FY18 SBIR IIB: Ionomer Dispersion Impact on Advanced Fuel Cell and Electrolyzer Performance and Durability

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- Los Alamos National Laboratory, Los Alamos, NM
- National Renewable Energy Laboratory, Golden, CO

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Project End Date: August 27, 2020

Overall Objectives

- Further develop nonaqueous ionomer dispersions for polymer electrolyte membrane (PEM) fuel cell and electrolyzer technologies to overcome catalyst and ionomer degradation within the catalyst layer under fuel cell and electrolyzer operating conditions.

- Evaluate down-selected ionomer dispersion (i.e., ethylene glycol [EG]) vs. baseline (water/1-propanol [NPA]) using high-performance catalysts for improved performance; identify ideal ionomer equivalent weight and ionomer to carbon (I/C) ratio for EG inks for improved performance and durability.

- Address the high boiling point of EG, which results in long drying times, by moving from decal catalyst-coated membranes to gas diffusion electrodes (GDEs) to enable more viable roll-to-roll (R2R) processing.

- Integrate GDEs with a dimensionally stable membrane (DSM) platform to create more durable membrane electrode assemblies (MEAs) for PEM fuel cells and electrolyzers.

Fiscal Year (FY) 2019 Objectives

- Correlate the catalyst ink rheology with electrode morphology and MEA performance.

- Double the durability of the MEA using nonaqueous ionomer dispersion.

- Develop the R2R processing of EG vs. water/NPA by switching from decals to GDEs to address the longer drying times of EG.

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]:

- Performance

- Durability

- Cost (develop R2R processing).

Technical Targets

The DOE 2020 technical targets and our current project status are listed in Table 1 for comparison.

FY 2019 Accomplishments

- Discovered the correlation between catalyst ink morphology and fuel cell performance.

- Fabricated fuel cell MEAs using ionomer dispersions in EG, and demonstrated improved performance and durability compared to water/NPA-based solvents.

- Optimized ionomer type and I/C ratio of EG-based inks to maximize fuel cell performance.

- Evaluated performance of EG vs. NPA-rich catalyst ink for PEM electrolyzers.

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

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

Characteristic	Units	DOE 2020 Targets	Project Status
Mass activity (H_2/O_2)	A/mg$_{PGM}$ @ 0.9 V$_{iR-free}$	≥0.44	0.64
Loss in initial catalytic activity	% mass activity loss	<40	21
PGM total loading	mg-PGM/cm²$_{geo}$	≤0.125	0.1 cathode; 0.2 anode
MEA performance (H_2/air)	mA/cm²$_{geo}$ @ 800 mV	≥300	375
Loss in performance at 0.8 A/cm	mV	<30	65
MEA performance (H_2/air)	mW/cm²$_{geo}$ @ 675 mV	≥1000	589

PGM – platinum group metal

INTRODUCTION

This DOE technology transfer project aims to commercialize nonaqueous ionomer technology developed at Los Alamos National Laboratory (LANL). In this project, Giner aims to transition LANL's innovative ionomer technology to successful commercialization by developing MEAs in more processable, scalable, and profitable ways. MEAs combining LANL's ionomer technology and Giner's DSM platform will be fabricated using methods suitable for mass production, such as the R2R process. We aim to investigate (1) the effect of ionomer dispersion on the fuel cell catalyst inks, electrode morphology and structures, and fuel cell performance/durability; and (2) the effect of ionomer dispersion on the electrolyzer catalyst inks, electrode morphology and structures, and electrolyzer performance/durability. In addition, the developed understanding of the catalyst ink rheology and morphology can help with R2R processing for both fuel cell and electrolyzer technologies.

From neutron scattering experiments at LANL it was found that although the proton form of Nafion has a similar size in both EG and water, it behaves quite differently when dispersed in these solvents. When Nafion is dispersed in water, its side chains tend to point outward, resulting in more electrostatic repulsion of the Nafion particles and poor chain entanglement. On the other hand, when Nafion is dispersed in a nonaqueous solvent, such as EG, its side chains turn inward, resulting in less electrostatic repulsion of the Nafion particles, and good chain entanglement. This means that Nafion dispersed in EG will likely occupy a smaller space than Nafion dispersed in water. This has implications for the secondary pores size distribution of the electrode upon drying (i.e., the water-based electrode may develop cracks due to the higher electrostatic repulsion of Nafion). Nafion particles dispersed in nonaqueous solvents have been shown to form ionomer layers that can be up to 4 orders of magnitude stiffer than those dispersed in conventional water/alcohol solvents [1, 2]. Higher ionomer stiffness could result in lower water uptake (i.e., less ionomer swelling in the catalyst layer). A stiffer ionomer can also result in a more durable catalyst layer due to the lower water concentration next to the catalyst particle surface. Higher water concentrations can promote increased catalyst dissolution and migration of dissolved ion species, such as Pt^{2+} and Co^{2+}, during accelerated stress test (AST) cycling [3] due to their attraction to oxygen in water.

APPROACH

- Ionomers will be dispersed in a variety of solvents and their morphology will be studied by small angle neutron scattering.

- Catalyst inks prepared using various ionomer dispersions and processing conditions will be studied by rheometry, zeta potential, and laser diffraction analysis.

- MEAs using the above catalyst inks will be evaluated for their performance and durability, and electrode structures will be characterized by microscopy techniques.

- The correlation between the catalyst ink rheology, electrode structures, and MEA performance will be established.

- The optimal catalyst ink formulations will be used to direct R2R production of MEAs.

RESULTS

To address the durability challenges of catalysts used in fuel cells and electrolyzers, we compare the performance and durability of aqueous and nonaqueous ionomer dispersions. First, the EG dispersed ionomer was compared to a water/NPA dispersed ionomer. The ionomers used were N212 membrane (D2021) dissolved in EG and a commercial D2021 dispersion in water/NPA/isopropanol. TEC36F32, a PtCo catalyst on high-surface-area carbon, was used with 0.1 mg/cm^2 Pt loading. Rheology, zeta potential, and laser diffraction were used to characterize the inks before casting them on Teflon substrates. Both decals were fully dried and then hot pressed to a N211 membrane. A commercial 0.2 mg/cm^2 Pt anode was used to eliminate any effect on performance and durability from the anode. Rheology was performed on both inks, whereby all parameters were kept fixed, except for the solvents used. Rheology, zeta potential and laser diffraction were also used to establish the optimal ball milling times of both inks, whereby this inks displayed a decrease in phase angle, an increase in viscosity as well as elastic and viscous modulus, and an increase in the absolute zeta potential with time. Stable values for all three characterization methods were achieved after 3 days of mixing the water/NPA inks and 5 days of mixing the EG inks.

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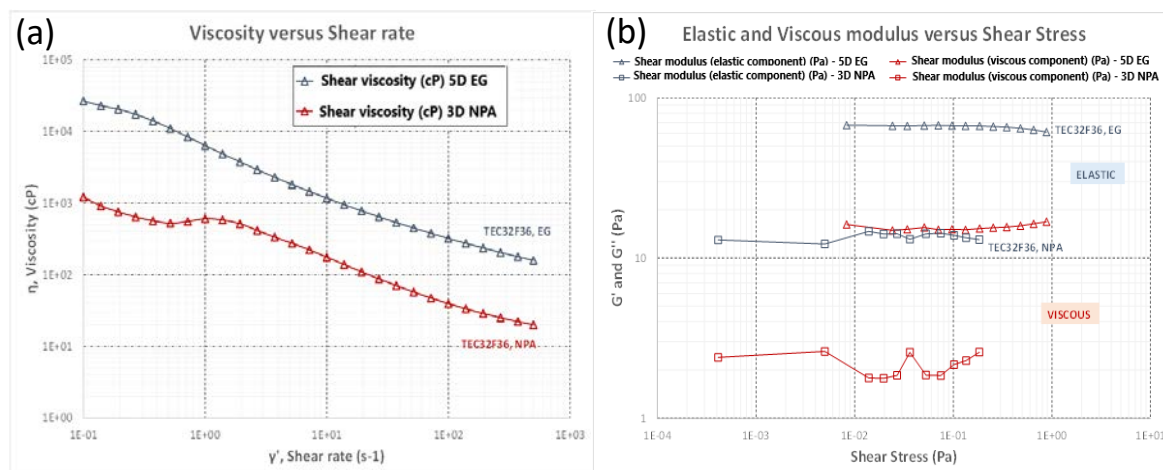

Figure 1. Rheology of fuel cell catalyst inks: (a) viscosity and (b) elastic and viscous modulus

The performance was tested at 80°C, 100% RH, using 1.5/1.8 stoichiometry at the anode and cathode, respectively, and 1.5/3 L/min fixed flows (shown in Figure 2a and 2b), where the trends were more pronounced. The EG electrode with overspray had the best initial performance, followed by the water/NPA-based electrode, then the EG electrode without Nafion overspray. An ionomer optimization study was performed for the EG, where D2021 was replaced by either D2020 or Aquivion, both also dispersed in EG. With all other aspects of the ink composition kept identical, the initial performance of both electrodes with D2020 and Aquivion ionomer was worse than with D2021. This was consistent with the higher elastic modulus of the D2021 inks. Next, the I/C ratio of the D2021 in the EG electrode was examined by increasing the I/C ratio from 0.9 to 1, which also resulted in poorer performance. Therefore, further studies continued with D2021 in EG at 0.9 I/C. The local oxygen resistance (R_{O2}) for the EG- and NPA-based ionomers was evaluated in a 5-cm^2 GM differential cell. The electrochemical surface area of the EG electrode was higher than that of the water/NPA electrode at 38 m^2/g vs. 28 m^2/g. The EG ink with Nafion overspray showed a local oxygen resistance of 10.6 s/cm (Non-Fickian resistance of 0.35 s/cm) vs. 6 s/cm (Non-Fickian resistance of 0.28 s/cm) for the water/NPA-based electrode, after subtracting the resistance from the gas diffusion layer and gas channels, which was estimated to be 0.076 s/cm. This may be due to the lower water uptake of the stiffer EG ionomer, reducing the oxygen permeability through the ionomer film. The overall performance improvement of the EG with Nafion overspray, however, indicates that the optimal secondary pore size distribution and lower swelling at high current densities compensates for the higher local R_{O2}.

All three MEAs were subjected to square wave accelerated stress test (SW AST) cycling from 0.60 V to 0.95 V. The results shown in Figure 2c and 2d are the averages of two repeats of the same AST for each solvent, using the EG electrode without Nafion overspray. The mass activity and 0.8 V performance of the cathode with the EG-based ionomer was twice as stable as the cathode with water/NPA-based ionomer. After 30k SW AST cycles, the mass activity of the EG electrode degraded by 21% vs. 46% in the case of the water/NPA catalyst. At 0.8 V the performance loss of the EG electrode was 26% vs. 44% for the water/NPA electrode. Interestingly, the EG electrode with Nafion overspray degraded similarly to the water/NPA electrode at 0.8 V, losing 40% of its initial performance. A methanol based Nafion overspray solution is being investigated in order to preserve the higher performance of the EG electrode as well as its superior durability. All three electrodes showed high mass activities. The water/NPA electrode had the highest mass activity, 0.65 A/mg$_{Pt}$, followed by the EG electrode with Nafion overspray, 0.64 A/mg$_{Pt}$, and the EG electrode without Nafion overspray, 0.56 A/mg$_{Pt}$.

The microstructure of the electrodes is compared before and after durability cycling, shown in Figure 3. The ionomer distribution of the EG electrode is more uniform compared to that of the water/NPA electrode as there was less ionomer aggregation in the EG electrode after 30k SW AST cycles. At beginning of life (BOL), primary porosities of 49% and 54% were observed for the NPA/water-based and EG system, respectively, using transmission electron microscopy (TEM). The secondary porosity (43%) of the water/NPA electrode was much higher than that of the EG electrode (30%); this is in good agreement with the proposed lower electrostatic interactions of Nafion dispersed in EG. The initial size of PtCo particles was smaller in the EG electrodes than in the water/NPA electrode, consistent with the higher viscosity of the EG ink observed with rheology. More PtCo dissolution was observed in the case of the EG electrodes vs. water/NPA during the 30k SW AST, but their final particle sizes are still smaller than that of the water/NPA electrode at end of life (EOL). The PtCo particles in the EG electrode without Nafion overspray grew by 58%, from 3.52 ± 1.79 nm to 5.58 ± 1.83 nm, while 66% particle growth was seen in the EG electrode with Nafion overspray (3.30 ± 1.09 nm grew to 5.50 ± 1.65 nm). The water/NPA electrode displayed 45% particle size growth (6.25 ± 1.86 nm to 9.04 ± 3.93 nm). The water/NPA electrode suffered severe cathode thinning by 31% (6.96 ± 7.11 μm to 4.8 ± 0.61 μm) and the EG cathode did not experience thinning at all (7.39 ± 0.777 μm to 7.74 ± 0.48 μm).
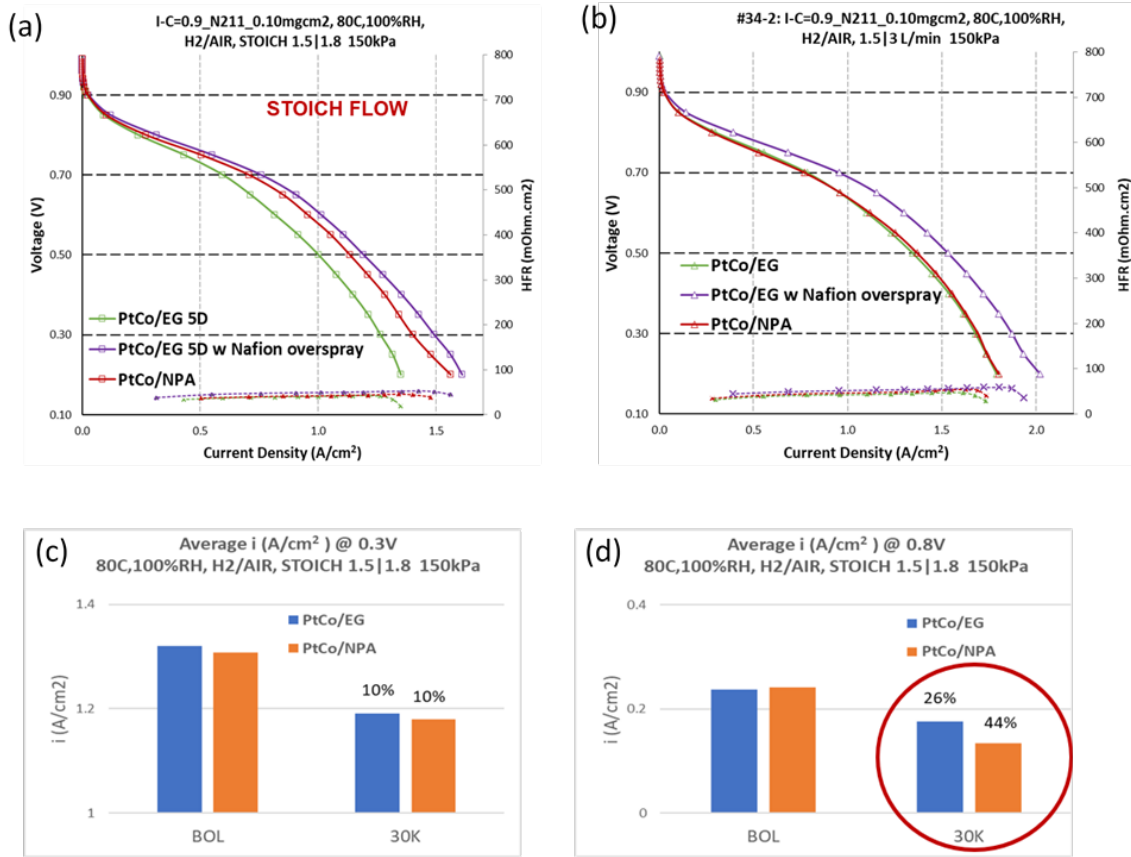
Figure 2. (a) H2/air performance with stoichiometric flows and (b) fixed flows for catalysts showing the performance of the EG-based electrode (with and without Nafion overspray) vs. the water/NPA electrode. (c) Performance drop during 30k SW AST at 0.3 V and (d) at 0.8 V.
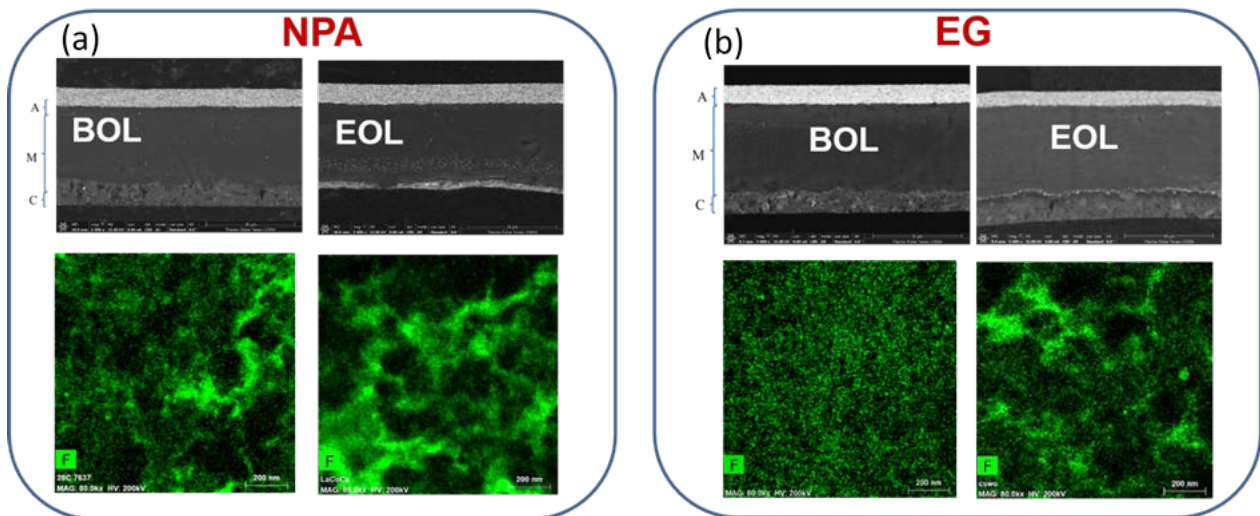

Figure 3. Microstructure at BOL and EOL of (a) NPA vs. (b) EG electrode using scanning electron microscopy (SEM) and TEM. EG-based electrodes show smoother electrode (from SEM), better initial ionomer distribution (from TEM), as well as less ionomer aggregation over 30k SW AST for the EG electrode.

Additional studies were conducted with electrolyzer inks where the ionomers were dispersed in EG and water/NPA. Inks were mixed using a water-rich, NPA-rich and EG solvent for Ir and IrOx catalysts. A 1 mg/cm^2 Ir or IrOx anode was used in combination with a 0.2 mg/cm^2 Pt/XC72 cathode and Nafion 115 membrane. The electrolyzers were tested in 50-cm^2 fixtures and operated at 3 A/cm^2 for 3 weeks. The resulting electrolyzer performance for the Ir and IrOx electrodes is shown in Figure 4. The performance of the water-rich electrode was the best, followed by that of the NPA-rich solvent and the EG solvent. The performance of the IrOx electrode was significantly better than that of the pure Ir electrode. This was specifically true for the EG anode.
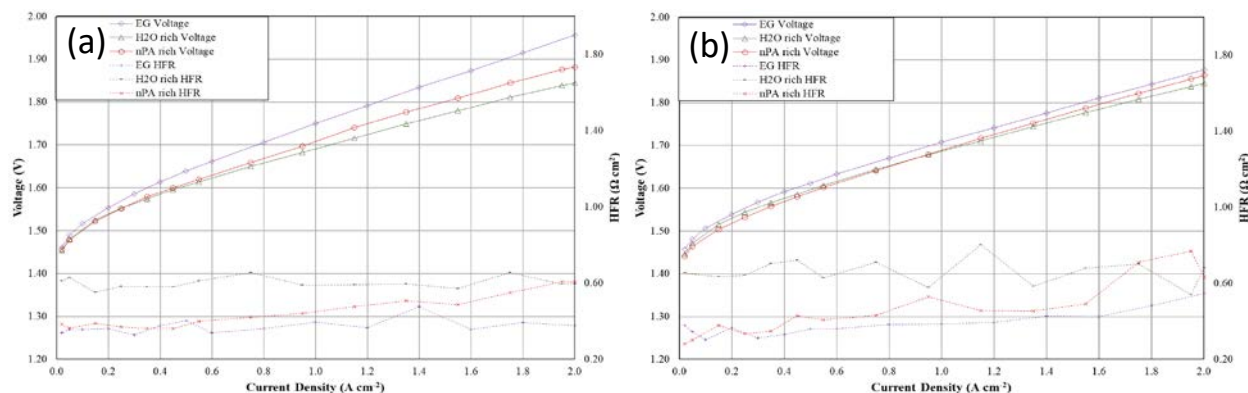

Figure 4. Performance of (a) Ir and (b) IrOx electrodes with EG, H2O-rich, and NPA-rich solvents after 3 weeks of operation at 80°C, 3 A/cm², where the H2O-rich electrode had the best performance followed by the NPA-rich and EG electrode.

CONCLUSIONS AND UPCOMING ACTIVITIES

In the PEM fuel cell portion of this work we have successfully shown that ionomer dissolved in EG resulted in a much more durable electrode compared to an ionomer dissolved in water/NPA; this has been correlated with observations of electrode ink rheology and electrode microstructure. In future work for the fuel cell, we will develop R2R processing using EG-based electrodes. We will address the long drying time by switching from a decal system to a GDE system. Initial dstudies have shown that the EG ink's drying rate was significantly faster on GDEs than on a decal. Initial MEA tests with EG-based GDEs have shown identical performance and high frequency resistance to those observed for decals. We are working closely with our R2R collaborator, National Renewable Energy Laboratory, to develop a viable R2R process for the EG electrode. RO$_2$ local studies before and after AST cycling will be used to monitor changes in oxygen resistance behavior of the ionomers.

Future tasks for the electrolyzer studies include the implementation of metal-oxide-supported Ir nanoparticle catalysts. Metal oxides that are highly stable under higher oxidation potential will be investigated as anode catalyst supports. Based on our previous work, W-doped TiO$_2$ has shown great potential as a stable anode catalyst support with reasonable conductivity. More aggressive testing protocols will be studied to accelerate the electrolyzer degradation process. Ink property studies will be performed on the new electrolyzer inks, including rheology, laser diffraction analysis, and zeta potential.

FY 2019 PUBLICATIONS/PRESENTATIONS

1. N. Macauley, F. Yang, M. Spinetta, S. Zhong, Y.S. Kim and H. Xu, "Correlating Catalyst Ink Rheology with Fuel Cell Performance and Durability," 236th ECS meeting, Atlanta, GA, 2019.

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2. Y.S. Kim, C.F. Welch, R.P. Hjelm, N.H. Mack, A. Labouriau, and E.B. Orler, "Origin of Toughness in Dispersion-Cast Nafion Membranes," Macromolecules 48 (2015): 2161−2172.

3. A. Kneer, N. Wagner, "A Semi-Empirical Catalyst Degradation Model Based on Voltage Cycling under Automotive Operating Conditions in PEM Fuel Cells," J. Electrochem. Soc. 166, no. 2 (2019): F120–F127.