V.B.4 FC-PAD: Ionomer, GDLs, Interfaces

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Overall Objectives

- Demonstrate improved performance and durability of fuel cells.
- Develop and implement characterization techniques for gas diffusion layers (GDLs), membranes, and ionomers.
- Characterize and understand the effects of interfaces and interfacial properties on fuel cell performance and durability.
- Elucidate and mitigate ionomer film resistances in the catalyst layer through model studies to better evaluate performance and durability of fuel cells.
- Explore and optimize transport phenomena related to liquid water.

Fiscal Year (FY) 2016 Objectives

- Characterize ionomer thin films to determine substrate interactions and impact of confinement.
- Initiate studies on ionomer thin film formation.
- Examine membrane durability strategies.
- Model impact of interfaces on transport phenomena and cell performance.
- Explore multiphase flow and interactions within the GDLs using advanced diagnostics and imaging.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan.

(A) Durability

(B) Cost

(C) Performance

FY 2016 Accomplishments

- Initiated studies on ionomer formation from inks using X-ray and light scattering and compared the impact of different solvents on electrode morphology.
- Characterized ionomer thin-film structure and properties for different conditions as a function of equivalent weight and side-chain length.
- Characterized Nafion® XL to understand the transport and mechanical properties and how they vary compared to standard Nafion.
- Explored changes due to hygrothermal ageing of membranes in terms of mechanical and transport properties.
- Correlated cerium movement and washout from membranes with cell-level performance.
- Examined composite membranes and reinforcement.
- Modeled the impact of interface effects for water droplets at the GDL/channel interface and water flooding at the catalyst layer/microporous layer (MPL) interface.

- Measured the interfacial resistance of ionomers as a function of humidity, temperature, and side-chain length.
- Measured and visualized water evaporation from GDLs using X-ray tomography.

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INTRODUCTION

The FC-PAD consortium was formed to advance performance and durability of polymer electrolyte membrane fuel cells (PEMFCs) to meet DOE targets and further enable their commercialization. The major challenge to be addressed by this consortium is to develop the knowledge base and optimize structures for more durable, high-performing PEMFC component technologies, while simultaneously reducing cost. In this project, we will develop validated models and advanced in- and ex-situ characterization techniques to further improve the performance and durability of fuel cells. We will also evaluate PEMFC component issues from low to operating temperatures of interest, including the impact of liquid water. We will characterize and understand components from the membrane to the porous media and their interfaces, with a focus on the ionomer within the catalyst layers.

APPROACH

The FC-PAD consortium incorporates national laboratory investigators with proven experience (developed in prior projects) related to durability, transport, and performance, and combines them into one highly coordinated effort. The effort is sub-divided into six thrust areas, including three materials-related thrusts and three cross-cutting thrusts. This report summarizes some of the work performed in the three cross-cutting thrust areas: 1) Modeling and Validation; 2) Operando Evaluation: Benchmarking, Accelerated Stress Tests, and Contaminants; and 6) Component Characterization and Diagnostics. The thrust areas of the consortium are highly integrated, and the work performed related to the various specific components is presented in the reports of the three materials thrust areas. The project will also benchmark the performance and durability of state-of-the-art membrane electrode assemblies provided by original equipment manufacturers and materials suppliers. Finally, the project will apply in situ and ex situ characterization techniques to reveal the performance losses and related degradation mechanisms operating in fuel cells and propose strategies to improve performance and durability.

Thrust 3 focuses on the membrane, GDLs, MPLs, catalyst-layer ionomer, and the interfaces between these components. The overall approach is to elucidate the governing phenomena using advanced diagnostics and continuum-level modeling, and use that knowledge to optimize performance and durability by mitigating the identified critical bottlenecks.

RESULTS

It is well accepted that low-Pt-loaded electrodes suffer from a local resistance that is due in part to mass transport [1,2]. It is believed that such resistance could be due to the ionomer films covering the reaction site, and thus we have investigated different ionomers to determine their properties and behavior. Going towards lower equivalent weight (EW) could enable better transport; thus, we have characterized 3M as well as Nafion perfluorinated sulfonic acid (PFSA) ionomers across lengthscales. In particular, we investigated their morphology and swelling as bulk membrane (>10 µm) and dispersion-cast thin film (<100 nm) to identify the roles of EW and side-chain length in phase separation across lengthscales. For the first time, humidity-dependent structural changes as well as different PFSA chemistries were explored in the thin-film regime, allowing for the development of a thickness-EW phase diagram as shown in Figure 1. Such a finding can serve as a basis for those trying to understand, synthesize, and improve these materials. It was also found that the ratio of macroscopic (thickness) to nanoscopic (domain spacing) swelling during hydration is affine (1:1) in thin films, but increases as the thickness approaches bulk, revealing the existence of a mesoscale organization governing the multiscale swelling in PFSAs. Ionomer chemistry, in particular the EW, is found to play a key role in altering the confinement-driven structural changes, including anisotropy, in PFSA thin films, with

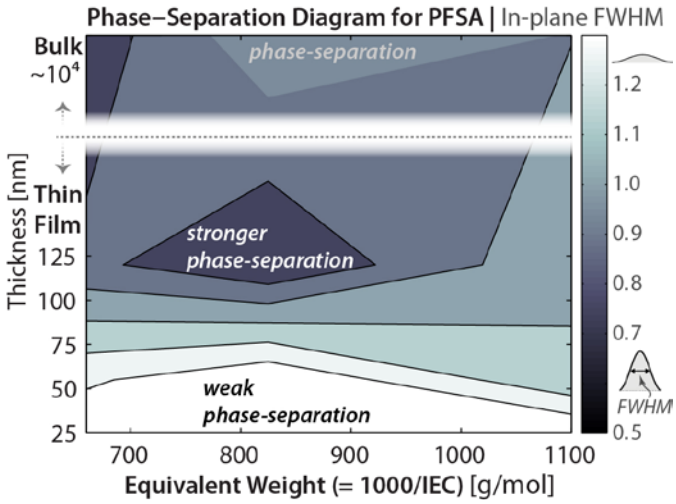

FIGURE 1. Phase-separation diagram generated from the full-width half max (FWHM) values of the ionomer peak determined from small angle X-ray scattering for bulk and thin-film PFSA ionomers

phase separation becoming weaker as the film thickness is reduced below 25 nm or as EW is increased. For the lower-EW 3M PFSA ionomers, confinement appears to induce even stronger phase separation accompanied by domain alignment parallel to the substrate. Finally, studies were initiated on the formation of these ionomer films in electrodes where detailed characterization of the inks and the resultant morphology were started. It was seen how the choice of casting solvent changes the colloid size and eventually the ionomer distribution in the electrode, where the LANL dispersion demonstrated the best Pt and ionomer distribution.

The ionomer thin films can also be related to suspected different interfacial morphology of bulk membranes. To analyze this interface, we developed a water-transport setup where the water flux is measured as a function of membrane thickness for differential humidity changes. This was accomplished with different EW and side-chain PFSAs. As shown in Figure 2, it is found that contrary to intuition, shorter side-chain ionomers demonstrate a larger interfacial resistance than Nafion. As membranes become thinner, such interfacial resistance can dominate the overall water response of the membrane and thus could limit transport. In addition, composite structures, including reinforced membranes, could exhibit multiple interfaces. On this last point, Nafion XL was studied to determine its various mechanical and transport properties, including anisotropic behavior, due to the reinforcement to establish structure/function/property relationships. It was also found that (pre)conditioning of the membrane by heating in water at different temperatures could have significant impacts on its structure/property relationship, in particular, the mechanical stability and conductivity, and its anisotropy.

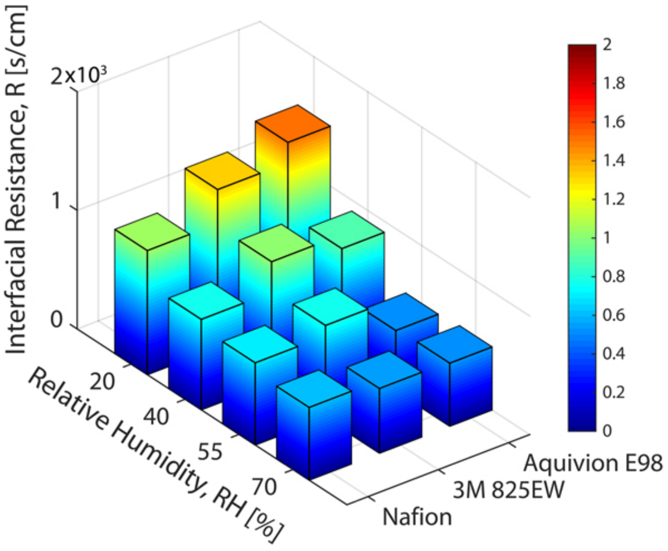

FIGURE 2. Membrane interfacial resistance for water transport as a function of humidity for three different PFSA ionomers

In terms of membrane durability, the impact of hygrothermal ageing on membrane properties was explored, where minor contamination resulted in the membrane becoming more brittle and having lower water uptake and conductivity. This was related to possible cross-linking between the ionic groups, and ageing at mid humidities provided the most severe effects. In terms of chemical durability, extensive work on the movement of Ce, a common radical scavenger, was conducted. It was determined that Ce moves quite rapidly through a membrane, especially when an ionic potential gradient is applied that effectively drives protons as well as water molecules through the membrane. The Ce content of membrane electrode assemblies was shown to migrate towards the gasket regions and the catalyst layers and was sustained there even after the applied potential was removed. In accelerated stress tests, it was shown how the fluoride emission rate was coupled to the Ce concentration (see Figure 3), thus implying that the Ce is removed to the liquid water once there are sufficient anions due to membrane fragmentation. Thus, there is a feedback where increased degradation results in more fluoride emission and hence less protection by Ce, leading to more degradation. As Figure 3 shows, this removal mechanism and degradation occur more rapidly for wet/dry cycling rather than different humidity holds, where saturated conditions provide the most stability for the membrane and Ce.

For exploring multiphase water interactions, both modeling and experimental studies were conducted. It was shown how poor contact between the MPL and catalyst layer can result in zones with a high propensity to flood, thus limiting performance, especially if they occur under the channels. Interestingly, constant-current simulations demonstrate a much larger performance decrease than constant-potential ones, thereby suggesting that cells in stacks (which are constant-current) may have different performance than single-cell tests (which are

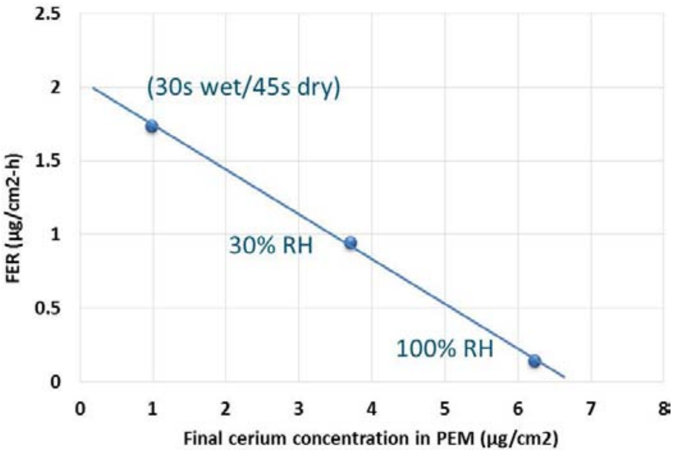

FIGURE 3. Fluoride emission rate after different cell testing—either cycling or hygrothermal ageing—as a function of final cerium concentration in the membrane (RH = relative humidity)

constant-potential). Also, the impact of water dynamics and droplet emergence from the GDL to the channel in terms of capillary pressure was explored, and a criterion for when time-averaging can be used for the boundary condition was developed. In terms of other interactions, an extensive study on evaporation kinetics and mechanisms was conducted for GDLs using a combination of theory and X-ray tomography imaging. Thus, the evaporation rate under different conditions was measured and correlated to the actual liquid/vapor interfacial area measured by the tomography (see Figure 4). The results demonstrate that once this area is considered, the evaporation rate is constant and not increasing as one would measure experimentally. In particular, the interfacial surface area is essentially linear with saturation or total water volume fraction. The concomitant modeling demonstrated that the evaporation was heat and mass-transfer limited and not kinetically limited; thus, the actual evaporation kinetics are rapid.

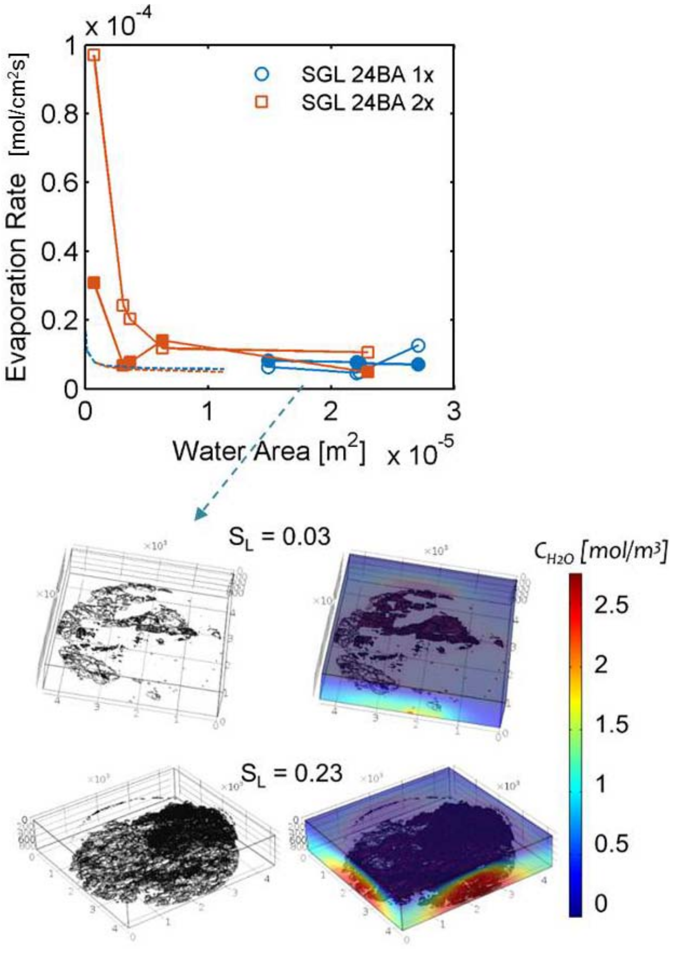

FIGURE 4. Measured evaporation rate as a function of measured water area for two different GDLs. The bottom shows the X-ray tomographs at two saturations and evaporation simulation results.

CONCLUSIONS AND FUTURE DIRECTIONS

To optimize performance and durability of fuel cell components, including ionomers, interfaces, and diffusion media, in this thrust of FC-PAD, we have enacted a synergistic combination of the crosscutting thrusts to explore component properties, behavior, and phenomena. Combined modeling and experiment to understand interfaces demonstrated the water-related issues, including blockage and droplet conditions, along with accurate measurements as to how interfacial area scales with saturation in GDLs. Newer shorter-side-chain and lower-EW ionomers demonstrate interfacial water-transport resistance as membranes and intriguing phase separation for thin films around the 50-nm range. For membrane durability, Nafion XL is promising, but there are concerns both with the mechanical reinforcement breaking as well as cerium migration to the electrodes and perhaps out the effluent water with membrane degradation products.

Going into the future work, the membrane focus on reinforcement and side chains will continue as well as further exploration of the relationship between cerium migration and durability, where the focus will be on understanding the relative influence of each migration mechanism and determining methods to stabilize cerium in the polymer electrolyte membrane and localize it to areas of highest radical generation. For the ionomer diagnostics, there is a continued need to understand thin films, develop a thin-film structure/property model, and explore the conditioning protocols for thin films relevant to catalyst-layer preparation. This last effort will be synergistic to understanding the impact of dispersions and casting on catalyst-layer performance, including direct observation of shear-induced transformation of dilute solutions and using model compounds to elucidate interactions during solvent evaporation with different solvents. Finally, for the various porous media, multiphase simulations with an emphasis on interfacial effects will be explored for both the membrane and GDL/channel.

FY 2016 PUBLICATIONS/PRESENTATIONS

1. Adam Weber, “Understanding Transport in Polymer-Electrolyte Fuel-Cell Ionomer,” Colloquium, U. Kansas, 2015. (invited)

2. Iryna V. Zenyuk, Ezequiel Medici, Jeffrey Allen, and Adam Z. Weber, “Coupling continuum and pore-network models for polymer-electrolyte fuel cells,” *International Journal of Hydrogen Energy*, 40, 16831–16845 (2015). doi: 10.1016/j.ijhydene.2015.08.009

3. Iryna V. Zenyuk and Adam Z. Weber, “Understanding Liquid-Water Management in PEFCs using X-ray Computed Tomography and Modeling,” ECS Conference, Phoenix, 2015. (invited)

4. Ahmet Kusoglu, Thomas J. Dursch, and Adam Z. Weber, “Nanostructure/Swelling Relationships of Bulk and Thin-Film PFSA Ionomers,” *Advanced Functional Materials*, 26, 4961–4975, (2016). doi: 10.1002/adfm.201600861

5. Ahmet Kusoglu and Adam Weber, "Exploring the Parameters Controlling the Crystallinity-Conductivity Correlation of PFSA Ionomers," APS Meeting, Baltimore, March 2016.

6. Ahmet Kusoglu and Adam Weber, "Understanding Ionomer Thin-Films in Fuel Cells," *MRS Meeting*, Phoenix, March 2016. (*invited*)

7. Iryna V. Zenyuk and Adam Z. Weber, "Understanding Liquid-Water Management in PEFCs Using X-Ray Computed Tomography and Modeling," *ECS Transactions*, **69** (17), 1253–1565 (2015). doi: 10.1149/06917.1253ecst.

8. Shouwen Shi, Thomas J. Dursch, Rod L. Borup, Adam Z. Weber, and Ahmet Kusoglu, "Effect of Hygrothermal Ageing on PFSA Ionomers' Structure/Property Relationship," *ECS Transactions,* **69** (17), 1017–1025 (2015). doi: 10.1149/06917.1017ecst.

9. Iryna V. Zenyuk, Prodip K. Das, and Adam Z. Weber, "Understanding Impacts of Catalyst-Layer Thickness on Fuel-Cell Performance via Mathematical Modeling," *Journal of the Electrochemical Society*, **163** (7), F691–F703 (2016). doi: 10.1149/2.1161607jes.

10. Shouwen Shi, Adam Z. Weber, and Ahmet Kusoglu, "Structure/property relationship of Nafion XL composite membranes," *Journal of Membrane Science*, **516**, 123–134 (2016). doi: 10.1016/j.memsci.2016.06.004

11. Ahmet Kusoglu and Adam Z. Weber, "Electrochemical/Mechanical Coupling in Ion-Conducting Soft Matter," *The Journal of Physical Chemistry Letters*, **6**, 4547–4552 (2015). doi: 10.1021/acs.jpclett.5b01639 (*perspective*)

12. Shouwen Shi, Thomas J. Dursch, Colin Blake, Rangachary Mukundan, Rodney L. Borup, Adam Z. Weber, and Ahmet Kusoglu, "Impact of Hygrothermal Ageing on Structure/Function Relationship of Perfluorosulfonic-acid membrane," *Journal of Polymer Science B: Polymer Physics*, **54** (5), 570–581 (2016). doi: 10.1002/polb.23946

13. Adam Weber, "Understanding Transport and Limitations in Fuel-Cell Catalyst Layers," FC Cubic, Tokyo, Japan, 2016.

14. A. Kusoglu and A.Z. Weber, "Understanding Ionomer Thin Films," MRS Meeting, Phoenix, 2016.

15. A.Z. Weber and A. Kusoglu, "Understanding Transport in Polymer-Electrolyte-Fuel-Cell Ionomer Thin Films," MRS Meeting, Phoenix, 2016.

16. A.Z. Weber, "Multiscale Modeling of Polymer-Electrolyte-Fuel-Cell Components," ECS meeting, San Diego, 2016. (keynote)

17. A.Z. Weber and R. Ahluwalia, "Modeling Performance and Durability in Polymer-Electrolyte Fuel Cells," CaRPE-FC, Vancouver, 2016.

18. Andrew M. Baker, Dusan Spernjak, Rangachary Mukundan, Rod L. Borup, Suresh G. Advani, and Ajay K. Prasad, "Cerium Migration during PEM Fuel Cell Accelerated Stress Testing," 228th ECS Meeting (2015).

19. Andrew M. Baker, Dusan Spernjak, Rangachary Mukundan, Rod L. Borup, Suresh G. Advani, and Ajay K. Prasad, "Cerium Migration during PEM Fuel Cell Operation," 2015 Fuel Cell Seminar and Energy Exposition (2015).

20. Iryna V. Zenyuk and Adam Z. Weber, "Understanding Liquid-Water Management in PEFCs using X-ray Computed Tomography and Modeling," 228th ECS Meeting (2015).

21. Ahmet Kusoglu and Adam Weber, "Correlating Transport And Stability Of Ion-Exchange Polymers Through Nanostructure," Pacifichem 2015 (2015).

22. Shouwen Shi, Colin Blake, Rodney L. Borup, Rangachary Mukundan, Adam Z. Weber, and Ahmet Kusoglu, "Effect of Hygrothermal Ageing on PFSA Ionomers' Structure/Property Relationship," 228th ECS Meeting (2015).

23. Iryna V. Zenyuk, Adrien Lamibrac, Jens Eller, Felix N. Büchi, and Adam Z. Weber, "Understanding Evaporation in Fuel-Cell Gas-Diffusion Layers with X-ray Computed Tomography," Interpore: 8th International Conference on Porous Media, Cincinnati, May 2016.

24. Rodney L. Borup, Rangachary Mukundan, Dusan Spernjak, David Langlois, G. Maranzana, A. Lamibrac, J. Dillet, S. Didierjean, O. Lottin, L. Guetaz, D.D. Papadias, R. Ahluwalia, and Karren More, "Material Degradation in PEM Fuel Cells," MRS Meeting, Phoenix, March 2016. (*invited*)

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