V.E.5 Open Source FCPEM-Performance and Durability Model: Consideration of Membrane Properties on Cathode Degradation

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Overall Objective

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

Fiscal Year (FY) 2015 Objectives

• Complete membrane sub-model development, integration, and validation within Fuel Cell Application Package for Open-source Long-Life Operation (FC-APOLLO)

• Complete open source model hosting for FC-APOLLO

• Complete data analysis for beginning of test (BOT), accelerated stress test (AST), and end of test (EOT) behavior of membranes/membrane electrode assemblies (MEAs)

• Dissemination of data via final report

Technical Barriers

This project addresses the following technical barriers from the Fuel Cell Technologies Office (FCTO) Multi-Year Research, Development, and Demonstration (MYRDD) 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 (indirect)

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 h

   – Stationary applications (1–10 kW$_e$): 60,000 h

• Electrocatalyst (transportation applications)

   – Support stability: <10% mass activity loss after 400 h at 1.2 V in H_2/N_2

   – Electrochemical surface area (ECSA) loss <40%

   – Precious group metal total loading: 0.125 mg/cm^2

FY 2015 Accomplishments

• Completed testing of membrane AST degraded MEAs

• Developed correlations for various behaviors of degraded MEAs and related diagnostics

• Completed hosting and release of the first versions of the open source code, FC-APOLLO

• Revised membrane sub-model and completed first validation against experimental data

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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 [1,2] 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 still exist with respect to catalyst layer degradation and an understanding of its driving mechanisms. In particular, acceleration of the mechanisms under different fuel cell operating conditions, due to different structural compositions/neighboring 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 is needed 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 rates.

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 FCTO MYRDD Plan [1]. 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; and (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 previous fiscal years a review of existing membrane sub-models and initial implementation was completed in order to down-select, evaluate, and initiate the full development of the membrane sub-model within the FC-APOLLO framework. The relational behavior of several models was evaluated in order to assess the ability to capture and/or predict various trends observed in the experimental data and it was found that the existing membrane sub-models within literature have several short comings in the ability to predict the behaviors observed in various aspects of the experimental data. In particular, many of the membrane sub-models are not implemented in a transient framework and do not adequately describe the rate of exchange between liquid and vapor phases; furthermore, many of the existing models contain parameters that are not tractable to determine, neither analytically nor from an ex situ or in situ experimental basis. Various forms of physics based membrane models do exist within the open literature; however, key coefficients that describe or control the behavior of the materials are generally not measurable or are unknown [7]. This project has adapted the work of Weber and Newman [8] as a starting point for a steady state implementation of the membrane sub-model and work in the last fiscal year has focused on the extension to a general transient, three-dimensional implementation in the context of a unit cell. Figure 1 shows the general schematic of the operating modes that the model captures and the interfacial resistance that exists related to the adsorption/desorption processes that occur at the interface of the ionomeric membrane and porous electrode. The implemented module attempts to capture the observations at steady state and, additionally, the time dependent behavior due to shifts in the chemical potential or state of water in either of the electrode regions over the course of operation. To date, initial implementation of the sub-model framework has been completed and the focus of the ongoing work continues to remain on the development of the interfacial resistance terms in such a way as to continue to capture the steady state
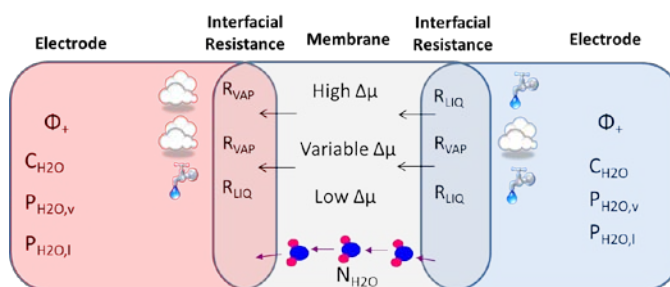
FIGURE 1. Water cross-over transport scenarios for the improved transient sub-model

behavior but additionally provide an explanation/capture the observed transient related effects relevant to AST cycling.

Experimental Parametric Studies

Experimental testing, characterization, and data analysis for the BOT, catalyst AST cycled, and membrane AST/ catalyst AST cycled was completed within this fiscal year. The project focused on the following types of membranes: Nafion® 211 (baseline membrane), Nafion® 212 (optional), experimental reinforced perfluorinated sulfonic acid (PFSA) membranes with low and high equivalent weights (EWs), and experimental reinforced partially fluorinated hydrocarbon (R-HFC) membranes of high and low EW. The intention of the testing in the project is to develop characterization and validation data for the simulation and modelling work and to generate data sets that can be used to correlate MEA performance and durability to membrane properties and key transport parameters.

A table of membrane properties/characteristics for the membranes considered in this project is shown in Table 1. Based on the theory/relationships of previous, existing, and to-be-implemented models, the membranes in Table 1 were characterized for behavior and properties related to water transport, uptake, and adsorption/desorption. The characterization of the membranes shown in Table 1 consisted of in-cell and ex situ testing including steady state polarizations, a membrane AST, a cathode catalyst AST, dynamic vapor sorption, and electrochemical impedance spectroscopy in order 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 previous project documentation.

TABLE 1. Properties of Examined Membrane Properties for Model Inputs

| Membrane	Acronym Used	EW (g/mol SA)	Density (g/mL)	Dry Thickness (µm)
Baseline: Nafion® NR211	NR211	1,099	2.0	25
Nafion® NR212	NR212	1,099	2.0	50
Reinforced PFSA High EW	R-PFSA-HEW	1,136	2.0	18
Reinforced PFSA Low EW	R-PFSA-LEW	872	2.0	14
Partially Fluorinated Hydrocarbon High EW	R-HFC-HEW	758	1.8	15
Partially Fluorinated Hydrocarbon Low EW	R-HFC-LEW	625	1.8	13

SA – sulfonic acid

In order to establish the effect of the catalyst AST and the combination of the membrane AST (pre-degraded membrane) and subsequent catalyst AST, a BOT performance was established. This test was done for MEAs with the different down-selected membranes at relative humidity (RH) of 60% and 100% and is shown in Figure 2. We see that each of the MEAs has in situ performance greater than 600 mV at current densities less than 1 A/cm^2. At 100% RH the R-PFSA-LEW MEA had similar performance as the baseline NR211 membrane. Lower performance was observed for the R-PFSA-HEW and NR212 MEAs consistent with the increased membrane thickness as compared to the performance of the R-PFSA-LEW and NR211 MEAs, respectively. At 2 A/cm^2 and 100% RH, a difference of 100 mV is observed between the baseline NR211 and the NR212 MEAs with the R-HFC membranes showing similar performance to the NR212 membrane; it is important to note that these membranes were thinner and had lower EW than the baseline. The R-HFC membranes' lower performance may have been a function of the structural pairing of dissimilar ionomers between the catalyst layer and the membrane.

After the BOT testing the MEAs were subjected to a cathode AST for 4,700 cycles. Figure 3 shows the results of the cathode AST on the performance of the MEAs. The range of performance differences observed at the BOT evaluation point was muted following the post-cathode AST performance (except for R-HFC-LEW) creating two pairing groups. This is largely due to the two top performing MEAs (the baseline NR211 and R-PFSA-LEW) having had
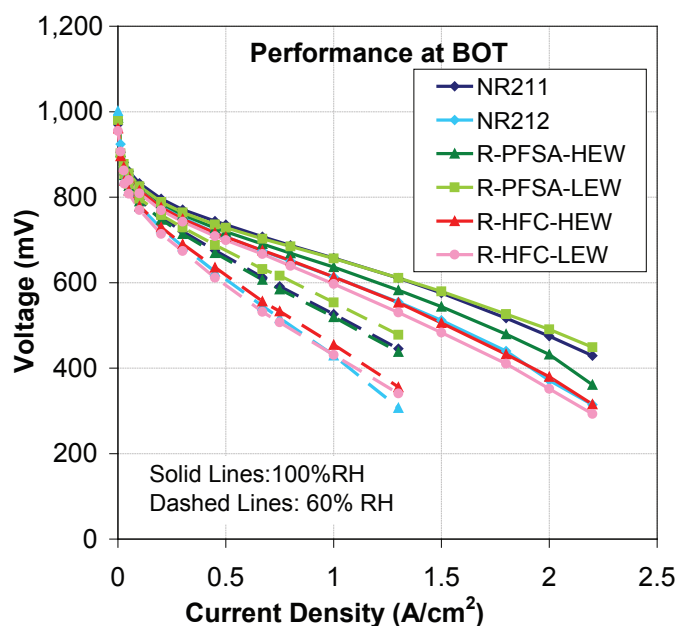
FIGURE 2. MEA performance at 100% and 60% RH at the BOT for the membrane/MEA types
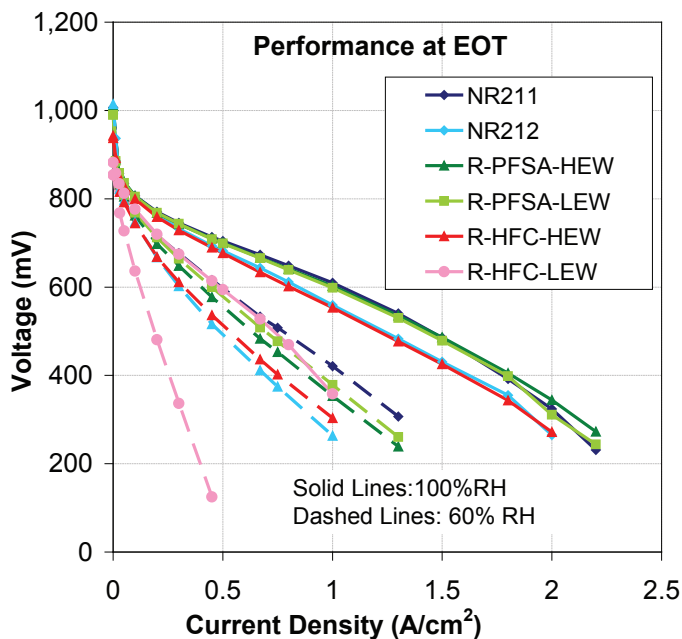
FIGURE 3. MEA performance at 100% and 60% RH after catalyst AST for the membrane/MEA types

higher levels of degradation than their thicker/higher EW counterparts and the R-HFC-LEW having had exceptionally high degradation and overall cell resistance. A voltage loss breakdown technique showed large ohmic loss increases for the R-HFC-LEW suggesting that membrane degradation had occurred during the cathode AST, which was subsequently confirmed by EOT membrane thickness measurements revealing a 50% thickness loss had occurred.

Following evaluation of the BOT and catalyst AST, a combination of membrane AST and catalyst AST was applied to a new set of MEAs (based on three down-selected membranes). These MEAs were subjected to three membrane AST cycles and then to a catalyst AST for up to 4,700 cycles. The ECSA and ECSA loss vs. AST cycles are shown in Figure 4. ECSA loss was observed to occur even during the course of the membrane AST which resulted in a lower starting ECSA entering the catalyst AST protocol. In order to assess the effect of the post-membrane AST state on the catalyst AST, the ECSA loss for post membrane AST samples was normalized to the ECSA at the start of the cathode AST rather than that of the fresh MEA. The results in Figure 4 show that the cyclic open circuit voltage degraded NR211 and R-PFSA membranes had lower ECSA losses after cathode AST cycling than the pristine samples. The NR212 showed similar results up to 700 cycles, but then had much higher ECSA losses for the degraded membrane which in part appears to be due to the development of an internal transfer. Failure analysis of the membranes/MEAs was done to quantify the platinum dissolution mechanism, and it was found that the Pt size did not grow and no platinum in the membrane (PITM) occurred with membrane AST. After both the membrane and cathode AST, the Pt size was higher and the PITM was much lower as compared to the data for the cathode AST alone, suggesting that the platinum migration was hindered by pre-existing membrane degradation and thus resulted in increased Pt agglomeration.

CONCLUSIONS AND FUTURE DIRECTIONS

The interim conclusions are as follows:

- Membrane degradation appears to influence the degree of agglomeration vs. formation of platinum in the membrane as compared to the baseline, catalyst AST only testing.

- Testing was completed on the effect of the combined membrane AST/catalyst AST on low loaded cathode catalyst layers and it was determined that the low loading was more severely affected by the catalyst AST
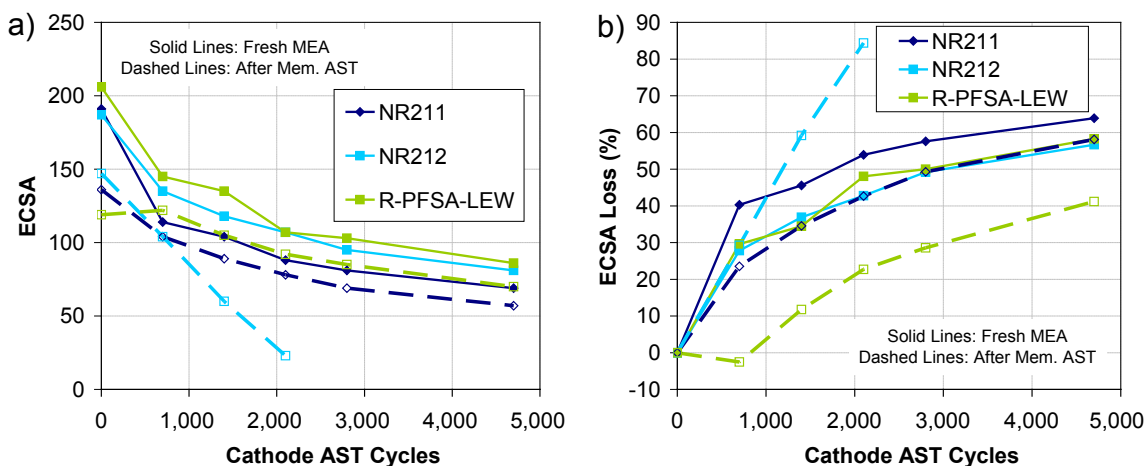
FIGURE 4. ECSA and ECSA loss for the membrane AST degraded MEAs subjected to catalyst AST cycling

as compared to the higher loading samples with the behavior of the samples in the combined membrane/catalyst AST showing similar degradation rates with the fresh samples.

Future directions include the following:

- Complete source code revisions for the improved membrane transport sub-model in FC-APOLLO based on new data for adsorption/desorption processes

- Release the documentation for FC-APOLLO

- Disseminate the validation data set for FC-APOLLO via the public hosting site

- Release revised FC-APOLLO model to www. sourceforge.net/projects/fcapollo

- Complete the project final reporting and publications.

FY 2015 PUBLICATIONS/PRESENTATIONS

1. Conducted FC-APOLLO Tutorial at the June 2015 DOE Annual Merit Review and Peer Evaluation in Arlington, VA.

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