

V.E.4 Open-Source PEMFC-Performance and Durability Model Consideration of Membrane Properties on Cathode Degradation

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Contract Number: DE-EE0006375

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Project Start Date: January 1, 2014
Project End Date: October 31, 2014

- Assess the membrane sub-model within FC-APOLLO and compare with assessment of to-be-implemented sub-model.
- Integrate the 'new' membrane sub-model into FC-APOLLO

Technical Barriers

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

(A) Durability

Pt catalyst and Pt catalyst layer degradation

- Effect of cathode structure and composition
- Effect of operational conditions

(B) Performance

- Effect of cathode catalyst structure and composition

(C) Cost

Technical Targets

In this project, fundamental studies of the Pt/carbon catalyst degradation mechanisms and degradation rates are conducted and correlated with membrane transport properties and operational conditions. The fundamental studies are used to facilitate the development and refinement of membrane model implementation within the open-source software FC-APOLLO. Furthermore, the 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
 - Electrochemical surface area (ECSA) loss: <40%
 - Pt group metal total loading: 0.125 mg /cm²

Overall Objective

Develop open-source, forward predictive models and conduct systematic cell degradation studies.

Fiscal Year (FY) 2014 Objectives

- Complete down selection of membrane types for analysis
- Measure and report material properties for down-selected membranes
- Evaluate beginning of test (BOT) performance and accelerated stress test (AST) behavior for down-selected membranes
- Evaluate BOT performance and AST behavior for membrane-AST-degraded membrane electrode assemblies (MEAs)

FY 2014 Accomplishments

- Completed down selection of membranes, with inclusion for perfluorinated sulfonic acid (PFSA), reinforced-PFSA, and hydrocarbon-based materials
- Reported on BOT performance and cathode catalyst AST testing for MEAs with the down-selected membrane materials
- Generated data for membrane-AST degraded MEAs for BOT performance and cathode catalyst AST testing
- Completed assessment of to-be-implemented sub-model and respective material relationship and predictions



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/neighbor components, 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 the membrane properties on the local conditions within the catalyst layer and the subsequent manifestation of those local conditions on performance and durability, in particular the catalyst layer degradation mechanisms and degradation rates, is needed.

The focus of this project is to develop open-source, forward predictive models and conduct systematic cell degradation studies that enable quantification of the cathode catalyst layer degradation mechanisms and rates and to correlate those rates and the degradation-derived changes in catalyst properties/composition to the materials properties of the chosen membranes.

APPROACH

This project addresses the performance and durability of Pt catalysts and catalyst layers which have been identified as key technical barriers in the DOE Fuel Cell Technologies Office Multi-Year Research, Development, and

Demonstration Plan. The project follows a parallel three-path approach of (1) theoretical simulations, (2) experimental investigations, and (3) material/component characterization (collaborative work) with the overall goal to advance the ability to simulate and design durable fuel cell products and subsequently reduce the iterative design/test cycle process for next generation fuel cell products.

The approach of the project includes: (1) Refinement of the membrane model that is an integral part of FC-APOLLO in order to describe changes in transport properties as a function of the change in membrane type (material characteristics); (2) Experimental assessment of the impact of membrane type, transport and materials properties on the MEA performance loss mechanisms and the Pt dissolution mechanism/rate; (3) Development of correlations that link membrane materials properties and catalyst layer effective properties to MEA/cathode performance and degradation loss mechanisms.

RESULTS

Model Development

During the first FY the review of the membrane models was the first step completed in order to facilitate integration into FC-APOLLO. To this end, several models within the literature were reviewed and partially implemented in a simplified framework in order to access the relational behavior of the parameters. Based on these reviews it was found that the existing membrane sub-models within the literature pose several challenges for use in unit-cell modelling. Many of the membrane sub-models are steady state and do not adequately describe the rate of exchange between liquid and vapor phases. Furthermore, many of the existing models contain parameters which are difficult, if not impossible, to measure quantitatively; for example, thermodynamic arguments like pressure and concentration are not compatible within a fixed-proton conducting polymer electrolyte and the surface activities which are generally defined by either pressure for gases or concentration for liquids, are not captured when both occur at the same time.

While physics-based membrane models do exist in the literature, the inherent coefficients are generally not measurable [7]; thus, in order to validate the model the coefficients need to be related to membrane properties that can be physically quantified. We have started to adapt the steady-state model proposed by Weber and Newman [8] with the intent to generate a general transient, three-dimensional implementation in the context of a unit cell. As shown in Figure 1, the module attempts to encode physics for the known transport processes taking place in the membrane as adapted by the work published by Weber and Newman. This module applies an inner iteration process to determine the state of the membrane (i.e. proton conductivity, diffusivity,

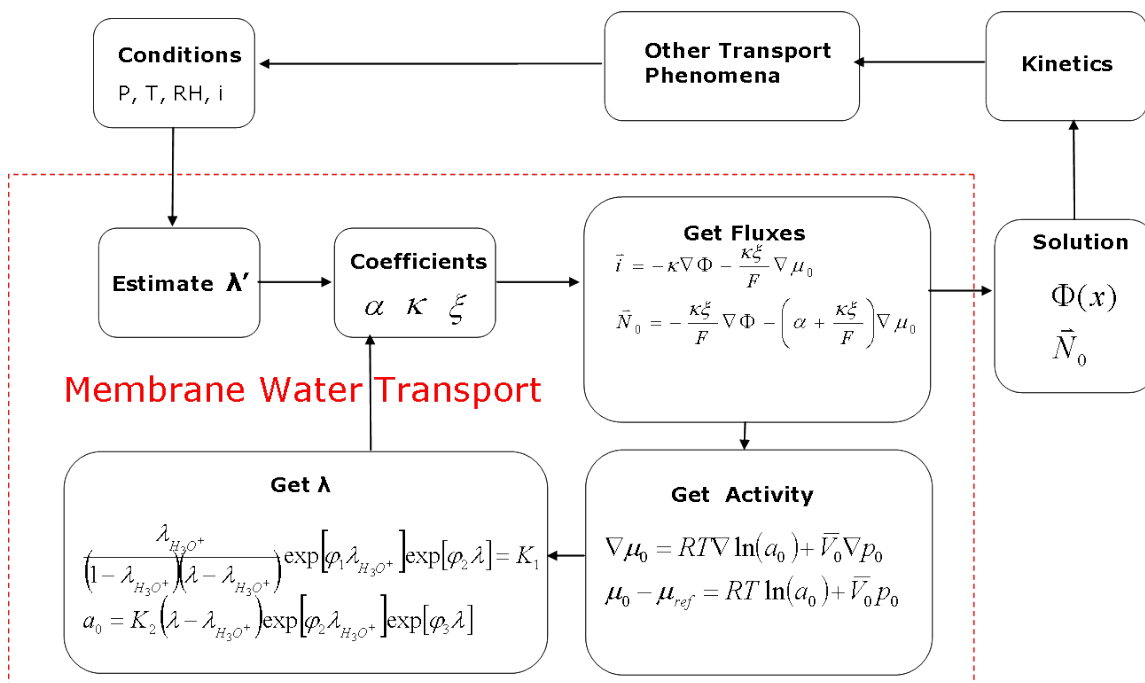


FIGURE 1. Membrane Water Modeling Approach

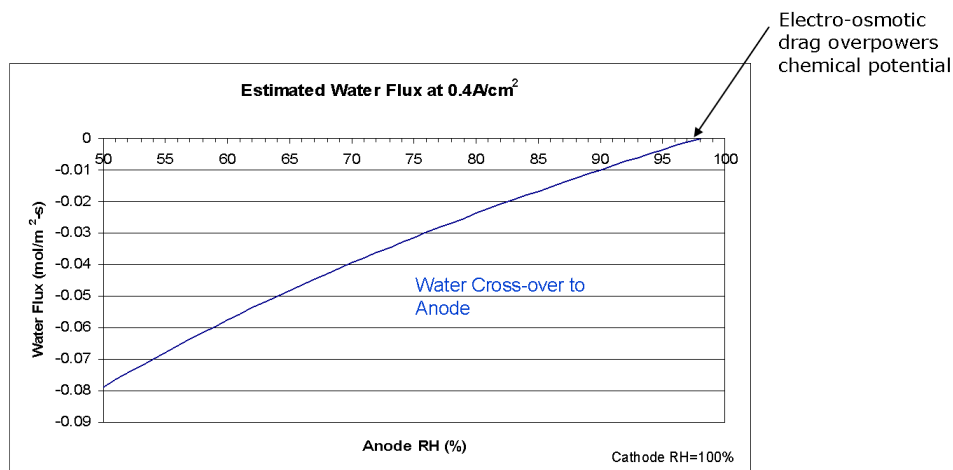


FIGURE 2. Simulated Water Flux

etc.) and an outer iteration to determine the solved variables (i.e. potential and fluxes) that external models, such as those for the oxygen reduction reaction kinetics, require.

An initial test to check the response of the numerical system and ensure that it behaved as expected is shown in Figure 2. In this test a current density of 0.4 A/cm² was applied at the membrane boundary with the water flux through the membrane determined as a function of anode relative humidity (RH), while the cathode RH was held constant. As expected, the current drove an electro osmotic flux which affected the net water flux to the anode

as indicated by the adjusted “zero” water flux conditions occurring increasingly towards a lower anode RH.

Experimental Parametric Studies

Experimental testing and characterization within this FY was conducted on the following types of membranes Nafion[®]211 (baseline membrane), Nafion[®]212 (optional), experimental reinforced PFSA membranes with low and high equivalent weights (EWs), and reinforced partially fluorinated hydrocarbon membranes of high and low EWs. The intention of the testing in the project is to develop

characterization and validation data for the simulation and modelling work and to generate datasets that can be used to correlate MEA performance and durability to membrane properties and key transport parameters.

A table of key membrane properties/characteristics was extracted (Table 1) based on the theory/relationships of previous/existing/and to-be-implemented models and this was used to guide the selection of experimental tests that are being conducted within the characterization component of the project.

In addition to the characterization of the membranes for the properties shown in Table 1, in-cell testing consisting of steady-state polarizations, a membrane AST and a cathode catalyst AST are used to elucidate differences and effects due to the use of different membrane materials and the associated effects on the cathode catalyst layer local conditions. The baseline MEA, the test hardware, the cathode AST, and suite of diagnostic tools are described in detail in the previous project documentation.

The BOT performance results for the MEAs with three different membranes at relative humidities of 60% and 100% are shown in Figure 3. We see that each of the MEAs has similar performance at current densities less than 1 A/cm². However, at current densities greater than 1 A/cm² the baseline membrane exhibits larger performance losses than the other PFSA materials. At 2 A/cm² and 100% RH a performance loss of as much as 80 mV emerges between the baseline membrane and the low EW PFSA membrane materials. The performance difference can be explained in part due to variations in the thickness of the membrane materials as the baseline material is the thickest of the three shown, while the differences seen at low RH are likely a

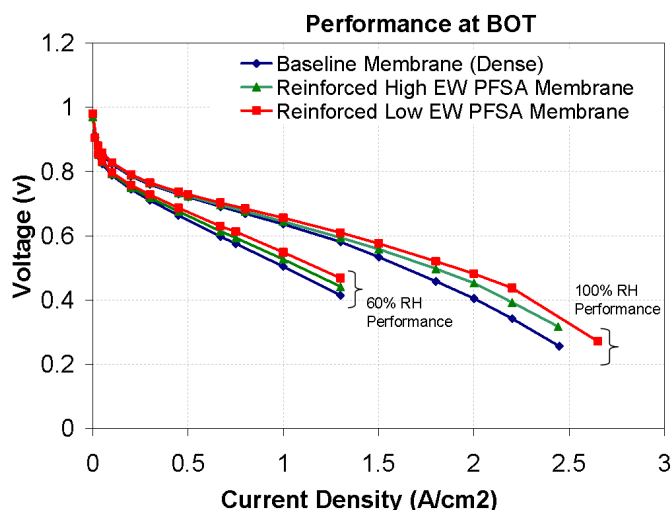


FIGURE 3. BOT Performance of MEAs with Different Membranes

more complex mix of the water transport, water content, EW, and thickness.

After the BOT performance benchmark, the MEAs were subjected to a cathode AST for 4,700 cycles. As seen in Figure 4(a), the performance throughout the current density range is very similar for the three membranes. Figure 4(b) shows that the ECSA losses are systematically offset between the different membranes and this offset appears to potentially be a function of the equivalent weight. There are also higher voltage losses for the high EW PFSA membrane MEA compared to the baseline MEA, with a loss of ~90 mV vs. 60 mV at 2 A/cm². It is also of note that the low RH performance is further depressed for the low EW PFSA membrane compared to the other membranes, again

TABLE 1. Membrane Properties for Model Inputs

Membrane Properties	versus	Required	Optional
Ion Exchange Capacity (EW)		x	
Density	dry, RH	dry	RH
Thickness	dry, RH	dry, RH	
Water Uptake/Content	T, RH, EW, time (rate of from dry state)	RH, time	T, EW
Proton Conductivity	T, RH, time (rate of from dry state)	RH, time	T, EW
O ₂ , H ₂ Gas/Dissolved Gas Diffusivity	dry, T, RH, EW		T, RH, EW
O ₂ , H ₂ Solubility	T, RH, EW		T, RH, EW
PtOH solubility/Diffusivity	T, RH, EW		T, RH, EW
Reactant Cross-over	T, RH	T, RH, system pressure	EW
Water flux (Constant System Pressure Anode/Cathode)	T, RH, EW, Pressure (cathode/anode)	RH, T, Pressure	EW
Water Permeation (Differential Pressure Anode/Cathode)	V/V, V/L, L/V, L/L		V/V, V/L, L/V, L/L
Thermal Relaxation			x
Interfacial Ionic Resistance (Between Ionomeric Materials)	T, RH, EW		RH, T, EW

RH calculated from P_{total}, P_{H₂O}, T

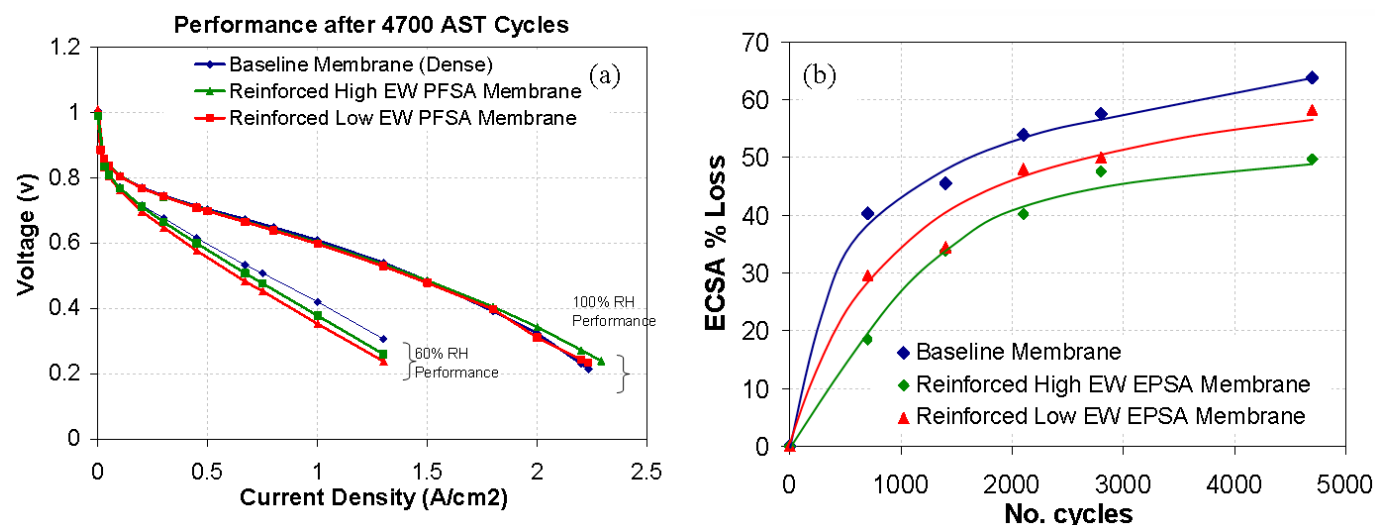


FIGURE 4. MEAs Containing Different Membranes after Exposure to Cathode AST, (a) EOT Performance, (b) ECSA Loss

indicating the potentially higher water content in the low EW PFSA membrane appears to be interacting with the catalyst layer degradation.

CONCLUSIONS AND FUTURE DIRECTIONS

The interim conclusions are:

- Platinum surface area losses appear to be affected by the EW of the membrane; this will be further explored within the project based on a set of theory in which the local solvation of the platinum complexes within the membrane are dependent on EW and may yield an increase or decrease in the amount of platinum complexes local to the catalyst thus affecting the driving force for the platinum dissolution reaction.
- Based on the results to date, the choice of membrane material results in differences in water-crossover and, subsequently, the local conditions around the platinum sites in the cathode catalyst layer. ECSA differences are observed over the course of AST cycling, however, the overall performance differences are not as large as was expected. This is due in part to a result that was observed from our previous project, in that the correlation between ECSA and cell performance showed a non-linear drop in performance which occurred for ECSA at ~ 80 or less. As a result, the current results and their impact on degraded performance are expected to be much more influential on lower loaded cathode catalyst layer designs, dependent on the membrane type used.

Future directions include:

- Complete implementation/revision of the “improved” membrane transport sub-model in FC-APOLLO

- Extend the Pt dissolution model to include coupling to address the water content effect and pH effect of different membranes
- Complete validation of FC-APOLLO with experimental data for the sub-model and cell performance/AST data
- Complete the membrane AST degraded, cathode catalyst AST testing for the various membranes
- Tabulate characterization data for membrane properties based on ex situ/in situ testing and compare to existing theory
- Release revised FC-APOLLO model to www.sourceforge.net/projects/fcapollo
- Develop design curves for catalyst degradation rates and catalyst changes to membrane transport properties

REFERENCES

- 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/>
- 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.
- 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.
7. G.J.M. Janssen. "A phenomenological model of water transport in a proton exchange membrane fuel cell", *ECS* 148 (12) A1313-A1323 (2001).
8. Weber, A.Z. & J. Newman. "Transport in Polymer-Electrolyte Membranes II. Mathematical Model". *ECS* 151 (2) A311-A325 (2004).