
Novel Ionomers and Electrode Structures for Improved Polymer Electrolyte Membrane Fuel Cell Electrode Performance at Low Platinum Group Metal Loadings

Andrew Haug (Primary Contact), Matthew Lindell, John Abulu, Mike Yandrasits, Grant Thoma, Andy Steinbach, Mike Kurkowski, Grant Weatherman, Israr Khan, Fuxia Sun, Matthew Krueger

3M Company, Corporate Research Laboratory
3M Center, Building 201-1W-28
St. Paul, MN 55144
Phone: 651-737-3579
Email: athaug@mmm.com

DOE Manager and Technical Advisor: David Peterson
Phone: 240-562-1747
Email: David.Peterson@ee.doe.gov

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Subcontractors:

- Michigan Technological University (MTU), Houghton, MI
- Tufts University (Tufts), Medford, MA
- Lawrence Berkeley National Laboratory (LBNL), Berkeley, CA
- Oak Ridge National Laboratory (ORNL), Oak Ridge, TN
- Argonne National Laboratory (ANL), Lemont, IL
- National Renewable Energy Laboratory (NREL), Boulder, CO
- Los Alamos National Laboratory (LANL), Los Alamos, NM

Project Start Date: October 1, 2016
Project End Date: September 30, 2019

Overall Objectives

- The overall objective is to develop electrodes containing new ionomers and oxygen reduction reaction electrocatalysts that exceed the following project-specific ionomer targets and DOE 2020 targets:
- Mass activity 0.44 A/mg_{PGM} or higher
- Platinum group metal (PGM) total content (both electrodes) ≤ 0.125 g/kW

- PGM total loading (both electrodes) < 0.125 mg_{PGM}/cm²
- Electrocatalyst mass activity durability of $< 40\%$ loss
- Metal stability accelerated stress test (AST) loss of performance < 30 mV @ 0.8 and 1.5 A/cm²
- DOE support targets
- An electrode ionomer 50% more conductive and bulk oxygen permeable over 3M825 perfluorosulfonic acid (PFSA)
- Membrane electrode assembly (MEA) robustness $> 70\%$ at cold, hot, and transient conditions.

Fiscal Year (FY) 2019 Objectives

- Develop an electrode ionomer 50% more conductive and bulk oxygen permeable than 3M825 PFSA.
- Achieve power targets of 0.125 g/kW.
- Achieve electrode activity targets of 0.44 A/mg_{PGM} with a nanostructured thin film (NSTF) catalyst greater than 25 m²/g_{PGM}.

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 Plan¹:

- A. Durability
- B. Cost
- C. Performance
- D. Operational Robustness.

Technical Targets

Table 1 summarizes 2019 project status against the relevant 2020 DOE targets and project targets. All reported status values are measurements made in

¹ <https://www.energy.gov/eere/fuelcells/downloads/fuel-cell-technologies-office-multi-year-research-development-and-22>

MEA format. So far, eight of the overall targets have been achieved. In this budget period (BP 3), a new imide-type ionomer (IMIDE#8) met the entire project targets, demonstrating a bulk oxygen permeability 64% greater than that of the 3M825 baseline while showing 73.6% more conductivity. Durable dispersed metal on carbon electrodes have achieved up to 0.36 A/mg_{PGM} while showing mass activity losses as low as 24%. Dispersed metal on carbon electrodes containing new ionomers achieved 0.661 V at 0.125 g/kW and up to 0.686 V at 0.125 g/kW at “elevated” automotive conditions (90/84/84°C, 21.6 psig). Low ionomer-to-carbon ratio (I/C) perfluoro imide-acid (PFIA) electrodes have allowed non-graphitized 10V50E systems to achieve support stability targets. Electrode optimization has ensured that dispersed NSTF and ionomer metal on carbon systems maintain operation robustness metrics.

FY 2019 Accomplishments

- Twenty-seven total ionomer types have been generated for this project.
 - Imide ionomer #8 met entire project targets with 64% and 73.6% improvements in oxygen permeability and ionic conductivity, respectively.
 - Imide ionomer #6 showed 105% gain in bulk oxygen permeability over the 3M825 baseline.
- PFIA has demonstrated unique and differentiated attributes, including: (1) demonstrating 8x more conductivity in an electrode vs. 3M825EW (Tufts); (2) maintaining its structure better as a thin film (LBNL); (3) improving dispersed NSTF performance (LANL, MTU); and (4) likely breaking up agglomerates more (ANL, 3M).
- Low I/C electrodes containing 3M PFIA have increased activity by as much as 61%, reduced local transport resistance by up to 57%, and reduced metal surface area loss from 91% to 59%.
- Low I/C PFIA + 10V50E electrodes allowed 5,000 DOE support cycles with 29 mV loss at 1.5 A/cm² compared to a baseline electrode that survived 2,000 cycles.
- Tufts demonstrated PFIA ionomer has 8x thin film conductivity compared to 825 PFSA.
- Dispersed NSTF is showing exceptionally low local gas transport resistance.
- Team collaboration led to the conclusion that dispersed NSTF electrodes suffer protonic conduction limitations. 3M electrode processing has reduced this effect and improved performance.
- An operational electrode pore network model (MTU/Tufts) showed that NSTF coverage by ionomer likely influences local protonic transport resistance.

Table 1. Status Against Technical Targets

Metric		2020 ^a Target	Project Target	March 2018	February 2019
PGM total loading, mg/cm ²		0.125	0.125	0.102 ^b	0.095 ^b
PGM total loading, g/kW [150 kPa abs]	NSTF	0.125	0.125	0.172 ^b	0.172 ^b
	ionomer			0.125 ^{b,d}	0.125 ^{b,d}
Mass activity @ 900 mV iR-free, A/mg	NSTF	0.44	0.44+	0.28	0.31
	ionomer			0.21	0.36
Support AST, % mass activity loss, 5k cycles	NSTF	<30	<30	<10% (Pt)	<10% (Pt)
	ionomer				27% (PtCo)
Electrocatalyst AST, mV loss @ 0.8 A/cm ²	NSTF	<30	<30	80 ^e	80 ^e
	ionomer			134 ^e	69 ^e
Electrocatalyst AST, % mass activity loss	NSTF	<40	<40	40% (Pt)	41% (Pt/Ir)
	ionomer			54.5%	24% ⁶
MEA robustness (cold/hot/cold transient)	NSTF	0.7/0.7/0.7	>0.7/>0.7/>0.7	0.93/0.84/0.90	0.93/0.84/0.90
	ionomer			0.97/0.90/0.94	0.97/0.90/0.94
Ionomer conductivity (S/cm, 80 °C, 50% RH)		---	0.087	0.070	0.099
Ionomer bulk O ₂ perm (mol-cm-s ⁻¹ -cm ⁻² -kPa ⁻¹), 80 °C, 50% RH		---	1.8E-13	2.3E-13	2.1E-13
^a All metrics and DOE 2020 targets are taken from DE-FOA-0001412		^d At 0.661 V for 80/68/68 °C, 7.5 psig and 0.686 V for 90/84/84 °C, 21.6 psig			
^b 0.025 mg Pt/cm ² anode		^e At 70/70/70 °C, 0 psig			
^c 3M transient protocols used for NSTF testing		^f Intermetallic PtCo alloy			

INTRODUCTION

Among the various recommendations for fuel cell performance enhancement at low precious metal loadings are increasing ionomer and electrode oxygen transport, as well as increasing ionomer hydrophobicity. Further proposed limitations include local (near catalyst) water generation and flooding and transport losses due to alloying (non-Pt) metal dissolution. Additionally, catalysts and electrodes with increased activity and durability are required to meet automotive performance and lifetime targets. The focus of this project is to develop electrode ionomers with improved oxygen transport, integrate these into electrodes containing durable, active NSTF powder, and achieve DOE 2020 power and durability targets.

In BP 2, several electrode-focused ionomers were generated and evaluated. Increased ionomer conductivity has led to improved electrode performance while lower ionomer content has shown activity and metal stability increases. For the first time, NSTF Pt/Ir catalyst powder is being integrated into a more classic electrode structure and showing good activity and excellent metal stability. Support from the Fuel Cell Performance and Durability Consortium, Tufts, and MTU is breaking down current NSTF performance limitations leading to the likelihood that local proton conductivity is limiting in dispersed NSTF systems. Integration and analysis of these novel materials continued in BP 3. Model development by MTU and Tufts has resulted in a model that is being validated against data and is probing the transport mechanisms of electrodes containing these novel materials.

APPROACH

The approach is to develop novel electrode-specific ionomers aimed at increasing oxygen permeability, conductivity, and cathode performance. Ionomer development is proceeding along three paths: developing and evaluating multiacid sidechain materials, imide-only materials (BP 1,2), and more novel oxygen-permeable ionomer structures (BP 2,3). NSTF will then be integrated into this ionomer-containing electrode framework. The best high-activity, durable *ultra-thin-film (UTF) alloy powder* having a minimal number of monolayers (i.e., maximum electrochemical surface area) potentially achieves areas approaching 70 cm²_{PGM}/cm²_{planar} with specific activities as high as 4 mA/cm² with 0.105 mg PGM/cm². This is a theoretical mass activity entitlement of 2.5 A/mg_{PGM}, a 5x increase beyond the DOE 2020 0.44 A/mg PGM mass activity target. Activity losses stabilizing UTF powder against cyclic decay and integrating UTF powder into an ionomer-containing electrode

are expected, but such UTFs can lose over 80% activity and still achieve DOE 2020 targets. Finally, optimization of the electrode framework containing novel ionomers and optimal NSTF will be completed to achieve the above targets. Guiding this development at every stage will be state-of-the-art characterization and modeling including nano-computed tomography imaging, grazing incident small-angle X-ray spectroscopy, transmission electron microscopy, water imbibition, and pore hydrophobicity/philicity measurements.

The proposed work is broken down into five tasks: electrode ionomer development and characterization (Task 1), advanced NSTF electrode development and characterization (Task 2), integration of novel ionomers and NSTF into electrodes (Task 3), model development (Task 4), and project management (Task 5). The project contains three 12-month BPs. NSTF development will focus mainly on the integration of state-of-the-art NSTF catalyst powder into an ionomer-containing electrode architecture.

RESULTS

For Task 1, IMIDE#8 ionomer has been shown to exceed entire project targets for bulk oxygen permeability and conductivity simultaneously—showing 64% and 73.6% improvements in oxygen permeability and ionic conductivity over the 3M825 PFSA baseline. As shown in Figure 1, IMIDE#6 achieved the highest recorded bulk oxygen permeability. New, more novel ionomers are being developed to further increase permeability. LM9/703 is the first material to successfully demonstrate bulk film permeability improvements. New materials of this kind are being made with hopes of furthering these gains.

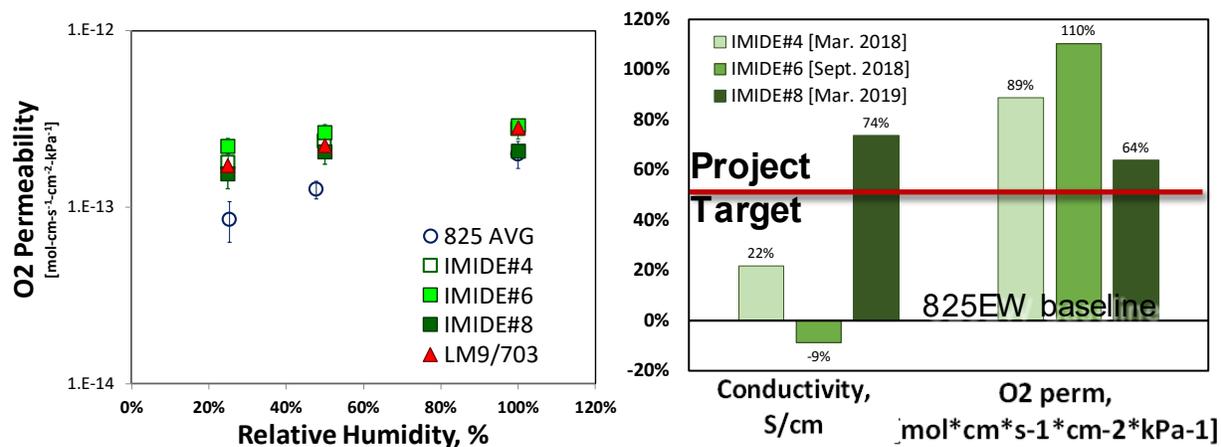


Figure 1. Combined oxygen permeability and conductivity (right) and oxygen permeability (left) of baseline PFSA and novel imide ionomers. Measured for bulk films at 80 °C, 50% RH.

Tufts found that for electrodes containing carbon and ionomer, PFIA ionomers are showing 8x thin film conductivity gains over 3M825 at 70% RH. These gains are beyond just ion exchange capacity improvements and may be due to larger, and perhaps better oriented, ionic domains as measured by LBNL using grazing incident small-angle X-ray spectroscopy. The gains enable $I/C_{\text{PFIA}} = 0.4$ to show similar proton conduction as $I/C_{825} = 0.8$. Reducing I/C in this way decreases local oxygen transport resistance as shown by local oxygen transport studies by 3M, NREL and LBNL. This reduced local transport resistance has been directly correlated to high current performance gains. Further, lowering I/C has been shown to reduce local oxygen transport for dispersed NSTF and dispersed metal on carbon systems as shown in Figure 2. Local transport resistance has been shown to be reduced as much as 57% by reducing the I/C ratio to 0.3.

For 3M825, the lowest oxygen transport resistance was shown at $I/C = 0.4$; below this the resistance increases. ANL has shown that for very low I/C ratios, carbon agglomeration increases. This may be why local transport resistance increases at $I/C = 0.2$ —agglomeration is so severe that some catalyst is deactivated at sub-saturated conditions. 3MPFIA was shown to reduce agglomeration vs. 3M825. As a result, transport resistance continued to decrease down to $I/C = 0.2$. While lowering I/C has shown transport gains, the improved bulk

oxygen permeability shown in IMIDE#6 has not yet translated to local oxygen transport gains, also shown in Figure 2. Further investigation is ongoing now.

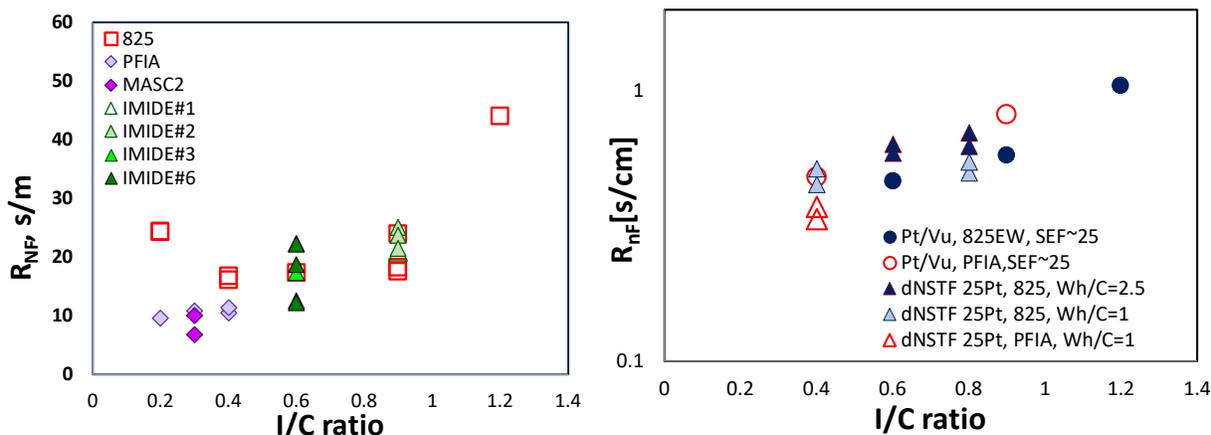


Figure 2. Left: Local cathode electrode transport resistance gains measured at 85 °C, 75% RH. Cathodes contained a 1:3 blend of 10V50E and XC72 carbon, 0.050 mg_{Pt}/cm². Right: Similar trends of local transport vs. I/C are shown by NREL for NSTF + Vulcan systems (shown as Pt/Vu systems).

These local transport and conductivity gains allow less ionomer to be used in the electrode. For low I/C 10V50E systems, this has allowed activity to increase from 0.15 to 0.22 A/mg_{Pt} and support stability to increase from 2,000 cycles with 300 mV loss to 5,000 cycles with 29 mV loss (Figure 3), and it has resulted in metal electrochemical surface area loss to drop from 91% to 59%. Further, both activity and durability have been improved using these electrodes. Activity gains of up to 61% have been made with graphitized Pt on carbon. Metal area loss has been reduced from 91% to 57% as shown in Figure 4. Through Task 3, integration of these ionomers with alloy catalysts have further reduced metal area loss to 36%, and stable metal alloys further reduced activity loss to 24%. Further improvements are expected here with better catalysts, new ionomer integration, and electrode configurations.

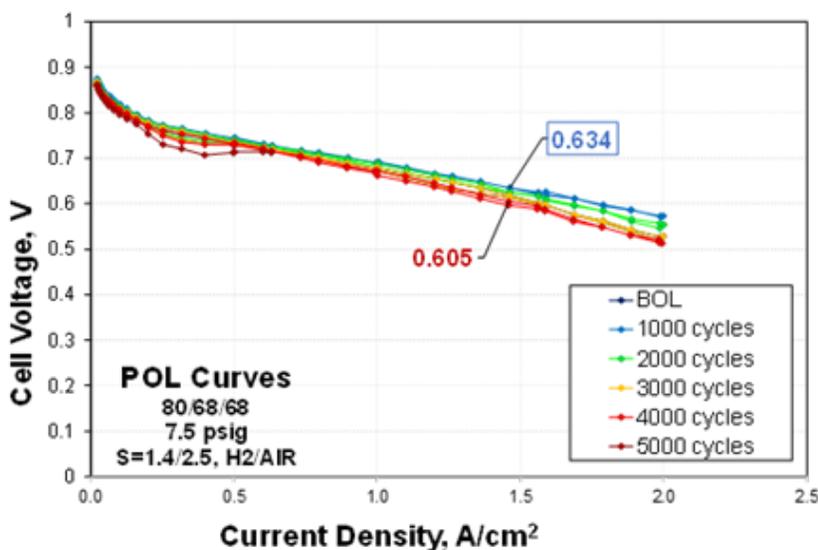


Figure 3. DOE support stability AST test, 10V50E, PFIA, I/C = 0.3, 0.188 mg_{Pt}/cm². Cycles are from 1.0–1.5–1.0 V, 80 °C, 100% RH, 800/500 sccm H₂/N₂. Polarization curves are at 80 °C, 68/68 °C AN/CA dewpoint, stoichiometry = 1.4/2.5 H₂/air, 7.5/7.5 psig AN/CA.

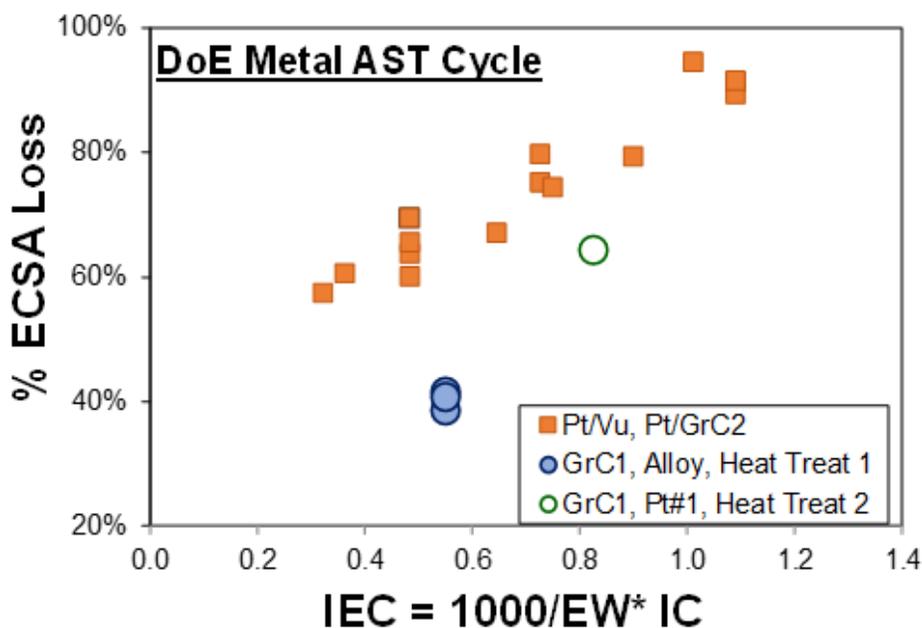


Figure 4. DOE catalyst stability AST test. Cycles are from 0.60–0.95 V, 80°C, 100% RH, 800/500 sccm H₂/N₂, 30,000 cycles. Polarization curves are at 80°C, 68/68°C AN/CA dewpoint, stoichiometry = 1.4/2.5 H₂/air, 7.5/7.5 psig AN/CA. Pt/Vu = 10V50E, GrC = graphitized carbon catalyst.

Task 2 work with dispersed NSTF electrodes has progressed significantly in BP 3. Integrating new Pt/Ir NSTF alloys has been very promising for several reasons: (1) exceptional metal stability as shown in Figure 4, (2) increased surface area vs. Pt-only NSTF electrodes, and (3) the catalyst is transition metal free, which eliminates the concern for leached transition metals corrupting catalyst coated membrane performance and water management.

Significant effort has focused on identifying and overcoming dispersed NSTF cathode performance limitations. While activity and lower-current-density operation has been good, resistance-like performance losses have been high. ANL has used ultra-small angle X-ray scattering to show that metal-free Vulcan XC72 carbon agglomerates 50 times more severely than 10V50E. LANL has shown, using transmission line impedance, that dispersed NSTF has significantly higher protonic resistance losses than 10V50E while gas transport is good. NREL and 3M have shown that local oxygen transport of dispersed NSTF + Vulcan carbon systems is as good as or better than similar 10V50E systems. Tufts and MTU showed, using their model, that poor ionomer coverage of NSTF would lead to resistance-style performance losses. All these data together suggest that severe electrode agglomeration of NSTF + Vulcan XC72 + ionomer electrodes leads to local protonic transport losses that reduce performance. The cause of these losses may be that due to agglomeration, the NSTF catalyst is not well covered or connected to the ionomer, leading to local protonic transport resistance.

Significant effort has been undertaken by 3M to incorporate more conductive ionomers and develop alternate electrode ink formulations and manufacturing processes aimed at reducing these resistance-style losses. Some gains have been made as shown in Figure 5. Specifically, processing focused on breaking up carbon agglomerates (Process 1) did not significantly change performance. Processing focused on increasing ionomer coverage of the whiskers did result in performance improvements (Process 2, 2a).

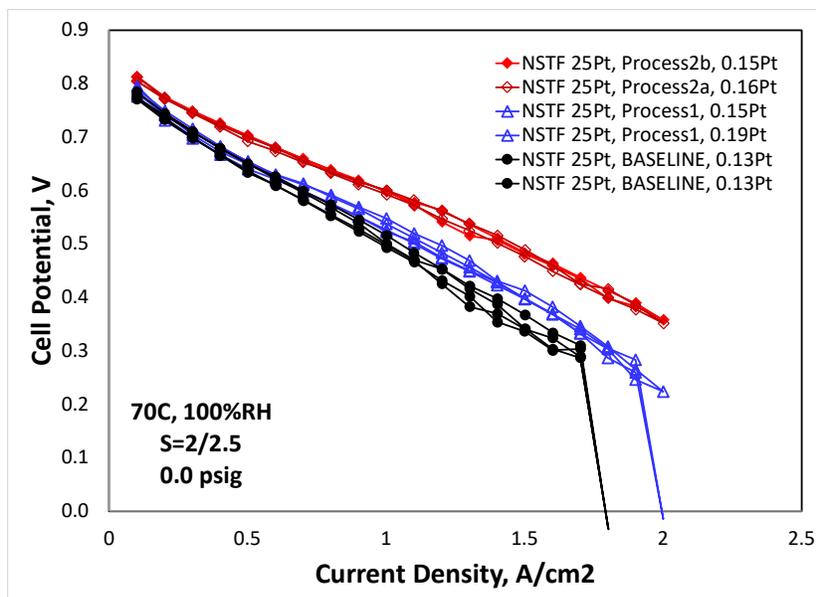


Figure 5. Dispersed NSTF + Vulcan XC72 + 3M725EW PFSA. I/C = 0.6, whisker/carbon wt % = 1.0, 70 °C, 100% RH, stoichiometry = 2.0/2.5 AN/CA, 0/0 psig AN/CA.

CONCLUSIONS AND UPCOMING ACTIVITIES

Newly developed electrode ionomers have exceeded all bulk oxygen permeability and bulk electrode conductivity project targets. PFIA thin film conductivity in electrodes has been shown to be 8x that of 3M825 PFSA, allowing reduction in I/C ratio from 0.8 to 0.4 without conductivity penalty. Performance, activity, support stability, and durability have been increased by reducing I/C ratio. Reducing I/C ratio and utilizing carbon free of platinum has resulted in increasing electrode agglomeration likely resulting in reduced protonic conduction near the catalyst. This has impacted metal on carbon systems at exceedingly low I/C ratios (<0.4) and dispersed NSTF + Vulcan XC72 systems. Processing focused on increasing catalyst-ionomer coverage has mitigated this limitation and improved performance.

Future work will build on these results, focusing on providing more protonic conductivity close to the NSTF catalyst surface. More advanced catalysts such as LANL's intermetallic PtCo on Vulcan system will be tested with PFIA at I/C = 0.3 in an attempt to achieve the entirety of the DOE project targets.

SPECIAL RECOGNITIONS AND AWARDS/PATENTS ISSUED

1. The National Institute of Standards and Technology has awarded neutron imaging beamtime to LANL and 3M through this project to study water location and concentration in a dispersed NSTF electrode system vs. typical 10V50E catalyst system.

FY 2019 PUBLICATIONS/PRESENTATIONS

Publications

1. S.J. Normile and I.V. Zenyuk, "Imaging Ionomer in Fuel Cell Electrodes with Two-Energies Transmission X-ray Microscopy Approach," *Solid State Ionics* 335 (2019): 38–46.
2. Gregory M. Su, Isvar A. Cordova, Jun Feng, Hiroshi Okuda, Cheng Wang, and Ahmet Kusoglu, "Chemical and Structural Origins of Water Uptake and Proton Transport in Perfluoro Ionene Chain Extended (PFICE) Ionomers," manuscript.

Presentations

1. "Understanding Fuel Cell Catalyst Layer Morphology and Its Transport Properties Via Advanced Diagnostics, Imaging and Modeling," PEFC&E 18 Symposia Plenary, Electrochemical Society Meeting, Cancun, Mexico (October 1, 2018).

2. I.V. Zenyuk, D. Sabarirajan, and P. Saha, “Understanding Ion Transport at Charged Interfaces with Application to Polymer Electrolyte Fuel Cells,” 69th Annual Meeting of the International Society of Electrochemistry, Bologna, Italy (September 5, 2018).
3. J. Liu and I.V. Zenyuk, “Bridging Micro and Nano Scales in Fuel Cell Electrodes Using Multi-Modal Imaging and Scale-Bridging Method,” InterPore 10th Annual Meeting and Jubilee, New Orleans, LA (May 15, 2018).
4. G. Su, I. Cordova, A. Kusoglu, and C. Wang, “Peering into Phase-Separated Perfluorinated Sulfonic-Acid Ionomers with Energy-Tunable X-rays,” APS Meeting, Boston, MA (March 2019).
5. A. Kusoglu, P. Dudenas, and A. Weber, “Effect of Side-Chain on Structure/Property Relationship of PFSA Ionomers,” APS Meeting, Los Angeles, CA (March 2018).
6. P. Dudenas, A. Weber, and A. Kusoglu, “Morphological Transitions in Ionomer Thin Films,” APS Meeting, Los Angeles, CA (March 2018).
7. A. Kusoglu, “Catalyst Ionomers in Fuel Cells,” ACS Meeting, Boston, MA (August 2018).
8. A. Kusoglu, “Interactions in Ionomers: Role of Chemistry and Confinement,” Asilomar PEMFC Conference, Asilomar, CA (February 2019).
9. A. Haug, “Novel Ionomers and Electrode Structures for Improved PEMFC Electrode Performance at Low PGM Loadings,” DOE Hydrogen and Fuel Cells Program Annual Merit Review and Peer Evaluation Meeting, Washington, DC (June 6, 2018).
10. “Novel Ionomers and Electrode Structures for Improved PEMFC Electrode Performance at Low PGM Loadings,” USCAR Tech Team Review (September 15, 2018).