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

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- Michigan Technological University, Houghton, MI
- Tufts University, Medford, MA
- Lawrence Berkeley National Laboratory, Berkeley, CA
- Oak Ridge National Laboratory, Oak Ridge, TN
- Argonne National Laboratory, Lemont, IL
- National Renewable Energy Laboratory, Golden, CO
- Los Alamos National Laboratory, Los Alamos, NM

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

Overall Objectives

The objective is to develop electrodes containing new ionomers and oxygen reduction reaction (ORR) electrocatalysts that exceed project-specific ionomer targets and the following DOE 2020 targets.

- Mass activity of 0.44A/mg_{PGM} or higher.
- Platinum group metal (PGM) total content (both electrodes) of ≤0.125 g/kW.
- PGM total loading (both electrodes) <0.125 mg_{PGM}/cm^2.
- Electrocatalyst mass activity durability of <40% loss.
- Metal stability accelerated stress test (AST) loss of performance <30 mV @ 0.8 and 1.5 A/cm^2.
- 2020 DOE support and start-up–shutdown (SUSD) targets.
- 50% ionomer conductivity and bulk oxygen permeability over 3M825EW.
- Membrane electrode assembly (MEA) robustness >70% at cold, hot, and transient conditions.
- Achieve a working electrode model investigating local water and gas transport through cathode electrodes.

Fiscal Year (FY) 2018 Objectives

- Develop an ionomer more conductive and 33% more oxygen permeable than 3M825.
- Achieve power targets of 0.175 g/kW.
- Achieve electrode activity targets of 0.35 A/mg_{PGM} with a nanostructured thin film (NSTF) catalyst greater than 25 m^2/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 Plan[1]:

(A) Durability

(B) Cost

(C) Performance

(D) Operational Robustness.

Technical Targets

Table 1 summarizes 2018 project status against the relevant 2020 DOE targets and project targets. All

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

reported status values are measurements made in membrane electrode assembly format.

So far, six of the overall targets have been achieved. This budget period (BP), a new imide-type ionomer (IMIDE#4) demonstrated a bulk oxygen permeability of 93% of the 3M825 baseline while showing 22% more conductivity. Dispersed metal on carbon electrodes containing new ionomers have achieved key performance targets while improving activity and metal stability.

The NSTF Pt/Ir catalysts developed in DE-EE0007077 (Steinbach) retain up to 70% of their metal activity when dispersed in ionomer-containing electrodes. The PtNiRu NSTF catalysts currently have achieved 0.31 A/mg$_{PGM}$ in the DOE 1,000-s hold activity test and higher (0.45 A/mg$_{PGM}$) in H_2/O_2 Tafel extraction. The NSTF Pt/Ir catalysts have demonstrated as low as 16% surface area loss and 33% activity loss. Dispersed NSTF electrodes with multiple support types have exceeded 5,000 DOE support cycles. Pt and PtCo on graphitized carbon supports have shown up to 45% activity increase (up to 0.30 A/mg Pt) in electrodes utilizing multi-acid side chain (MASC) ionomer at lower ionomer contents, and surface area losses as low as 36%. More active catalysts are being evaluated in this system with the goal of achieving activity and durability targets simultaneously.

FY 2018 Accomplishments

- Generated an imide-based ionomer with 92% more bulk oxygen permeability than the 3M825 baseline.
- Seven other novel ionomer types have been generated but have not shown oxygen permeability gains.
- Reduced electrochemical surface area (ECSA) loss from 90% (baseline) to 55% with base 10V50E and 10VA50E catalyst systems.
- Increased activity of 10VA50E by 45%.
- Tested an 10/10 Pt/Ir NSTF catalyst with 30 m^2/g_{PGM} ECSA that showed 15% surface area loss in the DOE metal AST.
- Tufts demonstrated 3M PFIA ionomer is inherently more conductive in an electrode than a perfluorosulfonic acid (PFSA) ionomer of similar ion exchange capacity.
- Identified a key protonic conductivity limitation of dispersed NSTF electrodes with Los Alamos National Laboratory.
- Los Alamos National Laboratory showed correlations between metal -containing and metal-free carbons and agglomeration.
- Michigan Technological University (MTU) correlated ionomer equivalent weight and electrode hydrophilicity.

Table 1. Status Against Technical Targets[a]

Metric	Units	Project Target	August 2018
PGM total loading	mg/cm^2	0.125	0.115[b]
PGM total loading, 150 kPa$_{abs}$	g/kW	0.125	0.125[b,d]
Mass activity @ 900 mV$_{iR\text{-}free}$	A/mg	0.44+	0.30/0.45
SUSD AST, % ECSA loss	%	<20	N/A
SUSD AST, loss @ 1.2 A/cm^2	mV	<5%	N/A
Support AST, mass activity loss	%	<30	<10% (Pt)
Electrocatalyst AST, mV loss @ 1.5 A/cm^2	mV	<30	80[e]
Electrocatalyst AST, % mass activity loss	%	<40	40% Pt, 33% Pt/Ir
MEA robustness (cold/hot/cold transient)[c]	%	>70/>70/>70	93/84/90
Ionomer conductivity (80°C, 50% RH)	S/cm	0.087 (+50%)	0.070 (+22%)
Ionomer bulk O_2 perm (80°C, 50% RH)	mol-cm-s^{-1}-cm^{-2}-kPa^{-1}	1.8E-13 (+50%)	2.3E-13 (+92%)

[a] All metrics and DOE 2020 targets are taken from DE-FOA-0001412.
[b] 0.025 mg Pt/cm^2 anode.
[c] 3M transient protocols used for NSTF testing.
[d] At 0.661 V, 80°/68°/68°C, 7.5 psig.
[e] At 70°/70°/70°C, 0 psig.
RH – relative humidity

INTRODUCTION

Among the various recommendations for fuel cell performance enhancement at low precious-metal loadings are increasing ionomer and electrode O_2 transport and increasing ionomer hydrophobicity. Further proposed limitations include local (near catalyst) water generation and flooding and transport losses due to alloying (non-platinum) 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 O_2 transport, integrate these into electrodes containing durable, active NSTF powder, and achieve DOE 2020 power and durability targets.

In Budget Period 2 (BP 2), several electrode-focused ionomers were generated and evaluated. Increased ionomer conductivity has led to improved electrode performance, and 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 Consortium for Performance and Durability, 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 is continuing in Budget Period 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 O_2 permeability, conductivity, and cathode performance. Ionomer development is proceeding along three paths: developing and evaluating multi-acid sidechain materials, imide-only materials (BP 1, BP 2), and more novel O_2-permeable ionomer structures (BP 2, BP 3). NSTF will then be integrated into this ionomer containing electrode framework. The best high-activity, durable ultra-thin film (UTF) alloy powders having a minimal number of monolayers (i.e., maximum ECSA) potentially achieve areas approaching 70 cm^2_{PGM}/cm^2_{planar} with specific activities as high as 4 mA/cm^2 with 0.105 mg PGM/cm^2. This is a theoretical mass activity entitlement of 2.5 A/mg_{PGM}, a 5-fold increase beyond the exceeding 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 more than 80% activity and still achieve DOE 2020 targets. Finally, optimizing 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 nanoCT imaging, grazing incident small-angle X-ray spectroscopy (GISAXS), transmission electron microscopy, water imbibition, and pore hydrophobicity/hydrophilicity 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 budget periods. 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#4 ionomer has been developed that exceed BP 2 targets and meet project targets for bulk oxygen permeability. As shown in Figure 1, IMIDE#4 showed a 92% increase in bulk oxygen permeability over the baseline. In general, the imide-based ionomers have shown increased oxygen permeability with IMIDE#2 and IMIDE#1 (not shown) showing improvements. New materials of this kind are being made in the hopes of furthering these gains. IMIDE#4 is showing the required conductivity improvements over 3M825 as well. Further, Tufts found that for electrodes containing carbon and ionomer, that multi-acid side chains are showing significantly improved conductivity over PFSA (3M825)—even when normalized to ion exchange capacity (Figure 2). Perhaps it is due to larger—and perhaps better connected—ionic domains as measured by

Lawrence Berkeley National Laboratory using GISAXS. Local oxygen-transport studies conducted by 3M, National Renewable Energy Laboratory, and Lawrence Berkeley National Laboratory have all confirmed that lowering the ionomer content of the electrode decreases local oxygen-transport resistance, which has been directly correlated to high current performance gains. It has not yet been validated that improved bulk oxygen permeability, inherent to the ionomer, results in local oxygen transport gains. That work presently is ongoing. Additional variables, such as choice of carbon support (Vulcan versus graphitized Vulcan), also seem to have an effect on local oxygen transport.

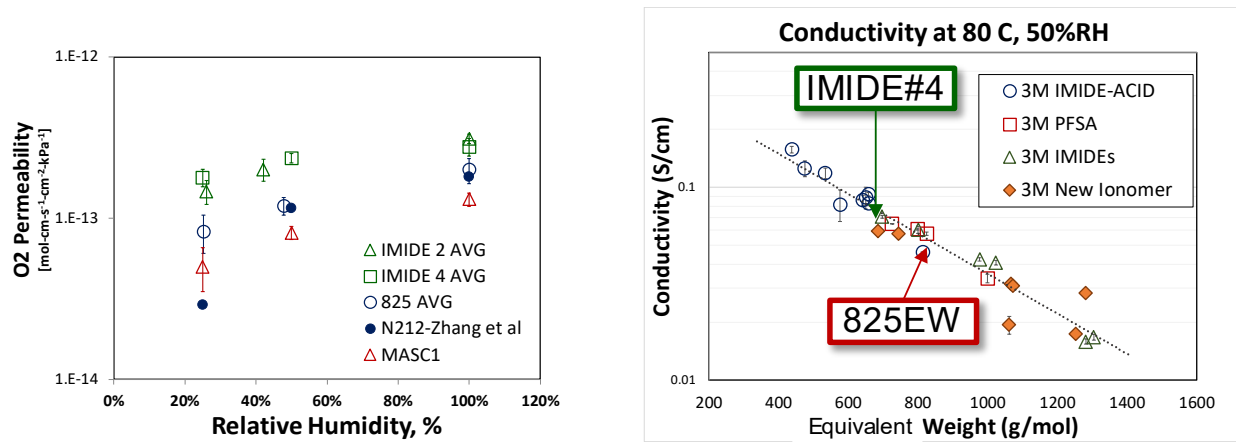

Figure 1. Conductivity (right) and oxygen permeability (left) of baseline PFSA and novel imide ionomers

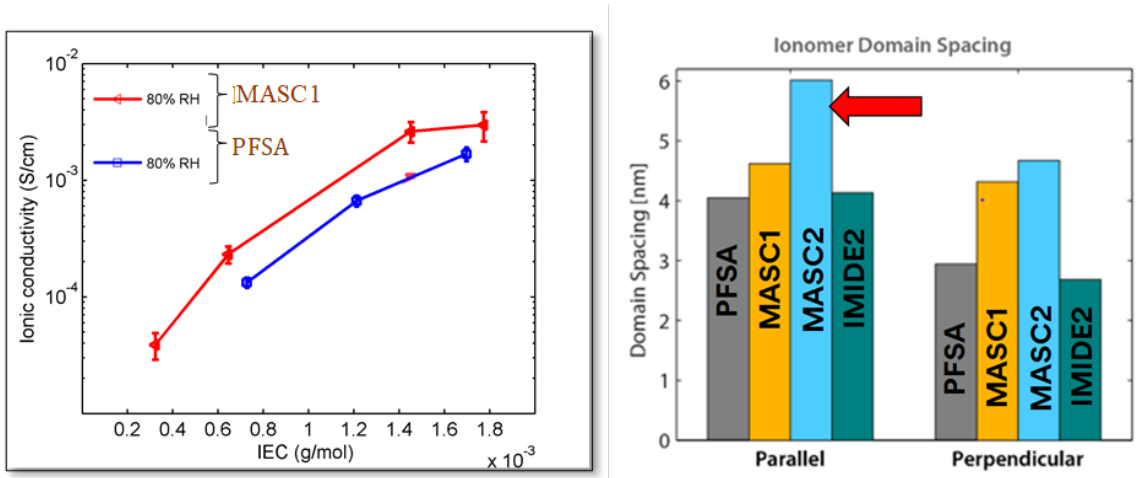

Figure 2. Conductivity normalized to ion exchange capacity of 3M825 PFSA versus multi-acid side chain 1 (MASC#1). Left is work by LBNL showing larger ionomer domains of MASC materials measured by GISAXS.

These gains have allowed less ionomer to be used in the electrode, giving rise to improved local oxygen transport in the electrode and improved performance, as shown in Figure 3. Further, both activity and durability have been improved using these electrodes. Activity gains of 45% have been made with graphitized Pt on C. 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 has further reduced metal area loss to 36%. Further improvements are expected here with better catalysts, new ionomer integration, and electrode configurations.

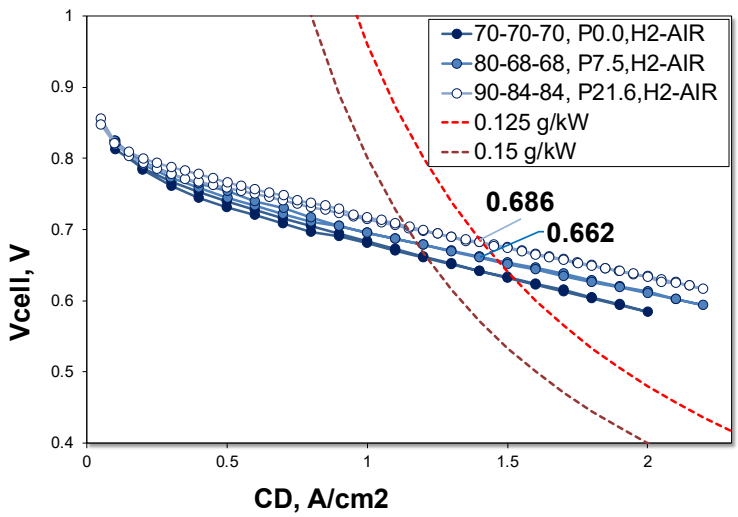

Figure 3. Performance at different conditions for best-in-class alloy at 0.095 mg Pt/cm² cathode loading

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

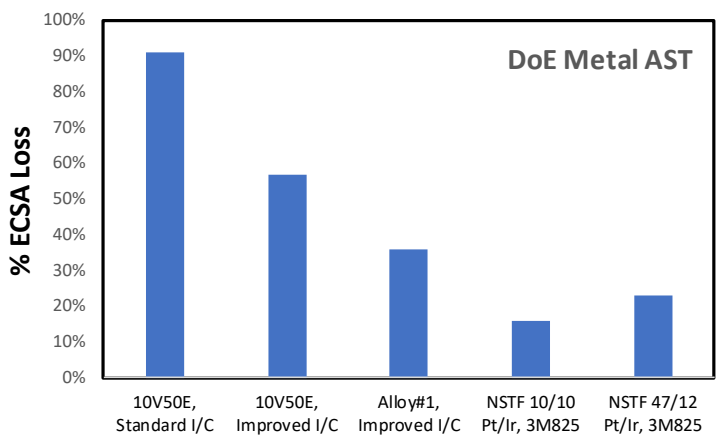

Figure 4. Cathode catalyst surface area loss occurring during DOE 30,000-cycle metal AST test (80 °C, 100% RH, H_2/N_2)

Task 2 work on electrodes has improved the activity retention when comparing classic NSTF Pt/Ir electrodes (whiskers laminated directly to a membrane) to dispersed ionomer-containing NSTF electrodes from ~33% to as much as 71%. Performance of a best-in-class 0.093 mg PGM/cm^2 NSTF cathode has achieved the target of 0.175 g/kW and demonstration surface area loss of only 23% in the DOE catalyst metal AST. Perhaps of more significance is that, despite the low surface roughness of this material, performance at moderate current densities is maintained, finally breaking the trend of performance versus surface roughness.

Performance of much of the dispersed NSTF materials has been reduced by what seems to be an additional resistance loss. Work with Los Alamos National Laboratory has investigated these materials utilizing advanced impedance techniques with the goal of possibly identifying this limitation. As shown in Figure 5, it is likely that dispersed NSTF electrodes suffer from an additional protonic transport limitation as compared to metal on carbon catalysts such as 10V50E (TKK). Based on the amount of ionomer present in the electrode (and ion

exchange capacity), this limitation more likely would be local to the catalyst. This is consistent with performance improvement seen utilizing lower-equivalent-weight ionomers. Work with multi-acid sidechain ionomers is shown to reduce this resistance loss, and now is being investigated using advanced impedance techniques. Analysis of this local transport loss is ongoing. MTU has used transmission electron microscopy analysis to show that it is highly likely that ionomer is present around the NSTF whisker in dispersed NSTF electrodes. Los Alamos National Laboratory also has demonstrated that gas transport in dispersed NSTF electrodes was quite good even at higher currents. This is consistent with work from Argonne National Laboratory that supports agglomerate more strongly. Agglomerated carbon-ionomer systems have many more regions where gas can pass unhindered by ionomer films, thereby incurring minimal bulk oxygen transport losses.

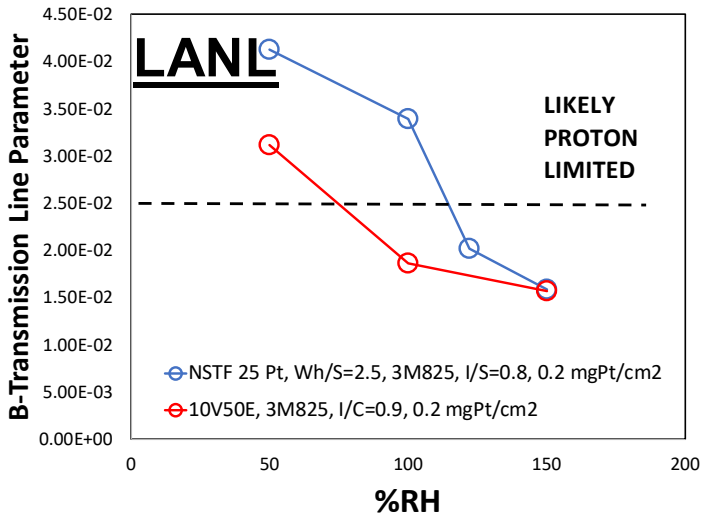

Figure 5. Transmission line impedance analysis of dispersed NSTF versus metal on carbon (10V50E) cathode electrodes performed by Los Alamos National Laboratory

In BP 2, Task 4 model development continued in collaboration with Tufts and MTU. Water generation and migration is being captured in the electrode. It is now being fitted against various data and parameters to better understand liquid water generation for different systems with different wettabilities.

CONCLUSIONS AND NEXT STEPS

New electrode ionomer development has exceeded oxygen permeability project targets with conductivity approaching overall targets. Led by understanding gained in multi-acid side chain ionomers in the electrode, local oxygen transport in the electrode has been reduced and performance increased. Metal-on-carbon stability has been improved by incorporating new ionomers. Dispersed NSTF stability and activity has been improved and local transport understanding is leading to performance gains. Key next steps are to continue the learning in the areas of local transport in electrodes and then apply this learning to best integrate the new ionomers and NSTF materials into the electrode in BP 3.

FY 2018 PUBLICATIONS/PRESENTATIONS

1. Abbou, S., K. Tajiri, E.F. Medici, and J. S. Allen, "Liquid Water Uptake and Contact Angle Measurement of Proton Exchange Membrane Fuel Cell (PEMFC) Electrodes," *Journal of the Electrochemical Society* (submitted).
2. Haug, A.T., "Novel Ionomers and Electrode Structures for Improved PEMFC Electrode Performance at Low PGM Loadings," USCAR Fuel Cell Tech Team, September 11, 2018, Detroit, MI.

3. Haug, A.T., 2018 Annual Merit Review, DOE Hydrogen and Fuel Cell Vehicles Technology Programs, Presentation FC143, June 2018, Washington, D.C.
4. Kusoglu, A., M. Tesfaye, D. Kushner, B. McCloskey, and A. Weber, "Thermal Transitions in Perfluorosulfonated Ionomer Thin Films," ACS Macro Letters (submitted).
5. Liu, J., 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, May15, 2018, New Orleans, LA.
6. Normile, S.J., and I.V. Zenyuk, "Imaging Ionomer in Fuel Cell Electrodes with Two-Energies Transmission X-ray Microscopy Approach," *Solid State Ionics* (Under Review, 2018).
7. Sabarirajan, D., and I.V. Zenyuk, Telluride Science Research Center Workshop: Interfacial Chemistry and Charge Transfer for Energy Conversion and Storage, July 22–27, Telluride, CO.
8. Saha, P., D. Sabarirajan, and I.V. Zenyuk, Gordon Research Conference: Electrochemistry, January 7–12, 2018, Ventura, CA.
9. Zenyuk, I.V., 3rd International Fuel Cells Workshop, Fuel Choices and Smart Mobility Summit, October 29–30, 2018, Tel Aviv, Israel.
10. Zenyuk, I.V., Electrochemical Society Meeting, October 1, 2018, Cancun, Mexico (PEFC&E 18 Symposia Plenary).
11. Zenyuk, I.V., Gordon Research Conference, Fuel Cells, July 29–August 3, 2018, Smithfield, RI.
12. Zenyuk, I.V., University of California, Irvine, Department of Chemical Engineering and Materials Science Engineering, February 23, 2018, Irvine, CA.
13. Zenyuk, I.V., University of South California, Aerospace and Mechanical Engineering, March 7, 2018, Los Angeles, CA.
14. Zenyuk, I.V., 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, September 5th, 2018, Bologna, Italy.