Durable High-Power Membrane Electrode Assemblies with Low Platinum Loading

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Contract No: DE-EE0007651

Subcontractors:
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• Giner, Inc., Newton, MA

Project Start Date: April 1, 2017
Project End Date: August 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) 2019 Objectives

• Verify performance, activity, and transport properties of 5-cm² and 50-cm² SOA MEAs at Fuel Cell Performance and Durability (FC-PAD) consortium partners for durability studies.
• Execute H₂-N₂ voltage cycling studies to evaluate the impact of operating conditions on electrode and membrane durability. Demonstrate >35% reduction in electrochemical surface area (ECSA) loss can be achieved by controlling operating conditions.
• Study membrane degradation factors such as operating conditions, cation migration, presence of local shorts, and membrane thickness.

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 Plan⁴:
• (A) Durability
• (B) Cost
• (C) Performance.

Technical Targets

The DOE technical targets and our current project status are listed in Table 1 for comparison.

FY 2019 Accomplishments

• The SOA MEA performance was verified in multiple single-cell platforms (5 cm², 10 cm², 50 cm²). The SOA MEA exceeds the criterion of 1 W/cm² @ 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 or 10 kW/gPGM was achieved (at 250 kPaₐ and 94°C).
• H₂-N₂ voltage cycling tests at various operating conditions were performed. Tests with a single-factor variable, such as relative humidity (RH), and multi-factor variables (as design of experiments) were executed.
• Reducing operating RH to 70% resulted in >35% reduction (go/no-go criteria) in ECSA

loss vs. 100% RH operating condition (as shown in Figure 1b).

- A combined highly accelerated chemical and mechanical stress test (HAST) was developed and failure mechanisms were proposed. Failure of Ce-free MEAs in HAST at similar locations highlighted a correlation between mechanical stress and chemical degradation.

- HAST studies at different operating temperatures indicated a ~7X higher degradation rate for a 20°C increase in temperature over 70°C.

- Transport of cations such as Ce\(^{3+}\) was found to be dominated by convection rather than diffusion. A cation transport model was developed, and transport coefficients were extracted by fitting with experimental data.

- A method to introduce local shorts by increasing cell compression and measure the same with a segmented cell was developed and tested. The use of X-ray computed tomography for identifying shorts due to gas diffusion layer fibers in MEAs was demonstrated at Lawrence Berkeley National Laboratory.

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

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Units</th>
<th>DOE 2020 Catalyst and MEA Targets</th>
<th>Project Status (50 cm(^2) cell) @ 94°C, 250 kPa(_a))</th>
<th>Project Status (50 cm(^2) cell) @ 80°C, 150 kPa(_a))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass activity</td>
<td>A/mg(<em>{\text{PGM}}) @ 0.9 mV(</em>{\text{R-free}})</td>
<td>≥0.44</td>
<td>0.65</td>
<td>0.65</td>
</tr>
<tr>
<td>Specific activity</td>
<td>µA/cm(^2)(<em>{\text{PGM}}) @ 0.9 mV(</em>{\text{R-free}})</td>
<td>≥720</td>
<td>1477</td>
<td>1477</td>
</tr>
<tr>
<td>I @ 0.8 V</td>
<td>A/cm(^2)</td>
<td>0.3</td>
<td>0.44</td>
<td>0.30</td>
</tr>
<tr>
<td>MEA performance</td>
<td>mW/cm(^2)(_{\text{geo}}) @ 675 mV</td>
<td>≥1000</td>
<td>1275</td>
<td>1000</td>
</tr>
<tr>
<td>Durability with cycling</td>
<td>hours @ &lt;10% V loss</td>
<td>5000</td>
<td>TBD</td>
<td>TBD</td>
</tr>
<tr>
<td>Q/ΔT</td>
<td>kW/°C</td>
<td>1.45</td>
<td>1.45</td>
<td>1.94</td>
</tr>
<tr>
<td>PGM total loading</td>
<td>mg(<em>{\text{PGM}})/cm(^2)(</em>{\text{geo}})</td>
<td>≤0.125</td>
<td>≤0.125</td>
<td>≤0.125</td>
</tr>
<tr>
<td>PGM content</td>
<td>g/kW rated mg/cm(^2) MEA</td>
<td>≤0.125</td>
<td>0.1</td>
<td>0.125</td>
</tr>
</tbody>
</table>

PGM – platinum group metal

INTRODUCTION

GM and other automotive MEA developers have achieved very impressive beginning-of-life (BOL) performance using low-Pt-loading (0.05–0.1 mg\(_{\text{Pt}}$/cm\(^2\)) 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 O\(_2\) 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 an 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. This will be achieved by systematic durability studies relying on advanced characterization tools and 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 best-in-class 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 durability of the MEA past 5,000 h for the DOE 2020 durability target.

RESULTS

In the previous year (BP 1), the SOA MEA was generated with use of best-in-class materials. As illustrated in Table 1 and Figure 1a, the SOA MEA performance exceeds the criteria of 1 W/cm² @ 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 or 10 kW/g PGM was achieved (at 250 kPa and 94°C). In the current year (BP 2), to demonstrate the potential of operating conditions on electrode and membrane degradation, H₂-N₂ voltage cycling tests were conducted at different operating conditions. Figure 1b shows the percentage ECSA loss mitigation and voltage loss mitigation by varying the relative humidity of the operating cell during voltage cycle durability test. A >35% ECSA loss mitigation and cell voltage loss mitigation was demonstrated. A design of experiment looking at different operating conditions such as temperature, RH, upper potential limit, hold time at upper potential, and lower potential limit was studied. Considering the brevity of the report, we will focus on single-factor study, namely RH.

Figure 1. (a) Performance of SOA MEA as measured in 50-cm² cell; 150 kPa, 80°C, 100% RH, and 250 kPa, 65% RH, 94°C. (b) ECSA and cell voltage loss mitigation as a function of relative humidity.

The SOA MEA was subjected to 30,000 voltage cycles in H₂-N₂ conditions at 80°C in a 5-cm² differential cell. A trapezoidal wave profile, between 0.6 V and 0.95 V, 0.7 V/s scan rate, 2.5 second hold time at both 0.6 V and 0.95 V, was used. The tests were performed at four different RH conditions, namely 25%, 50%, 75%, and 100% RH. As shown in Figure 2a, noticeable degradation of >100 mV at high current density (>2.0 A/cm²) was observed for voltage cycle tests at 100% RH. Conversely, the MEAs cycled at 25% RH showed minimal mV loss vs. BOL performance test. A similar trend was observed for ECSA loss as well (Figure 2b), with 30% ECSA loss observed for MEAs cycled at 100% RH vs. nearly zero ECSA loss at 25% RH operation, indicating even roughly 100% ECSA loss mitigation can be achieved by using benign operating conditions. While continuous 25% operation of a fuel cell is unlikely, even reducing the operating RH to close to 70% can result in >35% ECSA loss mitigation. The operating RH has a significant impact on the degradation of PtCo/C alloy catalysts. The trend is consistent with some of the earlier studies with Pt/C catalyst [1].
In addition to performance and kinetic measurements, diagnostics tests such as (a) CO stripping as a function of RH to estimate Pt utilization [2], (b) electrochemical impedance spectroscopy measurements in H₂-N₂ to quantify proton transport resistance [3], and (c) oxygen limiting current measurements to estimate bulk and local oxygen transport resistance were conducted [4]. Because SOA MEAs used porous high-surface-area carbon, in which the majority of PtCo particles are inside the carbon pores, CO stripping diagnostics (as shown in Figure 3a) indicate Pt utilization decreases with decrease in RH. Compared to beginning of test (BOT) samples, the degraded MEA shows improved utilization at low RH. This could be a result of increased accessibility of the micropores with aging. Electrochemical impedance spectroscopy measurements show no significant changes in proton transport resistance observed for BOT and end of test (EOT) samples [5]. At very low RH values, the EOT samples exhibit higher proton transport resistance. This could be from the dissolved Co due to voltage cycling. A marginal decrease in the local oxygen transport resistance is also observed from the oxygen limiting current tests [5]. This correlates well with the increased Pt accessibility in the micropores for EOT samples.

In addition to electrochemical diagnostics, the EOT samples, post 30k voltage cycling, were subjected to extensive analytical characterization such as transmission electron microscopy (TEM) for particle size measurements, energy-dispersive X-ray spectroscopy (EDS) for PtCo composition, and electron probe micro analysis (EPMA) for line scans to determine Co dissolution. Preliminary results from the EPMA are summarized in Figure 3b. The EPMA profile indicates a clear trend for higher dissolution of cobalt and migration of dissolved cobalt into the membrane. Measurable levels of dissolved Co were observed in untested fresh and BOL samples as well. The cobalt intensity in the membrane layer for EOT samples increases with increase in RH. This coincides with the higher ECSA loss observed for samples voltage cycled at higher RH. An increase in Pt/Co ratio for EOT samples cycled at higher RH was also observed in TEM-EDS measurements (data not shown here).

Figure 2. SOA MEA voltage cycled to 30k cycles at different RH. (a) H₂-air performance at 250 kPa, 65% RH, 94 °C. (b) ECSA of BOT (0k) and EOT (30k) samples.

Figure 3. SOA MEA voltage cycled to 30k cycles at different RH. (a) Pt utilization from CO stripping measurement as a function of RH. (b) EPMA profile for MEAs V-cycled to 30k cycles at different RH.
In the previous year, a HAST was developed to generate local stressful conditions that are both chemical and mechanical in nature. HAST generates maximum chemical stress occurring near the gas inlets and the maximum mechanical stress near the outlets. The chemical degradation failure of the membrane at the cell outlet, where mechanical stress was higher, was convoluted with the Ce³⁺ depletion. The tests were repeated on an MEA that has no Ce³⁺ in the membrane. Among several notable observations, an increase in crossover at the outlet of the cell was indicative of potential interaction between mechanical stress and chemical degradation. Another key objective of the study is to understand the impact of operating conditions on membrane degradation. HAST studies were conducted on the SOA MEA at different operating temperatures.

Figure 4a shows the H₂ X-over measurements for MEAs subjected to HAST at 70°C, 80°C and 90°C. Almost 7X acceleration in time to failure was observed at 90°C operating temperature relative to 70°C. This highlights the strong impact of operating temperature on membrane durability and could be optimized to prolong membrane life. Even though time to failure is almost 7X at either end, the failure location (outlet) and failure mode (thinning or diffusive crossover) is similar at all temperatures (Figure 4b).

The rapid movement of Ce³⁺ observed in HAST resulted in additional studies to understand the Ce³⁺ migration mechanism as well as quantify migration rates due to diffusion and convection. In the previous year, Ce³⁺ diffusion measurements were conducted by applying a droplet of Ce³⁺ solution of known concentration and monitoring its movement with Fourier transform infrared spectroscopy method [6]. In 2019, Ce³⁺ diffusion coefficients were measured as function of RH (λ) and temperature by using a more quantitative X-ray fluorescence (XRF) method. A two-chamber RH gradient cell as shown in Figure 5a was used to obtain Ce³⁺ migration rates by both diffusion and convection. Four thin strips of membranes with localized Ce were exposed to RH gradient in this cell and Ce³⁺ movement was monitored with the XRF method. The left chamber was exposed to 95% RH. The right chamber RH was varied—for example 95%, 75%, 50%, 25%. The Ce³⁺ movement was monitored at the end of 6 h, 12 h, 24 h, and 36 h using the XRF method. Figure 5b shows the Ce³⁺ migration at the end of 36 h using 50% RH on chamber 2. For strip 2, where the Ce patch is at the center of the 95% RH chamber, the Ce³⁺ migration happens via fast diffusion. For strip 3, where the Ce patch is at the center of the 50% RH chamber, the Ce³⁺ migration happens via slow diffusion. For strips 1 and 4, where the Ce patch is near the RH gradient, the Ce movement is dominated by convection and slow diffusion. RH has a strong effect on Ce³⁺ diffusion rates, and RH gradient promotes even faster Ce³⁺ movement via convection. Figure 5c shows the time resolution for Ce³⁺ migration on strip 4. A 1-D model was developed to account for both diffusion and convection. Measured data were fitted with a model to extract transport coefficients.
UPCOMING ACTIVITIES

For the remainder of FY 2019 and BP 3, the project will focus on electrode and membrane durability studies and modeling activities. Key activities will be conducted in collaboration with FC-PAD partners and are as follows:

- Complete the voltage cycling experiments to map the impact of operating conditions.
  - MEA characterization including EPMA, TEM, electron energy loss spectroscopy mapping (Oak Ridge National Laboratory, University of Texas).
- Obtain ex situ dissolution rates of Pt and Co and elucidate growth mechanisms (Argonne National Laboratory/National Renewable Energy Laboratory).
- Develop predictive models based on the experimental data with the fundamental understanding of degradation mechanisms—models for PtO growth, Pt and Co dissolution, Pt and Co transport, Pt shell thickness.
- Conduct accelerated stress tests of SOA and pre-shorted MEAs in segmented cells combined with visualization techniques such as XRF and X-ray computed tomography (GM/Lawrence Berkeley National Laboratory).
- Perform open circuit voltage and H2-O2 vapor cell tests to understand the impact of membrane thickness on chemical degradation rates and mechanisms.
- Refine the model for in-plane Ce migration during transient fuel cell operation.
- Develop a combined chemical/mechanical membrane degradation model based on experimental data and the fundamental understanding of degradation mechanisms.

FY 2019 PUBLICATIONS/PRESENTATIONS


REFERENCES


