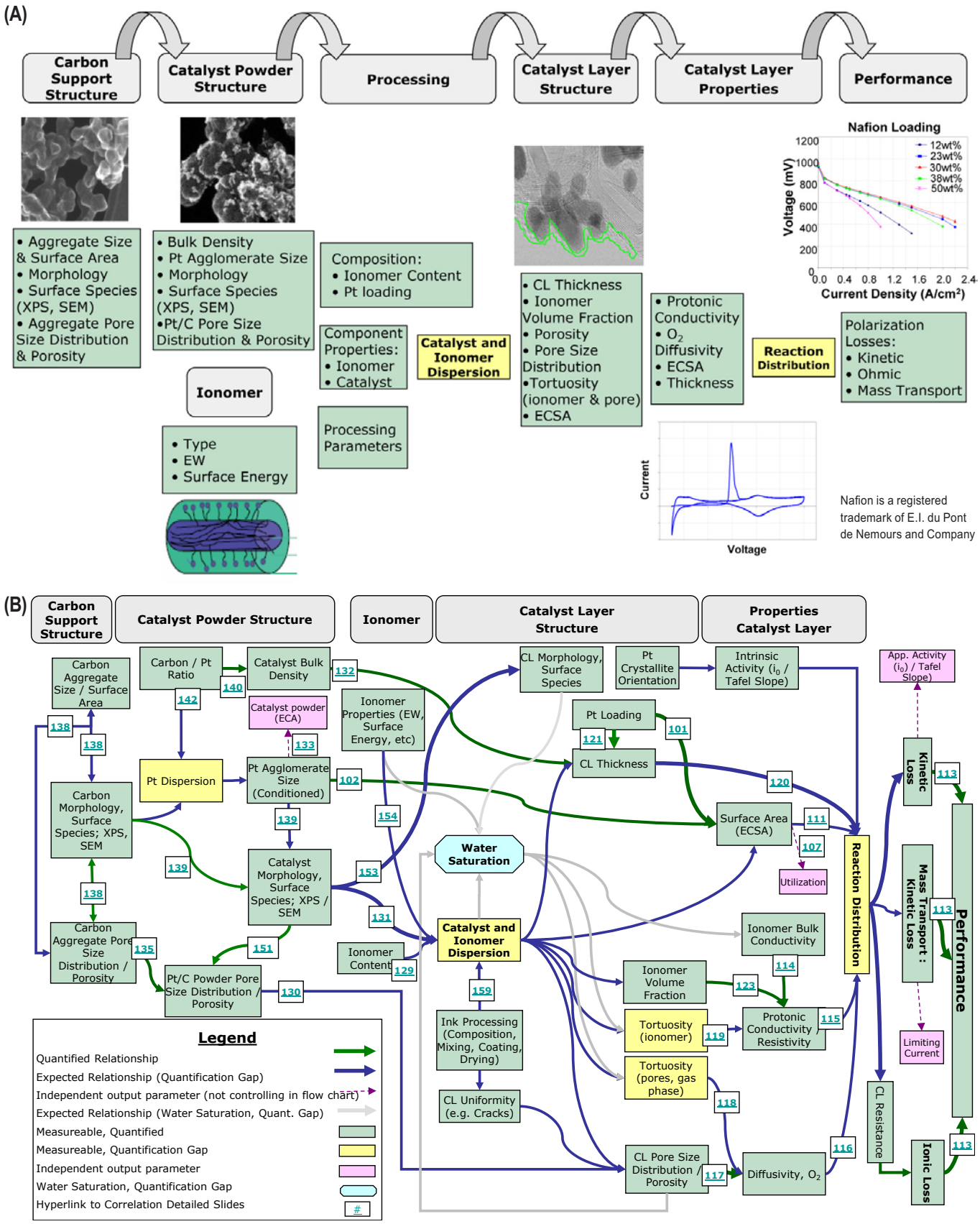

FIGURE 3. (A) Correlations approach flow chart. (B) Interactions and linkage of catalyst layer component characteristics, catalyst layer composition, structure, and effective properties and performance.

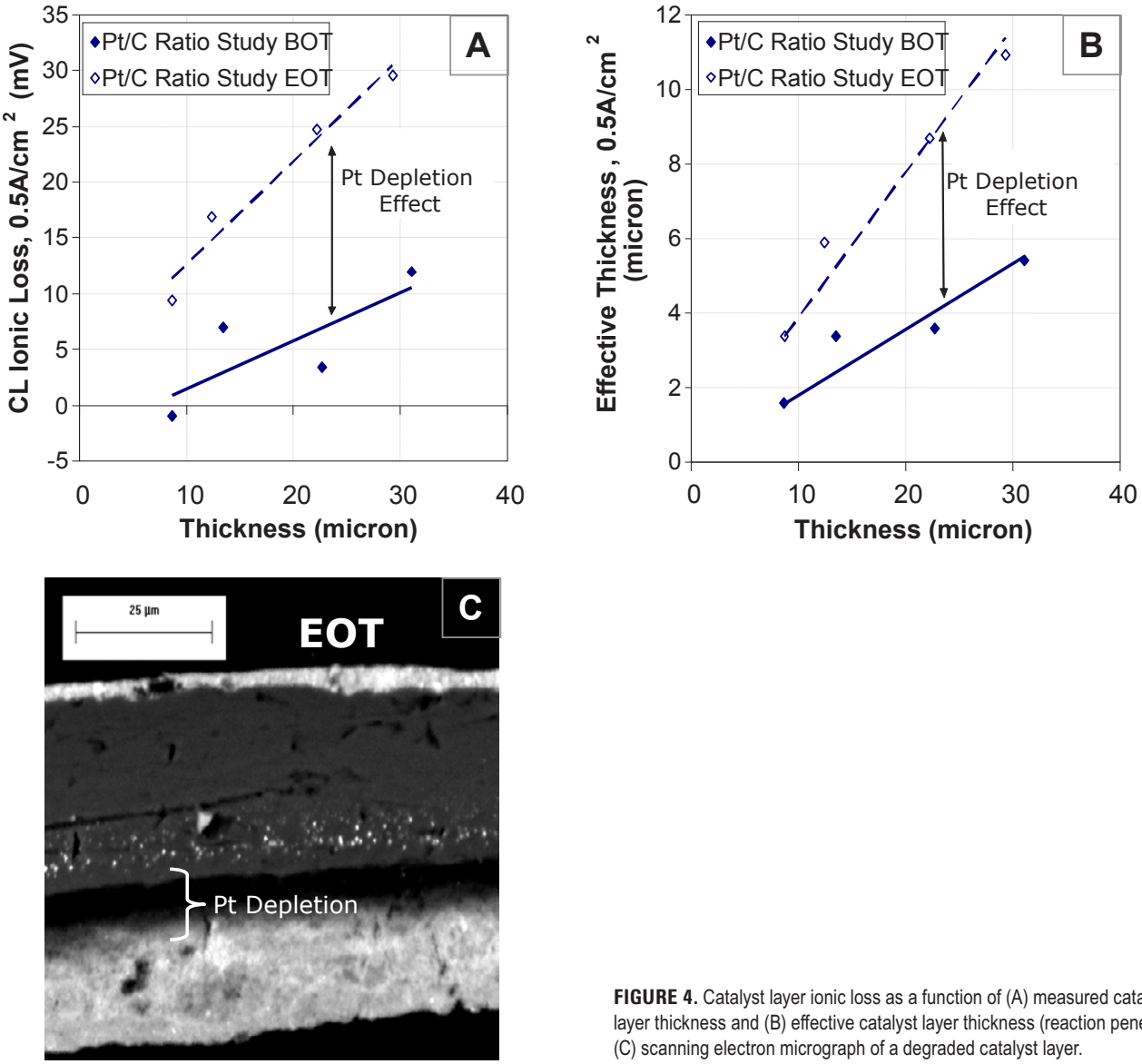

FIGURE 4. Catalyst layer ionic loss as a function of (A) measured catalyst layer thickness and (B) effective catalyst layer thickness (reaction penetration), (C) scanning electron micrograph of a degraded catalyst layer.

TABLE 1. Operational Durability Windows for the Baseline MEA (Pt50LSAC, 0.4 mg/cm^2 cathode loading)

Operational Parameter	Lower Level	Lower Level Time to 15% Performance Loss	Upper Level	Upper Level Time to 15% Performance Loss
UPL (100% RH, 80°C)	1.0 V	243 hours	1.4 V	7 hours
Temperature (100% RH, 1.4 V UPL)	60°C	46 hours	90°C	2.5 hours
Temperature (50% RH, 1.4 V UPL)	60°C	70 hours	90°C	5 hours
RH, cathode (1.4 V UPL, 80°C)	60% RH	11 hours	100% RH	8 hours
RH, cathode (1.2 V UPL, 80°C)	60% RH	1,500 hours	100% RH	200 hours

UPL - upper potential limit

insignificant. However, carbon corrosion is substantially affected by temperature and at an upper potential limit of 1.4 V, an increase in temperature from 60 to 90°C reduces the operational time ~18 times at 100% RH and 14% at 50% RH. Furthermore, changing the RH from 100% to 50% at constant temperature will approximately double the operational time to reach 15% performance loss. The effect of RH was found to be more significant for the Pt dissolution mechanism; a 7.5x increase in time to 15% voltage loss can be achieved by reducing the cathode RH from 100% to 60%.

CONCLUSIONS

The overall conclusions are:

- The lower corner and lower edge Pt atoms at the carbon interface were found to be the least stable and as such most likely to dissolve.
- The diffusion rates for PtO_2 and $Pt(OH)_2$ species were found to be very similar due to their similar size (activation energy of diffusion: -13 kJ/mol for $Pt(OH)_2$, -11 kJ/mol for PtO_2.
- Oxygen dissolution modeled within the catalyst structure showed that the ionomer films tend to be thin with little resistance.
- The effect of catalyst layer composition on local conditions is observed through the variation in transport parameters, with decreasing platinum loading, the transport resistance increases due to an increased 'localized' current demand and reduced ionomeric contact area.
- The correlations between materials properties, composition, structure, and effective properties of cathode components show similar trends for BOT and EOT MEAs.
- Design windows reveal durability acceleration factors for various operational conditions.

Overall, this work has provided significant advancements in the ability to model and design durable fuel cell products and to understand the role of catalyst layer morphology and structure on the durability of the MEA. The outcome of this project is subsequently assisting in reducing the iterative design/test cycle process for next generation fuel cell products via model simulations.

FY 2013 PUBLICATIONS/PRESENTATIONS

1. G. Brunello, J.I. Choi, S.S Jang, "Multi-scale First Principle Modeling of Three-Phase System of Polymer Electrolyte membrane Fuel cell", submitted abstract 222nd ECS Meeting, Honolulu, Hawai'i, October 7–12, 2012.

2. G. Brunello, J.I. Choi, S.S Jang, "Density Funcional Theory Study and Model development on Pt-Nano-particles", submitted abstract 222nd ECS Meeting, Honolulu, Hawai'i, October 7–12, 2012.

3. G. Brunello, J.I. Choi, S.S Jang, "Density Functional Theory Study of Pt Dissolution at Water-Pt Interface", submitted abstract 222nd ECS Meeting, Honolulu, Hawai'i, October 7–12, 2012.

4. V. Colbow, M. Dutta, A. Young, Z. Ahmad, D. Harvey, S. Wessel, "Performance Degradation and Structural Changes with Pt Cathode Catalyst layer Design", submitted abstract 222nd ECS Meeting, Honolulu, Hawai'i, October 7–12, 2012.

5. D.Harvey, A. Bellemare-Davis,K. Kunal, B. Jayansankar, J. Pharoah, V. Colbow, A. Young, S. Wessel, "Statistical Simulation of the Performance Degradation of a PEMFC Electrode Assembly" submitted abstract 222nd ECS Meeting, Honolulu, Hawai'i, October 7–12, 2012.

6. K. Artyushkova, P. Atanassov, M. Dutta, V. Colbow, S. Wessel, "Ex-situ Characterization of Degradation Mechanism of MEAs by iImaging XPS and SEM", submitted abstract 222nd ECS Meeting, Honolulu, Hawai'i, October 7–12, 2012

7. S.A. Stacy, J.S. Allen, Percolation in Catalyst Layer of PEMFC", submitted abstract 222nd ECS Meeting, Honolulu, Hawai'i, October 7–12, 2012.

8. R. Shahbazian-Yassar, "Membrane Electrode Assembly Degradation in Proton Exchange Membrane Fuel Cells: A View From Nanoscale", International Conferences of Young Researchers on Advanced Materials, July 1–6, 2012, Singapore.

9. M. Khakaz-Baboli, D.A. Harvey, J.G.Pharoah, "Investigating the performance of catalyst layer micro-structures with different platinum loadings", submitted abstract 222nd ECS Meeting, Honolulu, Hawai'i, October 7–12, 2012.

10. S. Wessel, V.Colbow, M. Dutta, A. Young, D. Harvey, "The impact of Materials Properties and Cathode Catalyst Structure/ Composition on MEA Performance and Durability", Hydrogen and Fuel Cells 2013, Vancouver B.C., June 16–19, 2013.

11. D. Harvey, A. Bellemare-Davis, B. Jayasankar, K. Karan, J. Pharoah, A. Young, M. Dutta, V. Colbow, S. Wessel, "Simulation of the ORR Multi-pathway and Catalyst Dissolution for a PEMFC: The Effect of Surface Coverage and AST cycling", Hydrogen and Fuel Cells 2013, Vancouver B.C.,June 16–19, 2013.

12. S. Wessel, "Water management in Low Temperature PEM Fuel Cells, Industrieworkshop: Wassermanagement in PEM-Brennstoffzellen, Freiburg (Germany), 31 January 2013.

13. K. Artyushkova, P. Atanassov, M. Dutta, D. Harvey, V. Colbow, and S. Wessel, "Structural Correlations: Design Levers for Performance and Durability of Catalyst Layers" submitted abstract 224th ECS Meeting, San Francisco, CA, October 27 – November 1, 2013.

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