V.B.4 Novel Ionomers and Electrode Structures for Improved PEMFC Electrode Performance at Low PGM Loadings

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Overall Objectives

- Achieve DOE 2020 targets for platinum group metals (PGM) total loading, mass activity, startup-shutdown accelerated stress tests (ASTs), catalyst support ASTs, electrocatalyst ASTs, and membrane electrode assembly (MEA) robustness.
- Develop novel, electrode-focused ionomers, focusing on combining conductivity with improved oxygen transport.
- Integrate nanostructured thin film (NSTF) catalyst powder into a dispersed electrode structure.
- Integrate novel ionomers with state of the art NSTF powder electrocatalyst to develop an advanced cathode of high activity, performance, and durability.
- Investigate electrode transport at bulk, intermediate and local levels for limiting effects including ionomer gas and proton transport, and impacts of hydrophilicity and the transition metal.
- Guide development with state of the art and novel characterization and modeling techniques, including in-operando nano-computed tomography (CT) and electrode pore network models.

Fiscal Year (FY) 2017 Objectives

- Generate
  - Initial imide and multi-acid side chain (MASC) ionomers (at least three over Budget Period [BP] 1).
  - Initial NSTF powders (more than 25 g).
  - Baseline catalyst coated membranes (CCMs) and electrodes, novel CCMs and electrodes.
  - Set up and validate DOE ASTs, local O_2 transport test, O_2 permeability test; test and characterize baseline CCMs.
  - Characterize novel ionomers using rotating disk electrode (RDE), grazing-incidence small-angle X-ray spectroscopy (GISAXS), four-point conductivity, and O_2 permeability.
  - Characterize baseline electrodes and dispersed NSTF electrodes using nano-CT, water imbibition and capillary pressure testing, scanning electron microscopy with energy dispersive spectrum (SEM-EDS), and transmission electron microscopy (TEM).
  - NSTF powder electrode achieves mass activities ≥0.30 A/mg Pt, electrochemical surface area (ECSA) ≥15 m^2/g, surface enhancement factor (SEF) >40 m^2/m^2, and 0.7 robustness factor.
  - Ionomer material developed exceeds the bulk O_2 permeability of the baseline 3M825 ionomer, with similar or better proton conductivity to 3M825.

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.

(B) Cost

(A) Durability

(C) Performance: operational robustness

Technical Targets

Relevant DOE technical targets and progress as of May 1, 2017, are listed in Table 1.

FY 2017 Accomplishments

- Engaged subs and the Fuel Cell Consortium for Performance and Durability (FC-PAD), finalized statements of project objectives (SOPOs), completed all non-disclosure agreements (NDAs), and commenced research.
- Generated electrode and CCM baselines utilizing 3M825 ionomer, TKK 10V50E catalyst, and an ionomer to carbon ratio of 0.9.
- Generated dispersed NSTF powder exceeding 50 total grams and generated baseline dispersed NSTF cathodes with different ionomers, supports, and whisker metal loadings.
- Generated more than seven novel ionomers for electrode development, including materials containing amides and MASC.
- Generated more than fifty electrode types (different ionomers from 520–1100 equivalent weight [EW], ionomer to catalyst [I/C] ratios from 0.3 to 1.2, loadings from 0.03 mg Pt/cm^2 to 0.35 mg Pt/cm^2).
- Developed a bulk membrane O_2 permeability test process based on General Motors method.
- Achieved 30 m^2/g dispersed NSTF ECSA in cell, exceeding Budget Period 1 (BP1) and Budget Period 2 (BP2) second quarter (Q6) targets; and dispersed NSTF surface roughness up to 90 cm^2/cm^2, also exceeding BP1 targets.
- Achieved dispersed NSTF activities >0.26 A/mg Pt utilizing PtCoMn and PtNi NSTF powders.
- Achieved fourth quarter BP2 power target of 5.7 kW/gPt with initial best in class dispersed NSTF down-select.
- Exceeded DOE electrode support stability project targets utilizing dispersed NSTF, achieving 20,000 cycles.
- Analyzed dispersed NSTF materials with nano-CT.
- Evaluated perfluoroimide acide (PFIA) ionomer utilizing GISAXS, demonstrating potential transport benefits.
- Began development of more novel ionomer types with initial prospects targeted for fourth quarter 2017 (Q4) delivery.

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INTRODUCTION

Among the various recommendations for fuel cell performance enhancement at low precious metal loadings are increasing ionomer and electrode O_2 transport, and

TABLE 1. Progress towards Meeting Technical Targets for Electrocatalysts and MEAs for Transportation Applications

METRIC	2020[1] Target	Integrated Cathode	PROGRESS
PGM total loading, mg/cm^2	0.125	0.125	0.102[2]
PGM total loading, g/kW [150 kPa abs]	0.125	0.125	0.172[2]
Mass activity @ 900 mV iR-free, A/mg	0.44	0.44+	0.28
SUSD AST, % ECSA loss	<20 %	<20	N/A
SUSD AST, % mV loss @ 1.2 A/cm^2	<5%	<5%	N/A
Support AST, % mass activity loss	<30	<30	28% (Pt)
Electrocatalyst AST, mV loss @ 1.5 A/cm^2	<30	<30	NA
Electrocatalyst AST, % mass activity loss	<40	<40	45% (Pt)
MEA robustness (cold/hot/cold transient)	0.7/0.7/0.7	>0.7/>0.7/>0.7	0.6/NA/0.6[3]

[1]All metrics and DOE 2020 targets are taken from DE-FOA-0001412
[2]Assume using 0.025 mgPt/cm^2 anode
[3]3M transient protocols used for NSTF testing
abs – absolute; iR – internal resistance; SUSD – startup-shutdown; NA – not available

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 O_2 transport, integrate these into electrodes containing durable, active NSTF powder, and achieve DOE 2020 power and durability targets.

In BP1, several electrode-focused ionomers were generated and evaluated. Increased ionomer conductivity has led to improved electrode performance while lower ionomer content has shown some activity increases. For the first time, NSTF as a powder is being integrated into a more classic electrode structure. Most of its industry leading activity and durability has been maintained; DOE electrode support stability targets have been exceeded. Advanced NSTF alloys are showing promising activities and initial characterization of these electrodes by nano-CT, SEM and TEM, and mathematical models are underway. Integration efforts of these novel ionomers with dispersed NSTF has begun and will continue into BP2 and BP3 with the goal of meeting DOE performance and durability targets. The expected outcome is a cathode electrode and integrated CCM with increased activity, performance, and operational robustness over current state of the art, and which is suitable for stationary and automotive applications.

APPROACH

The approach will be to develop novel electrode-specific ionomers aimed at increasing O_2 permeability, conductivity, and cathode performance. Ionomer development will proceed along three paths: developing and evaluating MASC materials, imide-only materials (BP1, BP2), and more novel O_2 permeable ionomer structures (BP2, BP3). 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 ECSA) will 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 5X 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 UTF's 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-CT imaging, GISAXS, TEM, water imbibition, and pore hydrophobicity/philicity measurements.

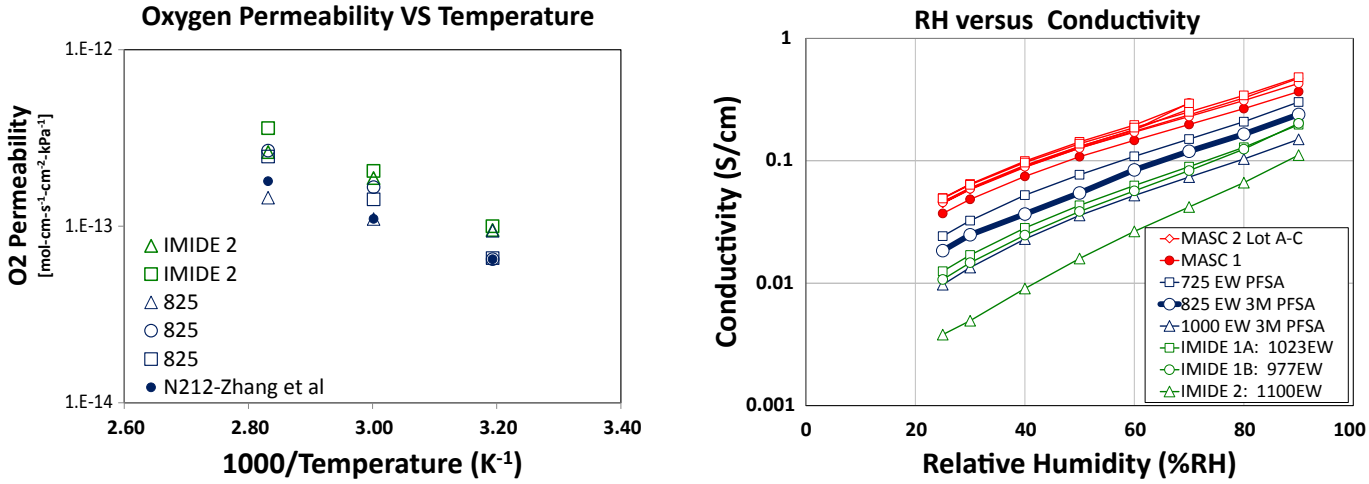
The proposed work is broken down into five tasks: electrode ionomer development and characterization (Task 1), advanced NSTF electrode development and characterization (Task 2), integration of novel ionomers and NSTF into electrodes (Task 3), model development (Task 4), and project management (Task 5). The project contains three 12-month 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

More than seven new ionomers and 25 g of NSTF powder have been generated, along with electrodes and CCMs of these under Tasks 1.1, 2.1, 2.3. Ionomers as low as 520 EW have been built into CCMs and evaluated. Additional carbon-ionomer electrodes (free-standing) of various types have been provided for evaluation. A procedure for measuring oxygen permeability of ionomer membranes has been developed in 3M based on the paper by Zhang et al [1]. Local oxygen transport techniques were adapted based on the work by Baker et al [2].

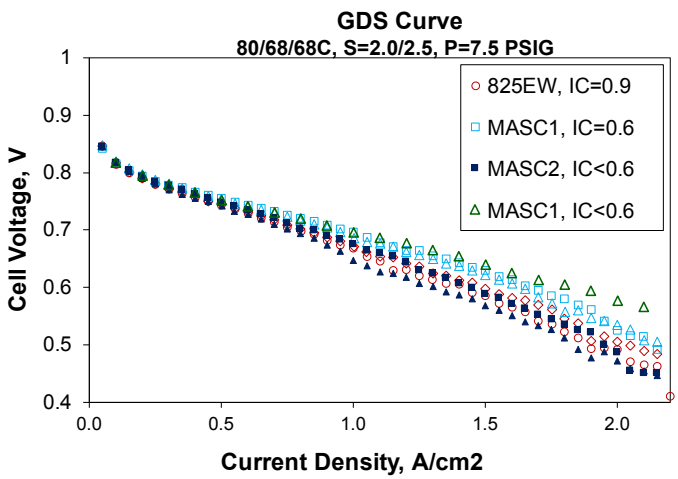
Initial conductivity and oxygen permeability tests were run on the new ionomers. As shown in Figure 1, Imide 2 is demonstrating oxygen permeability slightly above the baseline while Imide 1 is approaching baseline 3M825 perfluorinated sulfonic acid (PFSA) conductivity. As expected, MASC ionomers are showing exceptional conductivities. These results demonstrate that ionomer work is leading toward a BP1 ionomer goal of exceeding baseline ionomer conductivity and permeability simultaneously. Newer ionomers are expected to exceed both targets.

The initial baseline electrode for this project is the TKK 10V50E, 3M825 PFSA ionomer, and an ionomer to carbon ratio of 0.9 at 0.2 mg Pt/cm^2. A future, lower loading baseline will use 10V20E. All new ionomers are initially tested with 10V50E at various I/C ratios and loadings. As shown in Figure 2, MASC 1 performance under DOE conditions has significantly improved upon the baseline. A combination of high inherent conductivity and lower ionomer content likely leads to reduced bulk and local transport losses. Testing at 6% O_2 at 1 A/cm^2 leads to 100 mV gain over the baseline, while local transport testing is showing significant reductions in O_2 resistance losses (less than 10 S/m for total resistance). This result is further enhanced by GISAXS results from Lawrence Berkeley National Laboratory showing that PFIA ionomer (a MASC ionomer) produces a more random thin film structure, thereby becoming less of a barrier to oxygen permeation. Exceptionally low I/C ratios are demonstrating good promise for lowering local gas transport and improving performance. Further, lowering ionomer contact does seem to offer modest (10–15%) activity gains, especially with



RH – relative humidity

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



GDS – galvanodynamic scan

FIGURE 2. Performance curves for 10V50E at 0.2 mgPt/cm^2 with various ionomers and ionomer to carbon (IC) ratios

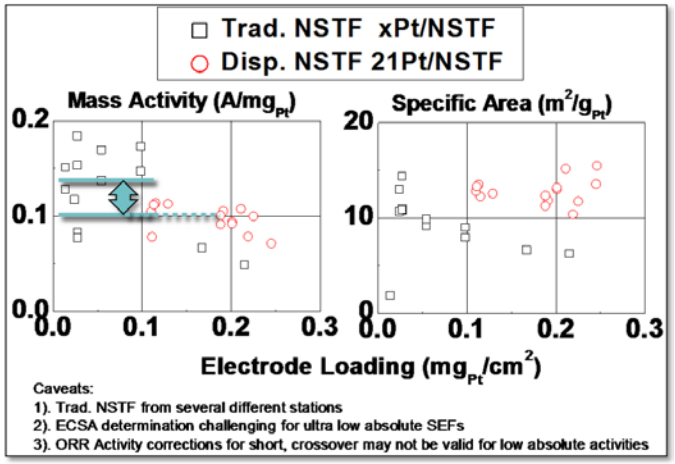
PFSA ionomers (725 EW and 825 EW). These down-selected materials will be further evaluated by transport testing and other means.

More conductive ionomers are showing some reduction in low temperature (40°C) performance. Baseline values at 0.4 V, 40°C are 1.6 A/cm^2, while MASC 1 at I/C = 0.9 is 0.9 A/cm^2. However, lowering I/C ratios are bringing these values up to >1.2 A/cm^2. An important part of upcoming work will be optimizing potentially more hydrophilic ionomers with wettable NSTF powder.

Initial work integrating powdered NSTF 2–25 µg/cm^2 Pt (geometric on liner) into an electrode resulted in cathodes that exceeded the initial surface area (ECSA) BP1 go/no-go of 15 m^2/g Pt. The ECSA of 15 ug/cm^2 Pt (geometric on liner) exceeded 25 m^2/g in fuel cell testing. It is clear that lowering the PGM on the whisker will increase the specific area to the point where Pt-only whiskers can achieve Milestone Q6 target of 25 m^2/g. Of greater significance is that the initial PtNi #1 sample down-selected from FC143 (A. Steinbach, Principal Investigator) [4] (28 ug/cm^2 Pt on liner as Pt38Ni62) shows 26-28 m^2/g ECSAs at relatively high Pt loadings on the whisker. Based on current data, a path to >35 m^2/g PGM seems probable. Down-selects from FC143 [4] show promise of further specific area increases. Further, surface roughness up to 90 cm^2/cm$^2_{GEO}$ have been achieved for powdered NSTF cathodes, well exceeding BP1 goals.

Electrodes containing powdered NSTF, support and ionomer have significantly improved operational robustness, especially at low temperatures, approaching the target of 70% peak power. Of more significance is that activity and durability, NSTF differentiators, can largely be maintained. Figure 3 shows roughly 33% mass activity is lost for NSTF electrodes containing ionomer. This is unexpected considering the ionomer has good opportunity to poison the NSTF surface, and encouraging for achieving project activity targets. Thus, mass activities of 0.28 A/mg Pt have been achieved with dispersed NSTF to date. Initial performance results with PtNi #1 are very promising. For a loading of 0.077 mg PGM/cm^2, and assuming and anode of 0.025 mg Pt/cm^2, a power output of 0.171 g/kW has been achieved. This exceeds the Milestone Q6 and BP2 go/no-go points. What is more significant about this result is that the dispersed package seems to handle the transition metals in the electrode.

Additionally, NSTF powdered electrodes have achieved support durability targets of 5,000 AST cycles with 5% activity loss. More than 20,000 cycles have been run without



ORR – oxygen reduction reaction

FIGURE 3. Mass and specific area comparisons for traditional NSTF and powdered NSTF electrodes. The left plot shows the mean differences in mass activity for comparable whiskers showing ~33% activity loss for the powdered NSTF electrode.

failure. NSTF powdered electrodes are also showing promise for achieving electrocatalyst durability targets, currently showing 50% metal area loss vs. 90% for 10V50E in the electrocatalyst AST.

Further, with new ionomers, and more knowledge about how to improve the dispersed NSTF cathode electrode package, it is likely that both performance, activity and power density will improve. Fundamental characterization of NSTF electrodes are underway as well, as shown in Figure 4. TEM and nano-CT can isolate NSTF materials. Imagery and data will be used to diagram ionomer, pore and solid structure of these electrodes. Resulting structures, performance differences, and the impacts of decay will be used in pore network model development.

In summary, ionomers novel ionomers are showing some promise for oxygen permeability, performance, and activity improvements. Dispersed NSTF is showing results for activity and durability above what was expected for the early stages of this project. Much of the NSTF electrode emphasis of this project will be to improve the power output of the NSTF material as a dispersed catalyst. Here is where the combination of 3M materials generation with Tufts, Michigan Technical University, and FCPAD's analysis will focus ionomer development, provide insight on electrode local transport, and integration.

CONCLUSIONS AND UPCOMING ACTIVITIES

Conclusions

- Initial dispersed NSTF electrode testing shows good operational stability. Low temperature performance issues of classic NSTF are eliminated as increasing support is added.
- Initial dispersed NSTF testing shows very little activity loss (0–25%) versus conventional NSTF. This is critical to the project's success and differentiation. Other unsupported catalysts show up to 95% activity loss.
- Initial dispersed NSTF alloy testing resulted in mass activities close to year one targets (0.28 A/mg Pt achieved with target of 0.30 A/mg Pt).
- Initial results show NSTF with support can exceed DOE support AST targets. Up to 20,000 cycles were achieved.
- Initial electrocatalyst durability cycling with low (25 ug/cm^2) whisker loading (0.1–0.2 mg Pt/cm^2 electrode loading) shows good catalyst stability. Down-selected samples from A. Steinbach [3] will likely improve upon this.
- Initial imide ionomers achieve good activity and performance. MASC ionomers show paths to improved performance and lower transport losses. Imide materials are showing good performance and moderate O_2 permeability improvements.

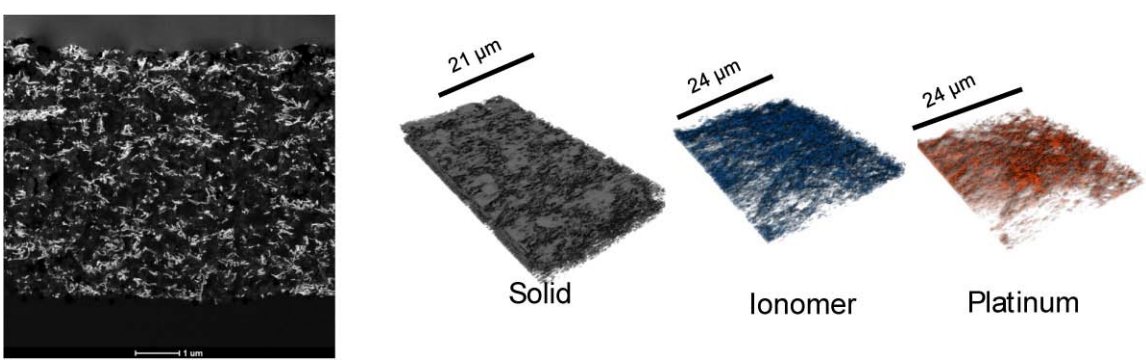


FIGURE 4. Characterization of powdered NSTF electrodes by TEM (Oak Ridge National Laboratory), and nano-CT (Tufts)

Upcoming Activities (BP2)

- Additional new ionomers with increasingly novel oxygen permeability-focused structures will be generated and evaluated.
- Transition metal impact of NSTF alloys on dispersed electrode performance will be evaluated and minimized.
- Quarterly testing of best-in-class NSTF down-selects from FC143 [4].
- Integration of dispersed NSTF with novel ionomers will commence.
- The pore network model is operational and and will begin its first predictions.
- An electrode water imbibition/capillary pressure diagram will be developed.
- In-operando nano-CT will continue to be developed.
- Additional new ionomers will be evaluated through GISAXS, including imide-only materials.
- Additional cathode baselines will be developed to better evaluate in-cell ionomer poisoning and lower loaded operation.
- RDE evaluation of novel ionomers for Pt poisoning will be conducted.
- Powdered NSTF electrodes will be evaluated with TEM for performance and decay characteristics.

FY 2017 PUBLICATIONS/PRESENTATIONS

1. FC155 at DOE's Annual Merit Review in Washington, D.C., on June 6, 2017.

REFERENCES

1. Zhang et al., J. Electrochem. Soc., 160, F616 (2013).

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3. A. Steinbach, GM DOE project FC144 entitled "Highly-Accessible Catalysts for Durable High-Power Performance." Award# DE-EE0007271.

4. A. Steinbach, 3M DOE project FC143 entitled "Highly Active, Durable, and Ultra-low PGM NSTF Thin Film ORR Catalysts and Supports." Award# DE-EE0007270.