
Durable High-Power Membrane Electrode Assemblies with Low Platinum Loading

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Subcontractors:

- University of Texas, Austin, TX
- Giner, Inc., Newton, MA

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Project End Date: March 31, 2020

Overall Objectives

- Identify best-in-class materials and generate a state-of-the-art (SOA) membrane electrode assembly (MEA) that meets DOE 2020 performance and cost targets.
- Study the impact of operating conditions on durability of SOA MEAs in differential cell conditions supported with advanced electrochemical and analytical characterization.
- Develop a predictive model for electrode and membrane degradation and recommend implementable benign operating conditions to prolong MEA durability to >5,000 h.

Fiscal Year (FY) 2018 Objectives

- Down-select and integrate best-in-class catalyst, ionomer, and membranes to generate SOA MEAs that will meet DOE 2020 performance and cost targets. Deliver 5-cm² and 50-cm² SOA MEAs to Fuel Cell

Consortium for Performance and Durability (FC-PAD) partners for durability studies.

- Conduct a systematic study to understand the role of catalyst and ionomer properties on measured polarization curve, activity, and transport properties of the catalyst layer.
- Initiate H₂-N₂ voltage cycling to study the effect of operating conditions on durability.
- Develop a combined accelerated chemical and mechanical stress test for membrane degradation. Explore degradation mechanisms.

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.

Technical Targets

Table 1 shows the DOE technical targets and current project status.

FY 2018 Accomplishments

- Several best-in-class catalysts, ionomers, and membranes were tested for activity and performance. The best-in-class materials were integrated to generate a SOA MEA.
- The final SOA MEA design exhibits >1.0 W/cm² and Q/ΔT <1.45 and platinum group metal (PGM) content (g/kW rated) of ~0.1 mg/cm² MEA or 10 kW/g PGM. Additional DOE metrics are shown in Table 1.
- Roles of carbon support on activity and transport properties were identified. Carbon micropore and macropore surface area was found to impact both oxygen and proton

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

- transport resistance. The expectation for an ideal carbon support was laid out.
- Performance variation due to ionomer distribution for different catalysts (HSC-a vs. HSC-g) and ink formulations (low to high alcohol fraction) was demonstrated by catalyst layer ionomer mapping studies at Oak Ridge National Laboratory.
 - Among different ionomer chemistries studied, the equivalent weight (EW) of the ionomer was the dominant factor in determining ionomer solution properties, catalyst ink properties, and catalyst layer performance. The side chain lengths considered in this study did not have a significant impact.
 - A combined highly accelerated chemical and mechanical stress test (HAST) was developed. The HAST indicates that higher mechanical stress can accelerate chemical degradation.
 - Several analytical methods involving Fourier transform infrared spectroscopy (FTIR), ultraviolet, and X-ray fluorescence (XRF) were developed to monitor Ce^{3+} movement. A two-chamber relative humidity (RH) gradient cell was devised at Giner to measure Ce^{3+} movement via convection.
 - Ce^{3+} movement via both diffusion and convection was measured. Initial studies indicate convection to be the dominant process.
 - Demonstrated use of X-ray computed tomography at Lawrence Berkeley National Laboratory for identifying shorts due to gas diffusion layer fibers in MEAs.

Table 1. Progress Toward Meeting Technical Targets for Electrocatalysts and MEAs for Transportation Applications

Characteristic	Units	DOE 2020 Catalyst and MEA Targets	Project Status (50 cm ² cell) 94 °C, 250 kPaa	Project Status (50 cm ² cell) 80 °C, 150 kPaa
Mass activity	A/mg _{PGM} @ 0.9 mV _{iR-free}	≥0.44	0.65	0.65
Specific activity	μA/cm ² _{PGM} @ 0.9 mV _{iR-free}	≥720	1,477	1,477
I @ 0.8 V	A/cm ²	0.3	0.44	0.30
MEA performance	mW/cm ² _{geo} @ 675 mV	≥1,000	1,275	1,000
Durability with cycling	Hours @ <10% V loss	5,000	TBD	TBD
Q/ΔT	KW/°C	1.45	1.45	1.94
PGM total loading	mg-PGM/cm ² _{geo}	≤0.125	≤0.125	≤0.125
PGM content	g/KW rated mg/cm ² MEA	≤0.125	0.1	0.125

INTRODUCTION

GM and other automotive MEA developers have achieved very impressive beginning-of-life performance using low-Pt (0.05–0.1 mg_{Pt}/cm²) loaded cathodes with PtCo alloys and thin (10–15 micron) membranes. Unfortunately, these MEAs are subject to life-limiting degradation during operation, especially at peak power, because of complex degradation mechanisms that are highly sensitive to the materials, MEA design, and fuel cell operating strategy. Specifically, power degradation of the cathode occurs via Pt and Co dissolution as well as deterioration of O₂ transport properties. Additionally, thin membranes are subject to failure due to manufacturing defects in the adjacent gas diffusion media and electrodes and the formation of membrane-attacking radical species caused by high gas crossover. This project is designed to systematically study these degradation phenomena in a SOA MEA, applying and extending diagnostic and modeling tools available at GM, its partners, and the FC-PAD consortium.

APPROACH

The project approach is based on our understanding that there is substantial opportunity to select operating conditions and voltage waveforms to reduce life-limiting electrode and membrane degradation rates. In this project, we intend to map the impact of operating conditions on SOA MEA durability for proton exchange membrane fuel cells (PEMFCs). This will be achieved by systematic durability studies relying on advanced characterization tools, degradation mechanism model development, and validation. Specifically, the project approach is to improve MEA performance and durability by executing the following work elements: (1) integrating the BIC materials to generate an SOA MEA in Budget Period (BP) 1, (2) incorporating systematic durability studies to assess the impact of operating conditions on MEA life, (3) conducting extensive postmortem characterization of MEAs to provide mechanistic understanding of MEA degradation along with developing and validating models to predict electrode and membrane degradation, and (4) recommending benign, yet realistic operating conditions to extend MEA durability past the 5,000-hour DOE 2020 durability target.

RESULTS

The goal of BP 1 was to generate a SOA MEA that meets or exceeds the DOE 2020 performance targets. Accordingly, in 2018, the SOA MEA was generated with use of BIC materials. As illustrated in Table 1 and Figure 1, the SOA MEA performance exceeds the criteria of 1 W/cm² at rated cell voltage of 0.67 V. The final SOA MEA design exhibits >1.275 W/cm² and Q/ΔT <1.45 and PGM content of 0.1 g/kW rated (10 kW/g PGM) at 250 kPaa and 94°C. The SOA MEA meets 1.0 W/cm² (rated 0.67 V) even at 80°C, 150 kPaa conditions, albeit at a less stringent heat rejection criteria of Q/ΔT = 1.94. The 5-cm² and 50-cm² MEAs were provided to the National Renewable Energy Laboratory (NREL) for confirmation testing and follow-up studies. As shown in Figure 1, the performance loss terms were quantified with differential cell diagnostics and use of an improved 1-D model. Such high performance, exceeding DOE targets, was achieved by systematic down-selections of catalysts (six), ionomers (nine), and membranes (three), followed by optimization using a design of experiment approach. The final SOA MEA design included a 12 μm perfluorosulfonic acid membrane with expanded polytetrafluoroethylene reinforcement, 30% PtCo/HSC-a on the cathode electrode with mid side chain ionomer (825 EW) at 0.9 I/C.

In addition to down-selection of the materials, one of the main objectives was to attain insights into the activity and transport properties of the catalyst layers. Measurements were conducted in 5-cm² differential cells with electrochemical diagnostics such as H₂-N₂ impedance for proton transport resistance [1], limiting current for oxygen transport resistance [2], CO measurements as a function of RH for Pt accessibility [3], and O₂ pol curve for activity measurements. Catalyst candidates were also characterized by transmission electron microscope measurements (University of Texas Austin) for particle size distribution and Brunauer-Emmett-Teller measurements for pore size distribution. The catalyst candidates are ~30 wt% PtCo (3:1 atomic ratio) supported on different carbon supports, both solid and porous carbon. Transmission electron microscope measurements indicate distinct advantage for porous high-surface-area carbon supports for a more uniform and smaller nanoparticle distribution. It is also reflected in the ECSA and mass activity measurements.

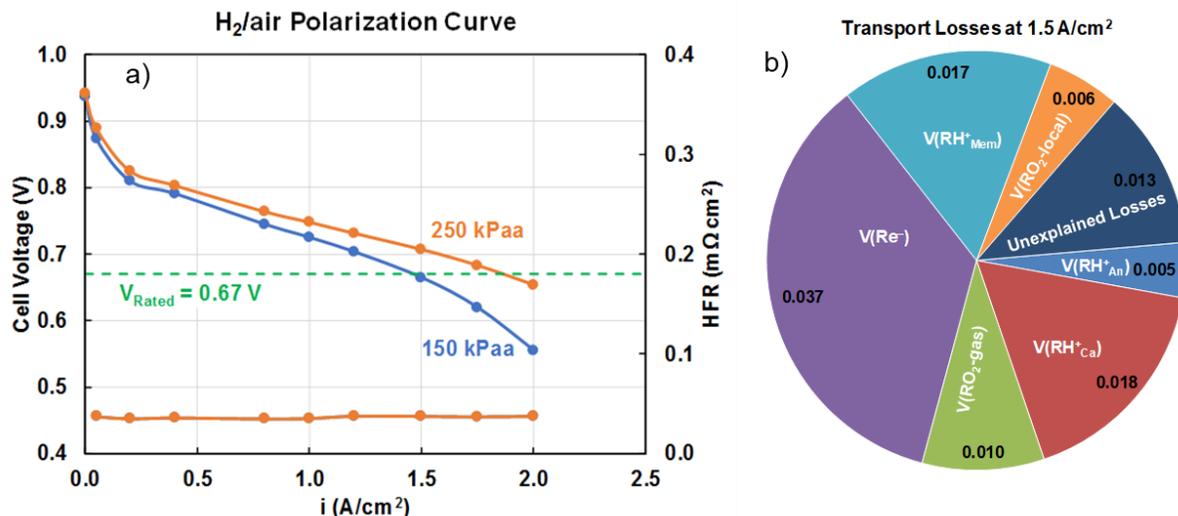


Figure 1. (a) Performance of SOA MEA as measured in 50-cm² cell. Conditions: 150 kPaa, 80 °C, 100% RH; and 250 kPaa, 65% RH, 94 °C. (b) Transport losses at 1.5 A/cm².

One important insight from this study is the impact of the carbon support on transport properties. Figure 2a shows the dependence of oxygen transport resistance and proton transport resistance on carbon surface area properties. Oxygen transport resistance is significantly reduced for catalysts with lower micropore surface area (<2 nm). Similarly, the proton transport resistance scales with macropore carbon surface area. In this study, macropore surface area is defined as pore size greater than 8 nm. So, an ideal carbon support should have a higher total surface area and mesopore surface area (4–7 nm) and lower micropore (<2 nm) and macropore (>8 nm) surface area.

For the ionomer study, several ionomer candidates at different EW and side chain length were considered. The ionomer solutions were characterized by advanced characterization methods such as ultra-small-angle X-ray scattering (USAXS) (at Argonne National Laboratory), grazing-incidence small-angle X-ray scattering (at Lawrence Berkeley National Laboratory), and other properties like molecular weight by size-exclusion chromatography, viscosity measurements, proton conductivity, and water uptake. All the measurements indicate that the impact of side chain length and chemistry considered in this study had minimal impact. The property variation was dominated by the equivalent weight of the ionomer. Scatterer size (nm) (from USAXS) indicative of ionomer aggregates was found to increase with EW. The lower scatterer size and smaller aggregates were found to reduce the particle size distribution of catalyst ink as measured by laser diffraction studies. For MEA tests, the ionomer content (I/C) was normalized to account for the difference in EW. The lower-EW ionomer had a significant improvement on performance at high current density as shown in Figure 2b. Despite I/C normalization in the catalyst layer, the lower-EW ionomers exhibited lower proton transport resistance and most of the performance improvement for lower-EW ionomers could be explained by the decreased transport resistance.

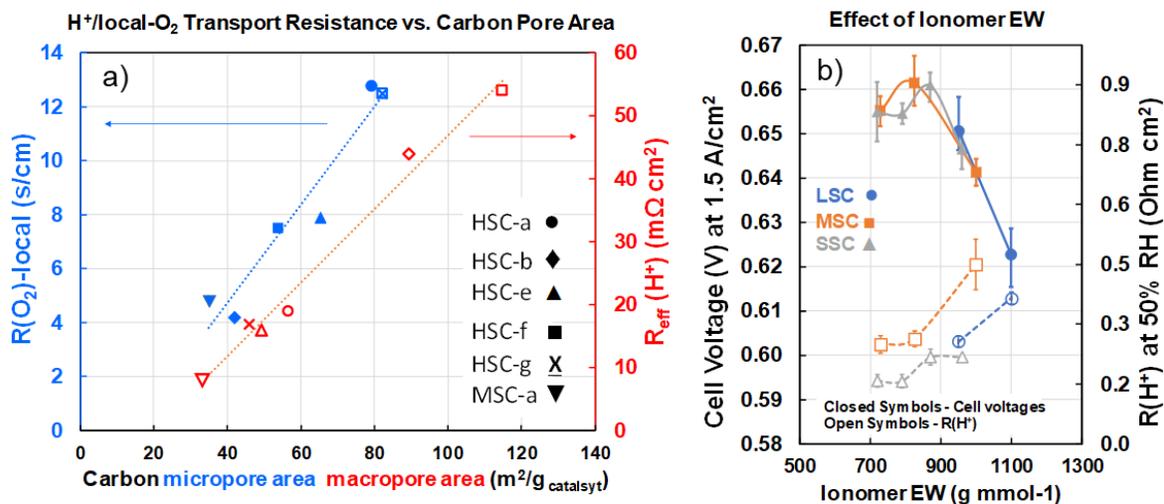


Figure 2. (a) Local oxygen transport resistance (closed symbols) and proton transport resistance (open symbols) dependence on carbon micropore and macropore surface area. (b) Proton transport resistance and cell voltage at 1.5 A/cm² as a function of ionomer EW.

A highly accelerated stress test (HAST) was developed to generate local stressful conditions that are both chemical and mechanical in nature. HAST involves a 50-cm² cell cycled between 0.05 A/cm² and 1.2 A/cm² with a low inlet RH in the co-flow configuration. This results in maximum chemical stress occurring near the gas inlets and the maximum mechanical stress near the outlets. The HAST was conducted using a current distribution tool providing a quantitative measure of mechanical stress (high frequency resistance [HFR]) and state of health (X-over measurement). Current, HFR, voltage, and water content (λ) profiles of the HAST are shown in Figure 3. The results indicate severe membrane thinning (chemical degradation in nature) at the outlet region where mechanical stress is high due to severe membrane hydration cycling. It was also found that the Ce concentration (measured by XRF) was depleted at the location of membrane failure (cathode outlet), possibly from the stronger water flux. To ascertain whether the chemical degradation of membrane was from Ce depletion due to stronger water flux, or increased mechanical stress due to humidity cycling, the test was repeated without the chemical mitigant—Ce. Preliminary tests of non-Ce-containing membranes exhibit chemical degradation at the same location indicating possible interaction between mechanical stress and chemical degradation.

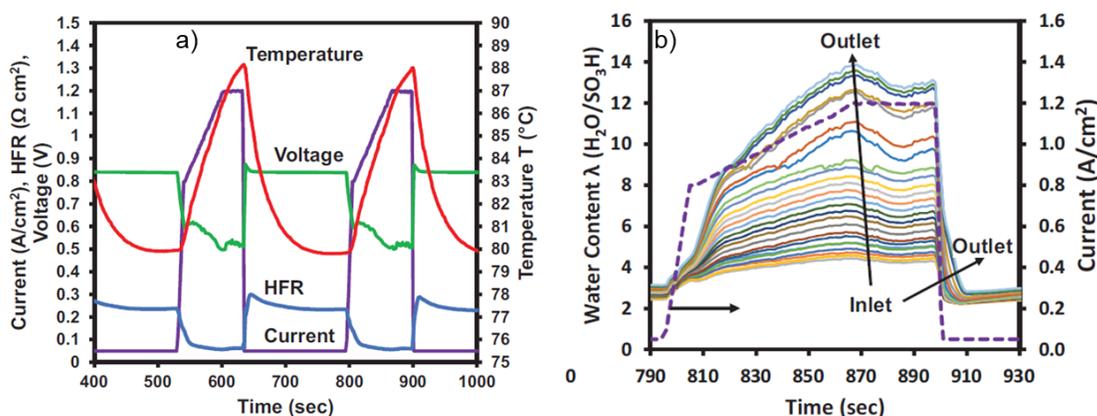


Figure 3. (a) HAST profiles of cell current, HFR, temperature, and voltage. (b) Close up of λ (solid) and current (dashed line) profiles from 790 to 930 sec.

The rapid movement of Ce^{3+} resulted in additional studies to quantify the Ce^{3+} migration mechanism as well as quantify migration rates due to diffusion and convection. Ce^{3+} diffusion measurements were conducted by applying a droplet of Ce^{3+} solution of known concentration and monitoring its movement with the FTIR method. The FTIR method uses the linear relationship between percentage Ce^{3+} complexation and absorbance at $1,726 \text{ cm}^{-1}$ [4]. Figure 4a shows the strong dependence of Ce^{3+} diffusion coefficient on RH (λ) and temperature. A 25-fold change in magnitude was observed between 100% and 50% RH followed by a further significant drop at lower RH. To quantify Ce^{3+} movement via convection, a two-chamber RH gradient cell as shown in Figure 4b was used. A thin strip of membranes with localized Ce was exposed to RH gradient in this cell and Ce^{3+} movement was monitored with the FTIR method. As shown in Figure 4c, the localized Ce^{3+} of Sample 1 near the RH gradient exhibited rapid movement from the high RH chamber to the low RH chamber. Sample 2 also exhibited movement to the low RH chamber after 36 h (not shown). The rapid movement due to RH gradient is indicative of the dominant role of convection in Ce^{3+} movement.

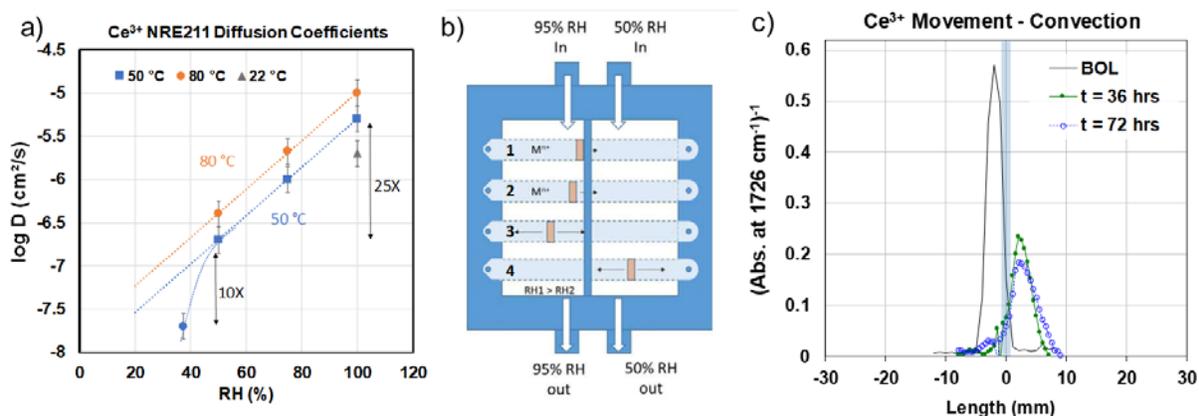


Figure 4. (a) Ce^{3+} diffusion coefficients as function of RH and temperature. (b) Two-chamber RH gradient cell. (c) Ce^{3+} profile as a function of time in the two-chamber RH gradient cell.

UPCOMING ACTIVITIES

For the remainder of 2018 and Budget Period 2, the project will focus on electrode and membrane durability studies. Key activities will be conducted in collaboration with FC-PAD partners and are as follows:

- H_2 - N_2 voltage cycling tests in various voltage waveforms and operating conditions at the National Renewable Energy Laboratory. Electrochemical diagnostics, including limiting current and others, to quantify voltage loss terms of the end-of-test MEA (GM/National Renewable Energy Laboratory).
- End-of-test MEA characterization for platinum dissolution, cobalt dissolution, particle size distribution quantification (GM/University of Texas Austin), and alloy structural changes (Oak Ridge National Laboratory).
- PtCo dissolution measurements at different potentials using an online inductively coupled plasma–mass spectrometer (Argonne National Laboratory).
- Confirm dominant Ce migration mechanism and quantify diffusion and convection coefficient to support Ce migration model and its incorporation in combined chemical and mechanical stress model.
- Open circuit voltage and H_2O_2 vapor cell tests to understand impact of membrane thickness on chemical degradation rates and mechanism.
- Conduct X-ray computed tomography on pre-shortened MEAs to visualize shorting and its propagation under HAST conditions (GM/Lawrence Berkeley National Laboratory).

FY 2018 PUBLICATIONS/PRESENTATIONS

1. N. Ramaswamy and S. Kumaraguru, “Materials and Design Selection to Improve High Current Density in PEMFC,” *ECS Transactions* 85, no. 13 (2018): 835–842.
2. F. Coms, S. Schlick, and M. Danilczuk, *The Chemistry of Membranes Used in Fuel Cells: Degradation and Stabilization* (Hoboken: Wiley, 2018): 75–106.
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5. C. Gittleman, Y. Lai and F. Coms, “Durability of Polymer Electrolyte Membranes for Automotive Application,” Invited presentation, AiMES 2018, Cancun, Mexico, October 2018.
6. N. Ramaswamy, V. Konduru and S. Kumaraguru, “Effect of Ionomer EW and Side Chain Length on Catalyst Layer Transport Resistances,” AiMES 2018, Cancun, Mexico, October 2018.

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