

V.B.1 Fuel Cell-Performance and Durability (FC-PAD) Consortium Overview

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Project Start Date: October 1, 2015

Project End Date: September 30, 2020

- Improve component durability (e.g., membrane stabilization, self-healing, electrode-layer stabilization).
- Provide support to industrial and academic developers.
- Development of new diagnostics, characterization tools, and models.
- Each thrust area has a sub-set of objectives which lead to the overall performance and durability objectives.

Fiscal Year (FY) 2016 FC-PAD Organizational Objectives

- Coordinate activities across the core national labs involved in FC-PAD, including in-person coordination meetings and regular conference calls.
- Develop data sharing approaches, including internal and external websites.
- Develop a structure to ease addition of industrial and academic partners, including streamlined multi-lab agreements.
- Conduct outreach to fuel cell developers and develop mutually beneficial collaborations.

Fiscal Year (FY) 2016 Technical Objectives

The technical objectives for FC-PAD are covered by the individual thrust areas, and are found in the separate annual reports for those thrust areas.

- Quantify gas-phase transport improvement of electrospun fibers in cathode electrode layer by electrochemical impedance spectroscopy.
- Compare the spatial distribution of reversible degradation during power cycling and constant power operation.
- Quantify cerium migration within the membrane in microns per second under both applied potential and applied current.
- Propose freeze/thaw protocol to DOE Fuel Cell Technology Team that simulates appropriate transportation shutdown/startup (SD/SU) conditions.
- Quantify by ex situ measurements the steady state concentration and dissolution rates of dissolved Pt and base metal from state-of-the-art Pt alloy catalysts.
- Develop and test protocol for characterizing performance and durability of state-of-the-art Pt alloy-based cathode catalyst layers.

Overall Objectives

- Advance performance and durability of polymer electrolyte membrane fuel cells (PEMFCs) primarily at a pre-competitive level.
- Develop the knowledge base and optimize structures for more durable and high-performance PEMFC components.
- Improve high current density performance at low Pt loadings.
 - Loading: 0.125 mg Pt/cm² total
 - Performance at 0.8 V: 300 mA/cm²
 - Performance at rated power: 1,000 mW/cm²

- Measure structural and transport properties of reinforced perfluorosulfonic-acid membrane including impact of hygrothermal ageing.
- Measure critical ionomer thin-film properties including simultaneous water uptake and swelling, gas permeability, and surface conductivity.
- Propose relevant diagnostic techniques for the identification of local Pt transport resistance.
- Fabricate, integrate, and evaluate electrode layers with modulated properties (e.g., catalyst wt%, carbon type) that can affect local Pt resistance in low-loaded PEMFCs.
- Quantify changes in local Pt transport resistance before and after durability measurements of down-selected electrode materials.
- Establish critical measurement protocol via cross-sectional transmission electron microscopy and scanning transmission electron microscopy with energy dispersive spectrum for several Pt-alloy catalysts to understand alloy catalyst degradation (dissolution) during testing.
- Study ionomer structural changes in low Pt-loaded membrane electrode assemblies (MEAs) subjected to extensive fuel cell operation.
- Establish complete database of Pt-alloy, Ce/ceria, carbon corrosion effects, and ionomer distribution observations as input data for model development.

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

A more detailed list of the Technical Barriers addressing A, B, and C above that this project addresses includes:

- The catalyst layer is not fully understood and is key in lowering costs by meeting rated power.
 - Mitigation of transport losses is required to improve performance.
 - Rated power at low Pt loadings reveals unexpected losses.
- The electrocatalyst remains a challenge for reducing the cost to meet system cost targets.
 - The catalyst, its interaction with other electrode components, the stability of alloying components,

and the effect of this instability are not fully understood and are key to achieving performance, cost, and durability targets.

- The ionomer presents challenges in terms of performance and durability.
 - Unknown membrane durability additive movement
 - Local losses associated with ionomer thin films
- Water and thermal management is needed, especially at lower temperatures.
- Tolerance to impurities and chemical and mechanical integrity has not been established.
- Sufficient durability of fuel cell systems operating over automotive drive cycles has not been demonstrated and is not fully understood.
- Development and implementation of accelerated stress tests (ASTs) are needed to shorten the time required to address durability issues.

Technical Targets

This project develops MEAs that meet the following DOE MEA targets (Table 1).

TABLE 1. Technical Targets: Membrane Electrode Assemblies for Transportation Applications

Characteristic	Units	2020 Targets
Cost	\$/kW _{net}	14
Durability with cycling	hours	5,000
Start-up/shutdown durability	cycles	5,000
Performance @ 0.8 V	mA/cm ²	300
Performance @ rated power (150 kPa _{abs})	mW/cm ²	1,000
Robustness (cold operation)		0.7
Robustness (hot operation)		0.7
Robustness (cold transient)		0.7

Meeting these targets enables the overall fuel cell system target for cost of \$40/kW.

FY 2016 Accomplishments

- FC-PAD consortium's core lab team operating with integrated thrusts.
 - Websites operational (internal and external)
 - Outreach activities, including >10 external presentation and site visits

- Collaborations with academic and industrial partners include ~20 different entities at various levels of interaction
- Expanded previous work in examining performance and durability of Pt-alloy catalysts.
- Fabricated multiple variations of electrode designs to optimize high current density performance.
- Conducted experiments related to thin-film ionomer for catalyst layer optimization with modeling supporting the experimental measurements.
- New durability ASTs were developed and accepted by DOE U.S. DRIVE Fuel Cell Tech Team.
- Experimental measurement of recoverable degradation and developed methods relating to recovering the reversible performance losses.



INTRODUCTION

Although fuel cells are being deployed in cars as part of demonstration fleets, they still fall short of the DOE targets for this technology, which are required for widespread consumer acceptance. The FC-PAD consortium was formed to advance performance and durability of polymer electrolyte membrane fuel cells (PEMFCs) at a pre-competitive level to further enable their commercialization. This consortium coordinates national laboratory activities related to fuel-cell performance and durability, provides technical expertise and harmonizes activities with industrial developers. The consortium serves as a resource that amplifies the Office of Energy Efficiency and Renewable Energy impact by leveraging the core capabilities of several labs.

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. Current research is focused on achieving high performance and durability in low Pt-loaded PEMFCs. The lower Pt-loading has already revealed several key performance and durability issues that need to be overcome for successful PEMFC commercialization. The low-Pt content and advanced alloys and structures used in the catalyst layer impose severe constraints on the optimization of MEAs. New transport and durability models and diagnostics that capture accurately the ionomer transport resistance in the MEA are required and being developed. Moreover, additives used in PEMFC components to increase durability can be mobile and further development is required to stabilize them. Finally, the interactions of the various low-cost components including metal bi-polar plates and gas diffusion layers with the MEA need to be optimized to meet all DOE targets simultaneously.

APPROACH

This 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 consortium formalizes already existing and effective collaborations amongst the national laboratories that have established leadership in PEMFC performance and durability research and development. The consortium coordinates work under the thrust areas defined in Figure 1. Three thrust areas are related to components (electrocatalysts and supports; electrode layers; ionomers, gas diffusion layers, bipolar plates, interfaces), and three thrust areas are cross-cutting in nature (modeling and validation; operando evaluation: benchmarking, ASTs, and contaminants; component characterization and diagnostics).

This project builds on existing capabilities at the five participating laboratories to improve the performance and durability of PEMFCs. Transport losses in advanced state-of-the-art MEAs will be identified and cell design will be optimized to maximize performance. Comprehensive multiphase transport models will be developed and then validated using novel diagnostic techniques. Degradation modes of individual material components will be identified and quantified providing detailed information to predict performance and durability. Interactions between the material components will be measured in terms of their effect on changing PEMFC performance. New ASTs will be designed to reflect accurately the degradation mechanisms observed during PEMFC operation. The research on degradation modes and performance will be used to define material requirements and enable future materials development.

RESULTS

FC-PAD is a newly developed consortium with a core team of U.S. national laboratories. The primary objective of this consortium is to implement improvements to PEMFCs and their components with respect to cost, durability, and performance. As a resource to DOE and industrial developers, the consortium will provide technical capabilities to future projects focusing on performance and durability of PEMFCs. This support will include providing relevant and validated testing protocols, critical information about material properties, advanced structures for performance improvements, and methods for mitigating performance losses due to degradation.

To coordinate effective collaborations, FC-PAD has been organized with a steering committee including Director (Rod Borup), Deputy Director (Adam Weber), and six thrust area coordinators: Deborah Myers, Shyam Kocha, Adam Weber, Rajesh Ahluwalia, Rangachary Mukundan, and Karren More. To speed the ability of FC-PAD to interact with outside organizations, a team of technology transfer specialists has

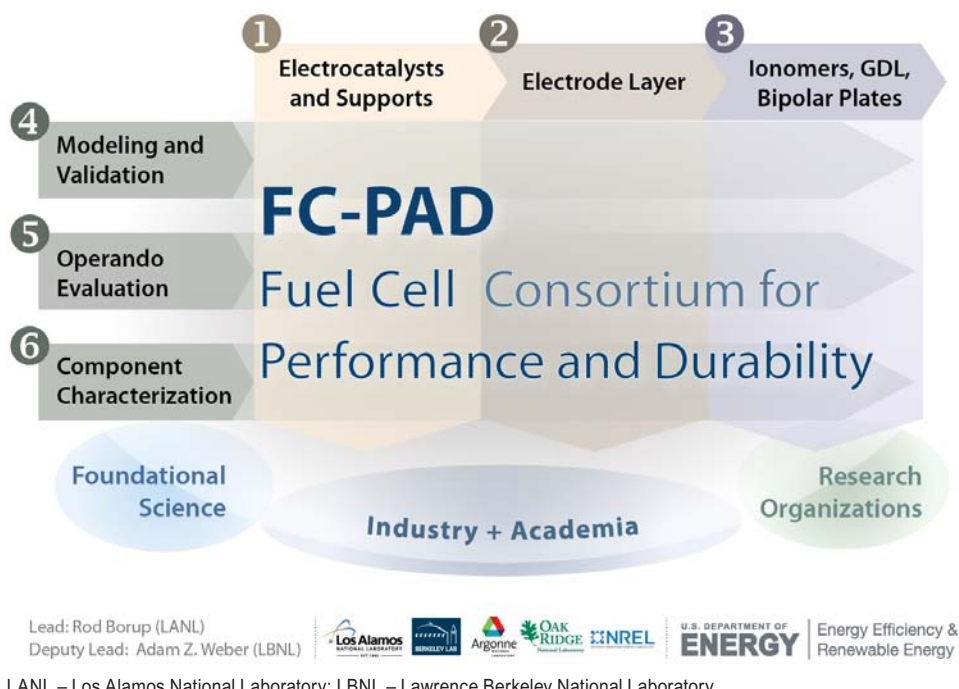


FIGURE 1. FC-PAD Structure. Structure is divided into three component thrust areas (1, 2, 3) and three cross-cutting thrust areas (4, 5, 6).

been formed, and are developing a set of multi-laboratory agreements, such as a multi-lab non-disclosure-agreement, to ease legal interactions with outside entities. Similarly, a set of individuals from the consortium members have been identified to identify methods for data analysis and sharing. The organizational structure of FC-PAD is depicted in Figure 2. Future additions will include Associate Steering Committee members from newly awarded FC-PAD projects from DE-FOA-0001412.

Key to the FC-PAD consortium success is successful coordination of research between the technical thrust areas. An example of successful coordination between FC-PAD thrust areas is shown in Figure 3. In this example, an experimental matrix related to drive cycle induced catalyst carbon corrosion was developed between various researchers representing catalysts, operando evaluation, modeling and characterization. With this inclusive approach, data was produced with feedback that was beneficial to all four of those thrust areas, and was the most valuable in terms of understanding the causes and mitigations to carbon corrosion during drive cycle operation.

Dissemination and collaboration is key to the success of FC-PAD. FC-PAD researchers have an extensive publication and presentation record, and substantial outreach during FY 2016 was conducted. FC-PAD has successfully developed an external website to help with dissemination of results at www.fcpad.org.

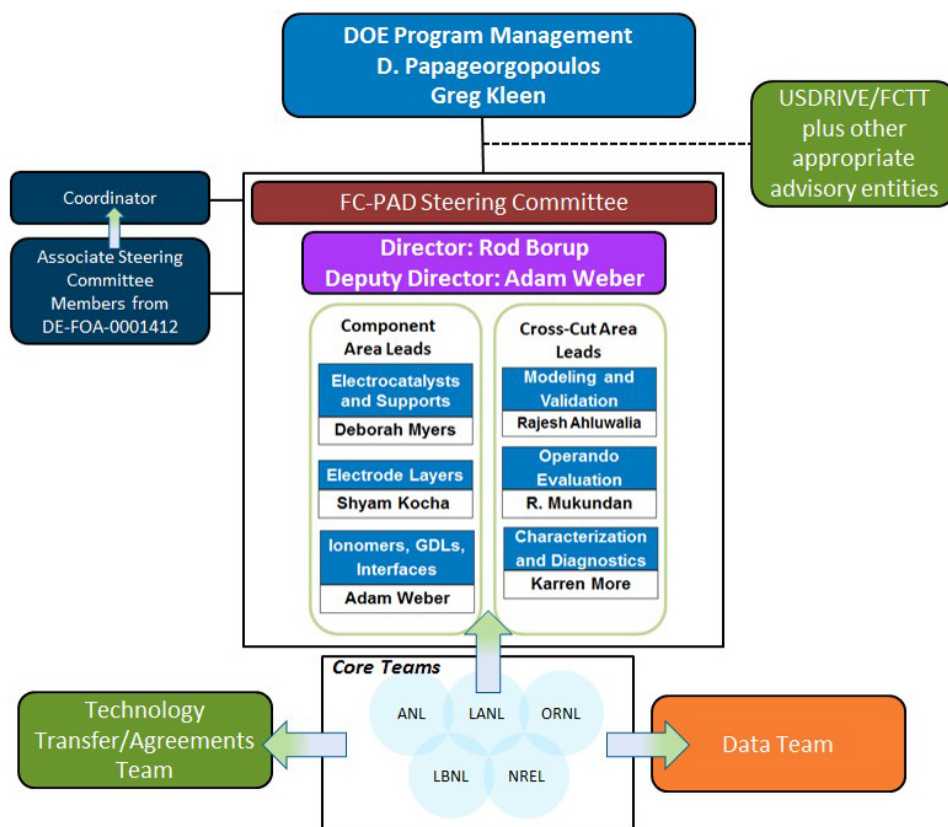
This website is currently being populated with new technical results, the FC-PAD organization and ways to collaborate with FC-PAD. In terms of collaboration, there are multiple paths available for collaboration. These include utilizing the vast array of characterization techniques and equipment that exist in the national lab system to examine material properties and characteristics, and validation of performance plus modeling support. The consortia is especially interested in new SOA materials to validate performance models, understand different material properties related to performance and durability and understand degradation mechanisms. An example of some of the capabilities related to FC-PAD is shown in Figure 4. Interested collaborators should contact the FC-PAD Director about methods for collaboration.

For other key technical accomplishments related to FC-PAD, readers should refer to the other FC-PAD thrust area related reports.

CONCLUSIONS AND FUTURE DIRECTIONS

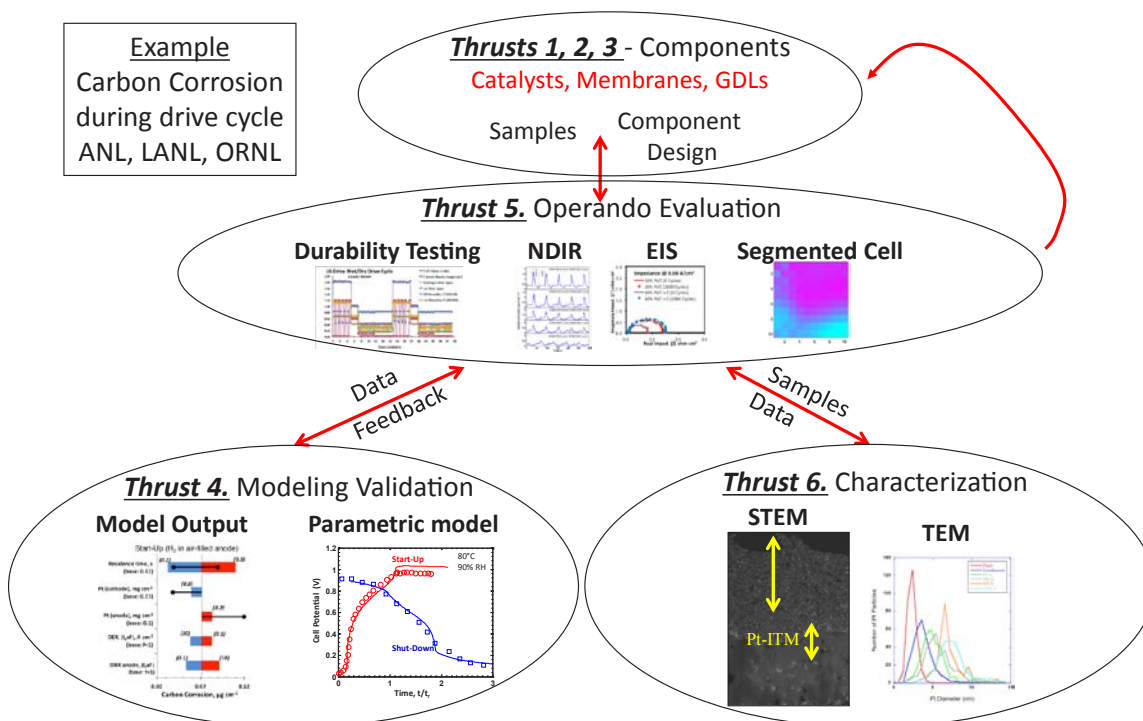
Additional technical details are found in the individual thrust area reports.

- Incorporate collaborators from DE-FOA-0001412 into FC-PAD.
 - Define mechanisms for collaboration.
 - Conduct lab and capability matching exercise.



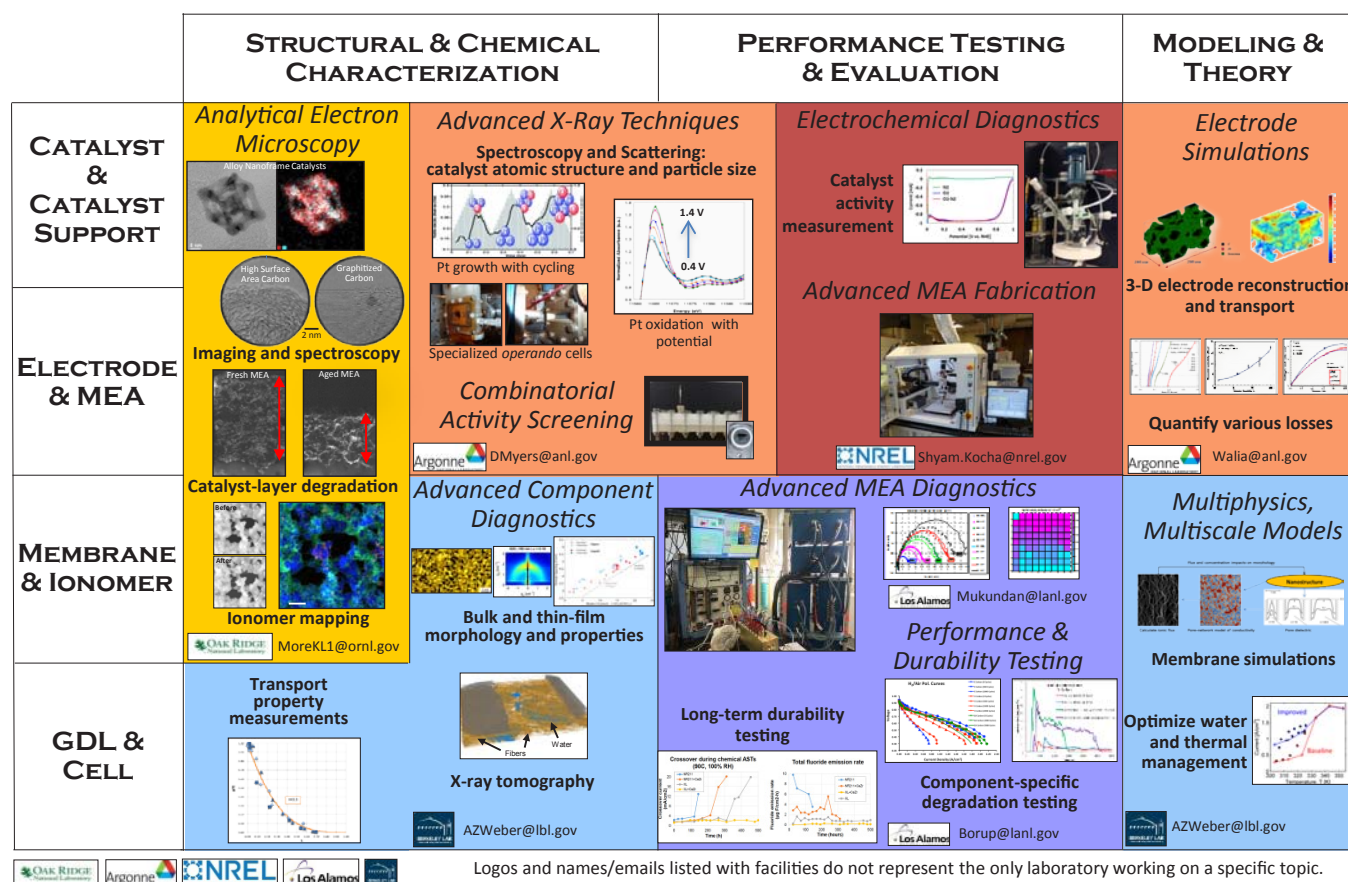
FCTT – Fuel Cell Tech Team; ANL – Argonne National Laboratory; ORNL – Oak Ridge National Laboratory; NREL – National Renewable Energy Laboratory; GDLs – Gas diffusion layers

FIGURE 2. FC-PAD organizational structure



NDIR – Nondispersive infrared sensor; EIS – Electrochemical impedance spectroscopy; STEM – Scanning transmission electron microscopy; TEM – Transmission electron microscopy

FIGURE 3. Example of how FC-PAD coordinates between component and cross-cutting thrust areas



3-D - Three dimensional

FIGURE 4. Capabilities related to FC-PAD at the consortium members. List is an example of capabilities and not meant to represent all capabilities.

- Identify roles for the FC-PAD core national labs for supporting roles.
- Develop milestones for the FC-PAD national labs related to newly awarded projects.
- Integrate new collaborators (industrial/academic/national laboratories) with core national labs.
- Continue outreach to develop new collaborators.
- Populate external FC-PAD website with relevant information.
- Thrust 1: Concentration on Pt-X alloys; developing understanding related to supports and durability.
- Thrust 2: Optimize catalyst layers with state-of-the-art catalysts; implement alternative designs for cathode catalyst layers.
- Thrust 3: Investigate side-chain chemistry effects; relationship between cerium migration and durability.
- Thrust 4: Thin-film structure and property modeling; modeling of catalyst layer/gas diffusion layer/channel interfaces.
- Thrust 5: Segmented cell evaluation of durability; adoption and development of differential cell protocols.
- Thrust 6: Characterization of catalyst layer structure; ionomer mapping and ionomer interactions with catalyst; provide characterization to collaborators.

SPECIAL RECOGNITIONS & AWARDS/ PATENTS ISSUED

1. Rod Borup received an award at 2016 DOE Hydrogen and Fuel Cells Program Annual Merit Review related to FC-PAD.
2. Andrew Baker won 1st place poster at the 2015 Fuel Cell Seminar. Poster Titled: *Cerium Migration during PEM Fuel Cell Operation*.
3. Andrew Baker won 2nd place for the Bernard Baker Award.
4. Peter Dudenias won 1st place poster for the PEFC 15 student poster competition at Electrochemical Society. Poster titled:

Heterogeneous Substrate Effects on Perfluorosulfonic-Acid Thin Films.

5. Rangachary (Mukund) Mukundan has been selected to receive the 2016 Sensor Division Outstanding Achievement Award from the Sensor Division of the Electrochemical Society (ECS).

FY 2016 PUBLICATIONS/PRESENTATIONS

Publications/Presentations Relevant to FC-PAD from Consortium Members:

1. Shouwen Shi, Thomas J. Dursch, Colin Blake, Rangachary Mukundan, Rodney L. Borup, Adam Z. Weber, and Ahmet Kusoglu, "Surface Anhydride Degradation-Induced Changes in Structure/Property Relationship of Perfluorosulfonic-acid (PFSA) membranes," *Journal of Polymer Science B: Polymer Physics*, (2016). doi: 10.1002/polb.23946.
2. 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.jpcclett.5b01639 (*perspective*).
3. 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.
4. 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," *ECS Meeting*, Phoenix, AZ, October 2015.
5. Ahmet Kusoglu and Adam Weber, "Characterization of Low EW Ionomers in Fuel Cells," *ECS Meeting*, Phoenix, AZ, October 2015.
6. Adam Weber, "Understanding Transport in Polymer-Electrolyte Fuel-Cell Ionomer," Colloquium, U. Kansas, 2015. (invited)
7. Ahmet Kusoglu, Peter Dudenas, Meron Tesfaye, and Adam Z. Weber, "Confinement Effects in PFSA Thin Films," *Pacific Polymer Conference 14*, Kuauai, December 2015.
8. Ahmet Kusoglu and Adam Weber, "Correlating transport and stability of ion-exchange polymers through nanostructure," *Pacificchem*, Honolulu, December 2015. (invited)
9. 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.
10. Iryna V. Zenyuk, Ezequiel Medici, Jeffrey Allen, and Adam Z. Weber, "Coupling Continuum and Pore-Network Models in Polymer-Electrolyte Fuel Cells," *European Fuel Cell Technology & Applications Conference - Piero Lunghi Conference*, Naples, 2015.
11. 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)
12. James A. Gilbert, A. Jeremy Kropf, Nancy N. Kariuki, Stacy DeCrane, Xiaoping Wang, Somaye Rasouli, Kang Yu, Paulo J. Ferreira, Dane Morgan, and Deborah J. Myers, "In-Operando Anomalous Small-Angle X-Ray Scattering Investigation of Pt₃Co Catalyst Degradation in Aqueous and Fuel Cell Environments," *Journal of The Electrochemical Society*, 162 (14) (2015) F1487–F1497.
13. L. Xin, F. Yang, A. Uzunoglu, T. Rockward, R.L. Borup, L. Stanciu, and J. Xie, "Highly Stable Hierarchical Polybenzimidazole (PBI) Grafted Graphene/Nanographene Hybrids As Catalyst Supports for Polymer Electrolyte Membrane Fuel Cells," Submitted to the 230th Meeting of the Electrochemical Society.
14. L. Xin, Y. Kang, F. Yang, A. Uzunoglu, T. Rockward, P.J. Ferreira, R.L. Borup, J. Ilavsky, L. Stanciu, and J. Xie, "Novel Catalyst-Layer Structures with Rationally Designed Catalyst/Ionomer Interfaces and Pore Structures Aided By Catalyst Functionalization," Submitted to the 230th Meeting of the Electrochemical Society.
15. K.C. Neyerlin, J.W. Zack, N. Macauley, R. Mukundan, R.L. Borup, K.L. More and S.S. Kocha, "Investigation of the Performance of PtCo/C Cathode Catalyst Layers for ORR Activity and Rated Power for Automotive PEMFCs," Submitted to the 230th Meeting of the Electrochemical Society.
16. D. Spornjak, R.L. Borup, D.S. Hussey, P. Zelenay, and R. Mukundan, "Imaging Fuel Cell Components: From Flow Field Channels to Catalyst Layers," Submitted to the 230th Meeting of the Electrochemical Society.
17. J.S. Spendelow, L. Castanheira, G. Hinds, T. Rockward, D.A. Langlois, R. Mukundan, and R.L. Borup, "Measurement of Local Electrode Potentials in an Operating PEMFC Exposed to Contaminants," Submitted to the 230th Meeting of the Electrochemical Society.
18. Andrew M. Baker, Dusan Spornjak, Rangachary Mukundan, Rod L. Borup, Elizabeth J. Judge, Suresh G. Advani, and Ajay K. Prasad, "Cerium Migration during PEM Fuel Cell Operation," Submitted to JECS.
19. 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, in press (2016). doi: 10.1149/2.1161607jes.
20. Ahmet Kusoglu, Thomas J. Dursch, and Adam Z. Weber, "Nanostructure/Swelling Relationships of Bulk and Thin-Film PFSA Ionomers," *Advanced Functional Materials*, in press (2016). doi: 10.1002/adfm.201600861.
21. 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, OH, May 2016.
22. Ahmet Kusoglu and Adam Weber, "Exploring the Parameters Controlling the Crystallinity-Conductivity Correlation of PFSA Ionomers," *APS Meeting*, Baltimore, March 2016.
23. Ahmet Kusoglu and Adam Weber, "Understanding Ionomer Thin-Films in Fuel Cells," *MRS Meeting*, Phoenix, AZ, March 2016. (invited)

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

25. Deborah J. Myers, James Gilbert, Nancy N. Kariuki, Xiaoping Wang, A. Jeremy Kropf, Zhiwei Yang, Mallika Gummalla, Mike Perry, Sarah Ball, Jonathan Sharman, Brian Theobald, Alex Martinez, Dash Fongalland, Somaye Rasouli, Kang Yu, and Paulo J. Ferreira, “Mechanisms of PEMFC Cathode Catalyst Dissolution and Degradation X-ray scattering and absorption studies of polymer electrolyte fuel cell cathode electrocatalysts,” 3rd International Workshop on Degradation Issues of Fuel Cells and Electrolysers, Santorini, Greece, September 30, 2015. (Invited)

26. F. Cetinbas, R. Ahluwalia, N. Kariuki (Argonne National Laboratory), K.L. More, D.A. Cullen, B. Sneed (Oak Ridge National Laboratory), R.P. Winarski, J. Ilavsky, V. De Andrade, and D.J. Myers (Argonne National Laboratory), “Structural Characterization and Transport Modeling of Pt and Pt alloy Polymer Electrolyte Fuel Cell Cathode Catalyst Layers.”