V.B.5 Durable High-Power Membrane Electrode Assemblies with Low Pt Loading

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Overall Objectives

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

Fiscal Year (FY) 2017 Objectives

- Down-select best in class catalyst, ionomer, and membranes to generate SOA MEAs that will meet DOE 2020 performance and cost targets.
- Systematic study to correlate catalyst layer structure formation from ink properties to its impact on measured polarization curve.
- Deliver 5 cm^2 and 50 cm^2 SOA MEAs to Fuel Cell Performance and Durability consortium (FC-PAD) partners for durability studies.

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.

(A) Durability

(B) Cost

(C) Performance

Technical Targets

See Table 1.

FY 2017 Accomplishments

- Several best in class catalysts, ionomers and membranes identified for evaluation.
- Initial activity measurement on several best in class catalyst exceeds DOE mass activity target of 440 mA/mg_{Pt}.

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

Characteristic	Units	DOE 2020 Electrocatalyst and MEA Targets	Project Status (5 cm^2 cell, differential conditions)
Mass activity (MA)	A/mg_{PGM} @ 0.9 $mV_{iR\text{-}free}$	≥0.44	0.60
Specific activity	$\mu A/cm^2_{PGM}$ @ 0.9 $mV_{iR\text{-}free}$	≥720	1,477
PGM total loading	$mg\text{-}PGM/cm^2_{geo}$	≤0.125	≤0.125
MEA performance	mW/cm^2_{geo} @ 675 mV	≥1,000	≥900
Electrocatalyst durability	% loss after 30,000 V-cycles	<40% loss in ECSA <40% loss in MA <30 mV loss @ 0.8 A/cm^2	*In progress*
Durability with cycling	Hours @ <10% V loss	5,000	*TBD*

TBD – to be determined; PGM – platinum group metals; ECSA – electrochemical surface area

- MEA performance of >900 mW/cm$^2_{geo}$ at 675 mV achieved for best in class catalyst materials. Identified gaps to meet >1,000 mW/cm$^2_{geo}$.
- PtCo alloy catalysts on porous high surface area carbon supports exhibit a distinct advantage in both activity and H_2-air performance over solid carbons.

INTRODUCTION

PtCo-alloy catalysts have achieved mainstream application approximately 20 years after they were first reported. Thanks to the recent high activity of these alloy catalysts [1], GM and other automotive MEA developers have achieved very impressive beginning of life performance using low-Pt (0.05–0.1 mg$_{Pt}$/cm^2) loading cathodes and thin (10–15 µm) membranes. Unfortunately, these MEAs are subject to life-limiting degradation during operation, and developers add twice the Pt and increase membrane thickness by 5–10 µm, substantially sacrificing cost, in order to achieve durability requirements.

These high performing MEAs suffer 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 FC-PAD.

APPROACH

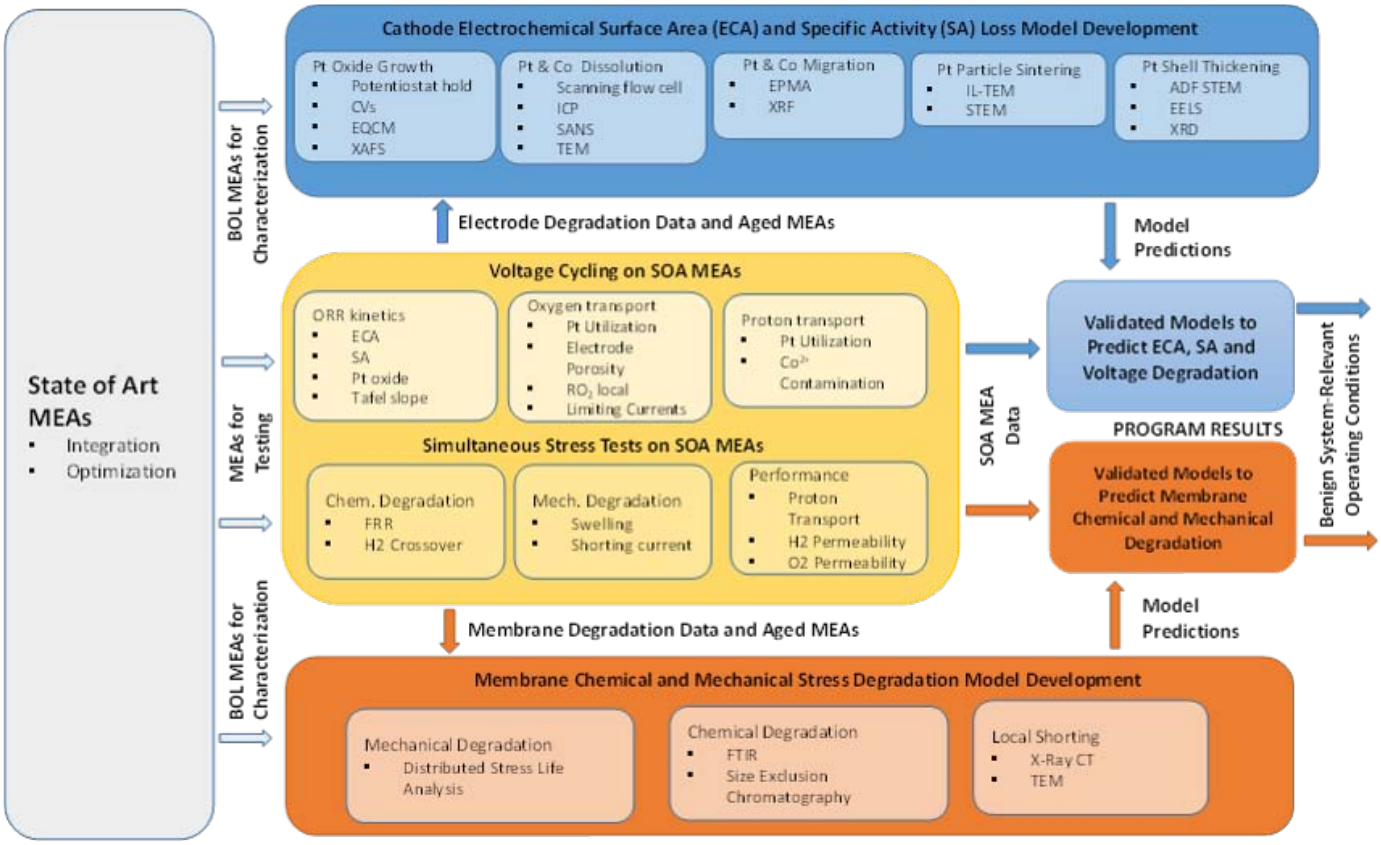
The project approach is based on our understanding that there is substantial opportunity to select operating conditions and voltage waveforms to reduce life-limiting electrode and membrane degradation rates. In this project, we intend to map the impact of operating conditions on SOA MEA durability for proton exchange membrane fuel cells. This will be achieved by systematic durability studies relying on advanced characterization tools, degradation mechanism model development and validation. The framework for the studies envisioned in the project is shown in Figure 1. 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, (2) incorporating systematic durability studies to assess the impact of operating conditions on MEA life, (3) conducting extensive post mortem 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 MEA past 5,000 h of the DOE 2020 durability target.

The output of the project will be a detailed understanding of operating condition sensitivity on cathode and membrane failure, critical for defining operating conditions and hybridization strategies that can guide system controls to maximize low-Pt MEA life. The project will utilize the expertise of GM, its partners, and FC-PAD to achieve project objectives.

RESULTS

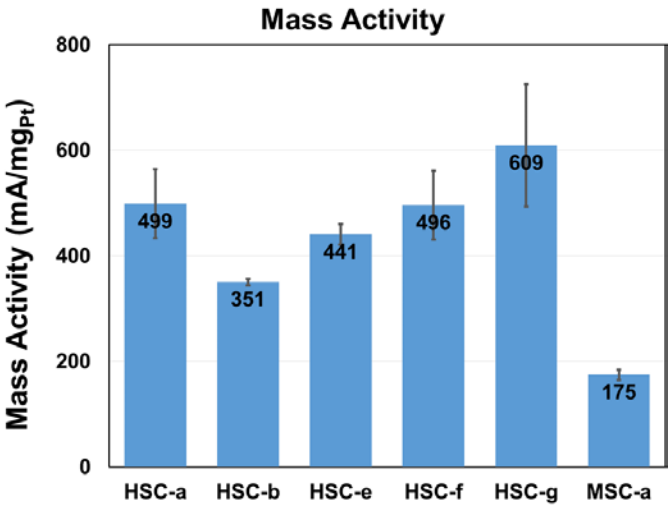
First year objective of the project is to procure best in class materials that can be optimized and integrated to generate an SOA MEA. In the first two quarters, few best in class catalyst candidates, like PtCo alloy from various suppliers and in house synthesis, have been studied for activity and performance. A few other high activity categories, such as faceted catalysts or core shell catalysts, are still early in development to be considered for this study. Location of the Pt particle (inside the pore vs. outside the pore) has been shown to have an impact on both activity and performance in the DOE project DE-EE0007271 (FC144 – Highly Accessible Catalyst). Recent scanning transmission electron microscopic tomography studies indicate the majority of particles are embedded inside carbon on high surface area carbon (HSC) supports, making them inaccessible during dry operation. Alternatively, solid carbon such as Vulcan or acetylene black would provide a majority of particles on the exterior surface of carbon, making them more accessible even during dry operation [2,3].

To address drawbacks and opportunities from this learning, high active PtCo catalysts on both porous HSC carbon and solid carbons like Vulcan were tested for activity and H_2-air performance. The catalysts were tested in MEAs fabricated as catalyst coated membrane with 0.1 mg$_{Pt}$/cm^2 on cathode electrode and 0.025 mg$_{Pt}$/cm^2 anode electrode laminated on 18 µm membrane. Initial test results (Figure 2 and Figure 3) indicate most of the PtCo alloy catalysts on various high surface area carbon supports exceeds DOE mass activity requirements of 440 mA/mg$_{Pt}$. Also, there are significant differences in activity for PtCo alloy catalysts on porous HSC like carbon supports compared with solid carbon like Vulcan. Activity of PtCo alloy catalysts on porous HSC catalysts are 3X higher (600 mA/mg$_{Pt}$ vs. 175 mA/mg$_{Pt}$) compared to solid carbon. Activity variations can be found even among several high surface area carbon supports. In the next few quarters, we will continue both electrochemical and analytical characterization of the MEAs to down-



CV – cyclic voltammetry; EQCM – electrochemical quartz crystal microbalance; XAFS – X-ray absorption fine structure; ICP – inductively coupled plasma; SANS – small angle neutron scattering; TEM – transmission electron microscopy; EPMA – electron probe micro analyzer; XRF – X-ray fluorescence; IL-TEM – identical location-TEM; ADF – annular dark-field imaging; EELS – electron energy loss spectroscopy; XRD – X-ray diffraction; FTIR – Fourier transform infrared; CT – computed tomography; STEM – scanning transmission electron microscopy

FIGURE 1. Project framework for electrode and membrane degradation studies



MSC – medium surface area carbon

FIGURE 2. Oxygen reduction reaction mass activity measurements at 0.9 V, 80°C, 100% relative humidity, H_2/O_2

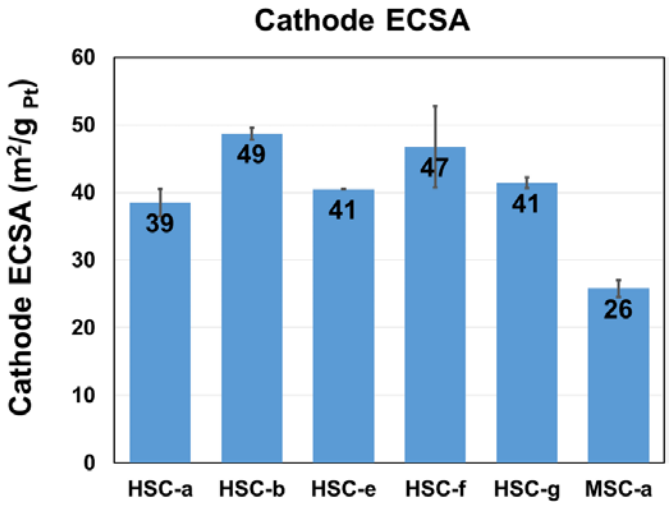


FIGURE 3. ECSA measurements at 25°C

select catalyst and other components such as ionomer and membrane for SOA MEA.

UPCOMING ACTIVITIES

For the remainder of the first year, the project will focus on generating the state-of-the-art MEA and deliver 5 cm^2 and 50 cm^2 MEA to FC-PAD. Key activities will be conducted in collaboration with FC-PAD partners to generate the SOA, including:

- Identifying catalyst, ionomers and membranes for improved performance and durability (GM) and MEA characterization (University of Texas at Austin).
- Electrochemical diagnostics including limiting current, etc., to quantify voltage loss terms of the MEA (National Renewable Energy Laboratory).
- Study ink properties using X-ray scattering methods (Argonne National Laboratory) and correlate with catalyst layer structure and ionomer interaction using advanced microscopy tools (Oak Ridge National Laboratory).
- Develop combined chemical and mechanical degradation test (GM and Giner) and explore use of advanced characterization method like X-ray micro CT (Lawrence Berkeley National Laboratory) to study membrane degradation.

The second and third years of the project will focus on electrode and membrane durability studies and MEA degradation model development.

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