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 @ 0.8 V: 300 mA/cm²
  - Performance @ rated power: 1,000 mW/cm²
- Improve component durability (e.g., membrane stabilization, self-healing, electrode-layer stabilization).
- Provide support to industrial and academic developers.
- Develop 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) 2017 Objectives

- Quantify cerium migration and diffusion within the membrane under both applied potential and applied current, including modeling of the migration.
- Demonstrate methods to stabilize cerium migration, improving membrane durability.
- Measure cation effects on membrane conductivity and water uptake.
- Measure effect of ionomer-cations on the oxygen reduction reaction (ORR).
- Establish database of 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

Technical Targets

This project develops membrane electrode assemblies (MEAs) that meet the targets in Table 1.

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Units</th>
<th>2020 Targets</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cost</td>
<td>$ / KWnet</td>
<td>14</td>
</tr>
<tr>
<td>Durability with cycling</td>
<td>Hours</td>
<td>5,500</td>
</tr>
<tr>
<td>Start-up/shutdown durability</td>
<td>Cycles</td>
<td>5,000</td>
</tr>
<tr>
<td>Performance @ 0.8 V</td>
<td>mA/cm²</td>
<td>300</td>
</tr>
<tr>
<td>Performance @ rated power (150 kPa)</td>
<td>m /cm²</td>
<td>1,000</td>
</tr>
</tbody>
</table>
FY 2017 Accomplishments

- Measured cerium migration in-plane, through-plane, and in in situ hydrogen pump mode.
- Analyzed cerium data to quantify migration and diffusion coefficients (at 100% relative humidity [RH]).
- Measured cation effect on conductivity and ORR in microelectrodes.
  - Measured reductions in microelectrode current due to cation content in ionomer.
- Identified Ce/carbon interactions as a likely cause for Ce stabilization in the catalyst layers.
- Measured a large improvement in membrane durability by incorporating Ce as CZO (cerium-zirconia) over similar concentrations of ion-exchange cerium.
- Measured perfluorinated sulfonic acid (PFSA) conductivity as a function of cation and water content.
  - Large/heavy cations → disrupt domains → lower uptake
  - Multi-valent cations → ionic crosslinks → restricted mobility
  - Conductivity scales with water per charge, not per poly(anion).
- Conducted a comparison study of perfluoroimide acid versus PFSA water uptake and conductivity.

INTRODUCTION

Although fuel cells are being deployed in cars with limited commercialization, 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 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.

For FY 2017, FC-PAD is represented by three annual merit review presentations and annual progress reports:

- FC135 FC-PAD: Fuel Cell Performance and Durability Consortium (this report)
- FC136 FC-PAD: Components and Characterization (primary contact: Karren More)
- FC137 FC-PAD: Electrode Layers and Optimization (primary contact: Adam Weber)

FC-PAD is an integrated consortia of five national laboratories with a large number of contributing staff scientists, research technicians, post-docs, and students. For FY 2017, FC-PAD contributors were:

- Argonne National Laboratory: Debbie Myers, Rajesh Ahluwalia, Nancy Kariuki, Dennis Papadias, C. Firat Cetinbas, J-K Peng, Xiaohua Wang
- Lawrence Berkeley National Laboratory: Adam Weber, Ahmet Kusoglu, Kelsey Hatzell, Lalit Pant, Huai-Suen Shiau, Anna Freiburg, Meron Tesfaye, Anamika Chowdhury, Sarah Berlinger, Andrew Crothers, Grace Lau, Michael Tucker, Clayton Radke, Thomas Chan
- Los Alamos National Laboratory: Rangachary Mukundan, Rod Borup, Natalia Macaulay, Mahlon Wilson, Yu Seung Kim, Sarah Stariha, David Langlois, Roger Luan, Siddharth Komini Babu, Andrew Baker, Joseph Dumont, Jacob Spendelow
- National Renewable Energy Laboratory: Shyam Kocha, KC Neyerlin, Nihal Shah, Jason Christ, Jason Zack, Jocelyn Mackay, Lawrence Anderson
- Oak Ridge National Laboratory: Karren More, David Cullen, Brian Sneed, Shawn Reeves

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 among the national laboratories that have established leadership in PEMFC performance and durability research and development. Three thrust areas are related to components: (1) electrocatalysts and supports; (2) electrode layers; (3) ionomers, gas diffusion layers, bipolar plates, interfaces; three additional thrust areas are cross-cutting in nature; (4) modeling and validation; (5) operando evaluation–benchmarking, accelerated stress tests (ASTs), and contaminants; and (6) component characterization and diagnostics.
Four FC-PAD projects from DE-FOA-0001412 were announced by DOE during FY 2017. Those projects are led by 3M Company, General Motors, United Technologies Research Center, and Vanderbilt University. The core national lab team is working to support those four projects with an equal level of effort utilizing national lab capabilities. A national lab primary point of contact was assigned for each project, with a statement of work negotiated for FY 2017. National lab work for those projects is represented in those project reports.

RESULTS

The results in this FC-PAD report are limited to our work related to membrane durability and understanding the membrane structure and performance.

Cerium is an additive used to improve the durability of fuel cell polymer electrolyte membranes (PEMs); however, migration of cerium (Ce) can be an issue. Cerium ions enhance the durability of PEM fuel cell components by rapidly and reversibly scavenging degrading radical species, which can be generated during operation. However, Ce migrates between the membrane and the catalyst layers (CLs). The migration of cerium is demonstrated in Figure 1, where a fresh MEA has a large concentration of cerium in the membrane (Figure 1a); however, after testing either by AST holding the cell at open circuit potential (Figure 1b) or operating the U.S. Drive Cycle Protocol (Figure 1c), little cerium remains in the membrane, with the majority residing in the catalyst layers, both anode (aCL) and cathode (cCL).

Hydrogen pump experiments were utilized in FY 2017 to understand the effects of potential gradients and proton/water flux on Ce migration. Figure 2 shows two-dimensional Ce maps during hydrogen pump experiments performed at 2 V and 100% RH for different amounts of charge transfer. The cerium concentration profiles show a progression of cerium migration to the counter electrode with time and charge transfer. After complete migration of the cerium, potential was removed and the corresponding time-dependent diffusion measured to define a cerium diffusion coefficient. With this cerium diffusion coefficient, a migration coefficient was modeled by the Nernst-Plank equation (Equation 1):

$$\frac{\partial c}{\partial t} + V \cdot (-Dc \cdot z \mu_m \cdot Fc \cdot \Phi_{ionic}) = 0$$  \hspace{1cm} (1)

The coefficients determined and used in the modeling (solid lines) were:

- Diffusion Coefficient 0.686 $[x10^{-10} \text{ m}^2 \text{ s}^{-1}]$
- Mobility 7.2±0.8 $[x10^{-15} \text{ s mol kg}^{-1}]$

To improve membrane durability to alleviate issues with migration, we have employed more effective radical scavengers in the cathode CL, nearest to the location of peroxide and reactive hydroxyl radical generation, based on CZO (cerium-zirconia) \cite{1}. CZO addition to the cathode CL at a loading of 10 µg/cm$^2$ improved the durability of Nafion XL PEMs, which is demonstrated by reduced electrochemical gas crossover, open circuit voltage decay, and fluoride emission rates (shown in Figure 3) during PEM chemical stability ASTs. Additionally, this improvement in durability counteracts undesirable Ce migration due to ionomer degradation. The overall degradation rate, indicated by average fluoride emission rate (FER) over the test duration, also correlates well to the final Ce content in the PEM after ASTs. This result is consistent with our hypothesis that during aggressive ASTs, Ce movement from the PEM into the CLs is affected by degradation of the Ce-containing ionomer, itself. Therefore, employing a highly effective radical scavenger, such as CZO, dramatically mitigates PEM degradation, which negates the effects of Ce migration due to side chain scission. MEAs with improved chemical stability, which do not compromise cell performance, as shown here, directly address barriers of lifetime and cost which currently hinder PEM fuel cell commercialization.

A large effect of cations such as cerium is the reduction of water uptake and loss of conductivity. A series of cations

![FIGURE 1](https://example.com/figure1.png)

**FIGURE 1.** Cross-section images by scanning electron microscopy (SEM) and cerium mapping by X-ray fluorescence (XRF) of (a) fresh MEA, (b) an MEA after the membrane open circuit potential AST, and (c) an MEA after the U.S. Drive Cycle test.
was examined to correlate the membrane conductivity to cation concentration and water content. The membrane conductivity versus water content is shown in Figure 4 for this series of cations. From this, we can determine that conductivity \( \text{scales with water per charge, not per poly(anion).} \) Overall, the cationic-interaction-dependent properties are strongly affected by hydration/RH to which the system is exposed, with the effect of the different cations being:

- Large/heavy cations \( \rightarrow \) disrupt domains \( \rightarrow \) lower uptake
- Multi-valent cations \( \rightarrow \) ionic crosslinks \( \rightarrow \) restricted mobility

Interestingly, cerium has an exceptionally high conductivity, higher than it expected from similar sized or valance cations. This is a fortuitous result as cerium is a cation of choice for radical scavenging, and these properties may limit deleterious effects of the cation on membrane and ionomer conductivity.

**CONCLUSIONS AND UPCOMING ACTIVITIES**

Significant progress is reported in this report related to understanding cerium migration in membranes and its potential effects on durability. Migration and diffusion coefficients were quantified at 50% and 100% RH. CZO is shown to enhance the membrane durability much better than adding cerium cations. Work also demonstrates advances in
modeling of membrane structures and detailing water uptake with various cationic species.

As a consortium, the future work planned is broad, but concentrates on developing the foundational science understanding of the MEA components:

- MEA/catalyst layer structure
  - Binary interactions that govern structure in an ink (polymer/solvent, Pt/C and solvent, Pt/C and ionomer, etc.).
  - Effect of interactions on catalyst layer morphology.
    - Microporosity, ionomer/carbon, and ionomer/Pt structure.
  - Catalyst layer restructuring during conditioning.
  - Cation effect on CL and ionomer structure (Ce, Co, Ni, etc.).
- Micro-continuum model for domain-scale physics
  - Nanoscale interactions: electrostatics, solvation, finite size, image charge, dispersion forces.
  - Effect of elected cations relevant to leaching, for thin film ionomers.
  - Isolation of nanoscale and mesoscale resistances.
- Durability: low catalyst loading and catalyst type effect
  - Comparative H₂O₂ and radical formation at lower loadings (2e⁻ versus 4e⁻).

Specifically related to this report, future work related to membrane durability includes:

- Membrane, membrane additives, and cation effects
  - In situ fuel cell operation with measurement of Ce concentration profiles.
  - Surface analysis of Ce/C catalyst supports to identify Ce bonding/stabilization.
  - Correlation or demonstration of no correlation of R_{CL} with Ce ionomer concentrations.
  - Better stabilization of Ce in localized areas of the membrane (CZO, Ce stabilized within fibers or capsules).
  - 2D (or 3D) modeling of the cation migration.
  - Model prediction of durability with Ce content and migration.

**SPECIAL RECOGNITIONS & AWARDS/PATENTS ISSUED**

- Ahmet Kusoglu received the Supramaniam Srinivasan, Early Career Award from the Energy Technology Division of the Electrochemical Society.
- Ahmet Kusoglu received a Toyota Young Investigator Award from the Electrochemical Society.
- Andrew Baker received the Bill Baron Fellowship in recognition of his contributions related to the renewable energy field from the University of Delaware.
- Rangachary (Mukund) Mukundan has been selected as a 2017 recipient as a fellow of the Electrochemical Society.

**REFERENCES**


**FY 2017 PUBLICATIONS/PRESENTATIONS**

1. Publications and presentations listed here represent the three FC-PAD annual merit review presentations and annual progress reports: FC135 (V.B.1), FC136 (V.B.2), and FC137 (V.B.3).
Publications Relevant to FC-PAD from Consortium Members


Presentations Relevant to FC-PAD from Consortium Members


33. Firat Cetinbas, Rajesh Ahluwalia, Nancy Kariuki, Karren More, David Cullen, Brian Sneed, Robert Winarski, Jan Ilavsky, Vincent De Andrade, and Debbie Myers, “Structural


44. R. Borup, Video: Science in 60–A Clean, Renewable Power Source, Los Alamos National Laboratory, Los Alamos, NM.


Microscopy Methods,” 230th Meeting of the Electrochemical Society.