

V.C.4 Ionomer Dispersion Impact on Fuel Cell and Electrolyzer Performance and Durability (SBIR Phase II TTO)

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- Demonstrate the durability advantages of using non-aqueous ionomers in the electrode.

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

Technical Targets

The targets of this project are to apply ionomer dispersion technology to make durable fuel cell and electrolyzer MEAs. DOE targets for PEM fuel cells are listed in Table 1.

TABLE 1. MEA Durability Targets

Characteristic	Units	DOE 2020 Target
Platinum group metal (PGM) total content (both electrodes)	g/kW	<0.125
PGM total loading (both electrodes)	mg-PGM/cm ² _{geo}	<0.125
Loss in catalytic (mass) activity	% Loss	<40
Loss in performance at 0.8 A/cm ²	mV	<30
Loss in performance at 1.5 A/cm ²	mV	<30
Mass activity @ 900 mV _{IR-free}	A/mg _{PGM}	0.44

Overall Objectives

- Further develop and commercialize LANL's non-aqueous solvent-based ionomer dispersion technology.
- Scale-up ionomer and dimensionally-stable membrane (DSMTM) production to allow for continuous roll-to-roll production of low platinum-group metals (PGM) membrane electrode assemblies (MEAs) for fuel cells and electrolyzers.
- Demonstrate the durability of polymer electrolyte membrane (PEM) fuel cell and electrolyzer MEAs at more extensive cycling and operating conditions.

Fiscal Year (FY) 2017 Objectives

- Characterize the influence of non-aqueous solvents on ionomer particle morphology and electrode layer structure.
- Fabricate MEAs using various non-aqueous ionomer dispersions from LANL and investigate the influence of the solvent on fuel cell performance.

For PGM electrolyzers, DOE has not set a target. Giner's targets are:

- Low PGM loading electrolyzer MEA demonstrates less than 20 mV loss (at 1.5 mA/cm²) after 50,000 cycles from 1.4 V to 1.9 V.
- Low PGM loading electrolyzer MEA demonstrates less than 20 mV performance loss after 1,000 hour test at 1.5 A/cm².

FY 2017 Accomplishments

- Upgraded electrode layer manufacturing from batch spraying to an ink-casting process. DSM-based MEAs were fabricated from selected ionomer dispersions.
- Characterized the non-aqueous solvent influence on ionomer particle morphology via small-angle neutron scattering measurements and electrode layer structure by high resolution transmission electron microscopy.

- Fabricated MEAs using various non-aqueous ionomer dispersions and established the ranking of the solvent influence on fuel cell performance.
- Demonstrated the durability advantages of using ethylene glycol (EG)-based ionomer in the electrode, with only 20 mV voltage loss at 1 A/cm² after 30,000 cycles in the accelerated stress test (AST).



INTRODUCTION

LANL has developed a revolutionary method of building an MEA for PEM fuel cells that can significantly reduce manufacturing costs and extend MEA lifetimes. This method incorporates unique polymer dispersions in non-aqueous liquids to produce superior electrode performance, stability, and durability during harsh fuel cell operating conditions [1–7]. The LANL-produced MEA has been evaluated and certified using an AST developed by DOE in conjunction with car manufacturers; the voltage loss of LANL’s MEA remained below 30 mV even after 70,000 cycles.

The ionomer dispersion work at LANL has great potential to significantly improve the lifetime of PEM fuel cells [2–4]. However, the ionomer dispersion used was Nafion® 1100 equivalent weight; there has been a strong push in the industry towards lower equivalent weight membranes that can increase proton conductivity. Low equivalent weight ionomers are less dimensionally stable and could benefit more from Giner’s well-established DSM™ technology. Also, the work at LANL has been done with dispersions of ionomer in the salt form, rather than in the proton form. This requires additional processing after membrane production to put the membrane in the acid form. Using dispersions from LANL in the acid form and utilizing Giner’s DSM technology, this Phase II program will validate these technologies towards viable commercial applications in advanced fuel cell and electrolyzer systems.

APPROACH

Conventional PEM fuel cell and membrane-based water electrolyzer technology suffers from a lack of durability, high manufacturing costs, and rapid performance degradation. In this project, Giner, in collaboration with LANL, investigates a revolutionary method of building membrane electrode assemblies for PEM fuel cells and water electrolyzers in order to reduce manufacturing costs and extend the lifetime of the electrochemical devices. In FY 2017, we focused on improving beginning of life (BOL) fuel cell performance using a single-dispersion-agent-processed electrode. This work is motivated by the fact that these electrodes showed good durability but limited BOL performance compared to the conventional water/isopropyl alcohol (IPA/H₂O)

processed electrodes. Our approach to obtain good BOL fuel cell performance is to (i) understand ionomer particle morphology in dispersion; (ii) investigate the electrode morphology, catalyst, and ionomer binder distributions in the electrodes; (iii) evaluate the electrode performance using various electrodes prepared from different dispersing agents. Giner and LANL prepared several perfluorosulfonic acid dispersions (proton form) from various single dispersion systems. Electrodes were made from different dispersions and tested both at Giner and LANL. Oak Ridge National Laboratory characterized the electrode morphology including polymer electrolyte and catalyst distribution to correlate the BOL performance with electrode morphology. Giner performed MEA durability tests following the DOE AST protocols.

RESULTS

First, laser diffraction particle size analysis was used to understand the various solvents’ impacts on catalyst ink structure (see Figure 1). It can be seen that n-propyl alcohol (nPA)/H₂O and EG solvent systems provide better ink structure, implied by much smaller agglomeration sizes. IPA/H₂O and pentanediol-based solvent systems exhibit large agglomerations in the ink, which may account for their poor quality. The laser diffraction particle size will be correlated with electrode structure and fuel cell performance later.

The electrode morphology and structures were characterized. Most of the electrodes demonstrate smooth coating surfaces and good quality (see Figure 2a), except that the cathode layer made from IPA/H₂O-based ink exhibits large “mud cracks.” Low magnification transmission electron microscopy element mapping was then used to characterize the ionomer distribution in these cathode layers, as shown in Figure 2b. The best ionomer distribution was found in the ethylene glycol-based sample, with ionomer aggregates <50 nm. On the other hand, the 3M ionomer/pentanediol

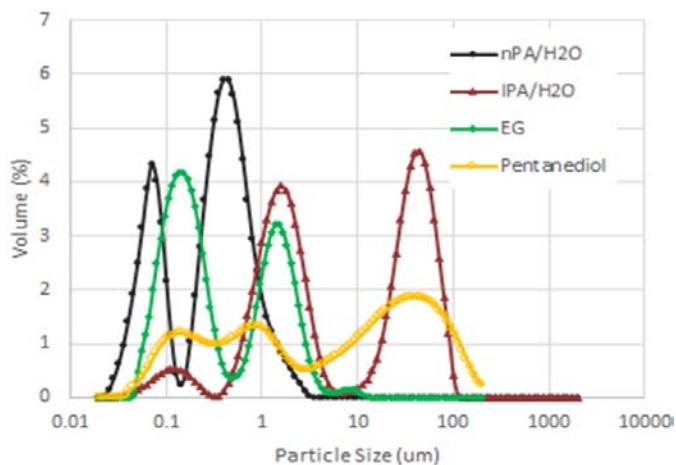


FIGURE 1. Particle size distribution in various solvents

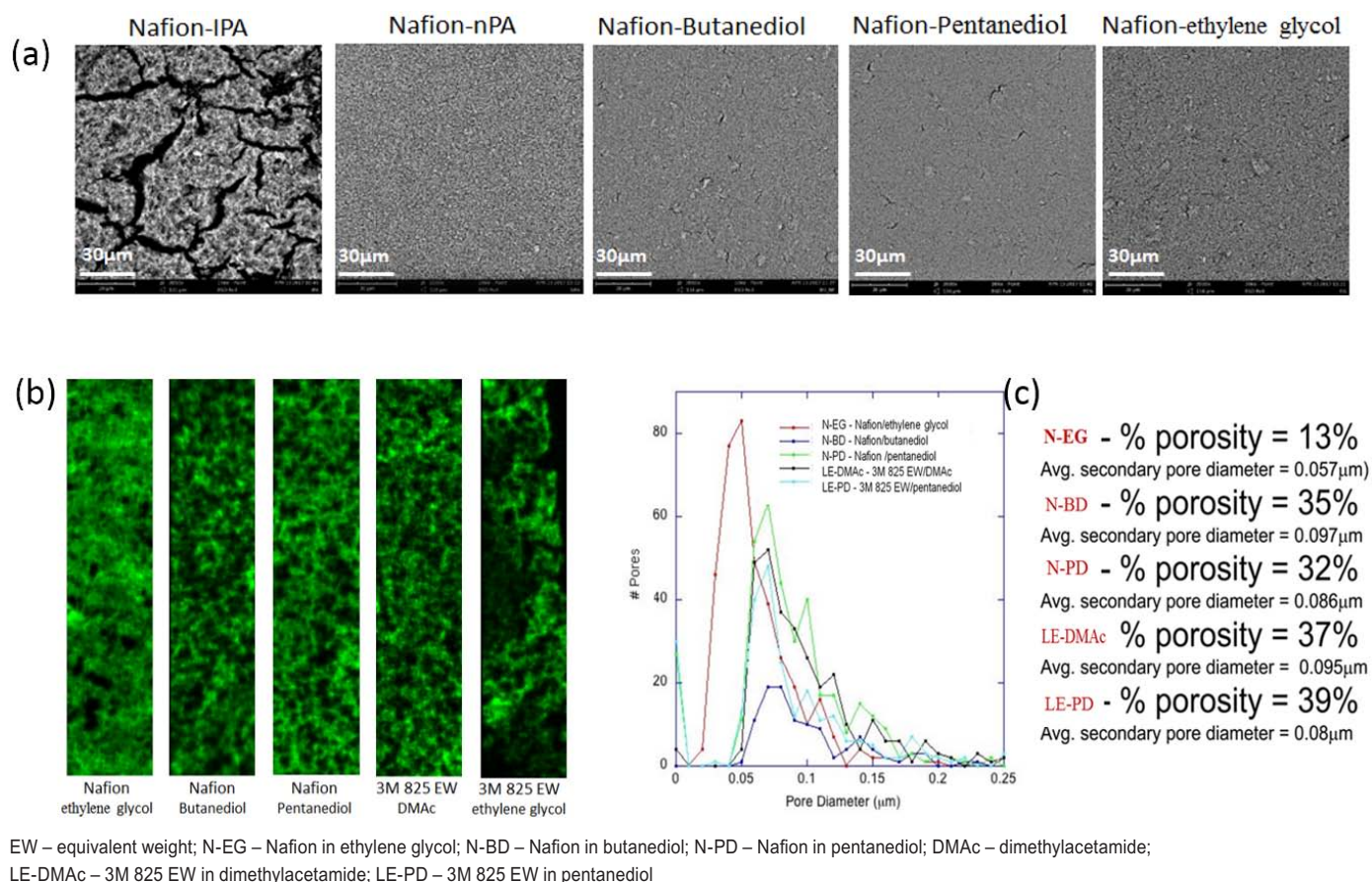


FIGURE 2. (a) Scanning electron microscopy images of catalyst layers prepared from different solvents. (b) Ionomer distribution in catalyst layers prepared from different ionomer dispersions. (c) Pore size distribution of the electrode layers.

sample showed the worst ionomer distribution, which was consistent with its poor coating quality. The porosity and pore size distribution of the electrode layers were also obtained from transmission electron microscopy image analysis, as shown in Figure 2c. The EG-based electrode shows the lowest porosity (i.e., 13%), indicating its high density. It also contains the smallest pore sizes and the highest number of pores. All the other samples have similar porosity, i.e., ranging from 32% to 39%. Among these electrodes, the 3M ionomer/pentanediol-based sample has the highest porosity.

The effect of the dispersing agents on initial fuel cell performance was investigated. In this experiment, four ionomer dispersions were used and compared with nPA/H₂O and IPA/H₂O. All MEAs had a Pt loading of ~0.20 mg_{Pt}/cm². The initial fuel cell performance is shown in Figure 3. The IPA/H₂O baseline shows very low performance especially in the mass transport region, which is probably attributed to its poor coating quality. The ionomer dispersions have shown significant influence on the fuel cell performance, with a general ranking as: nPA/H₂O > ethylene glycol > butanediol > pentanediol > pentanediol (3M). The ethylene glycol-based sample displays the best performance of all the non-aqueous

samples, and its performance is very comparable to the nPA/H₂O baseline. The cathode processed from butanediol showed relatively lower mass transfer performance than the ethylene glycol-based sample.

Based on the initial fuel cell performance, the ethylene glycol-based sample was selected for durability testing according to the DOE AST voltage cycling protocol: voltage cycles between 0.6 V and 1.0 V; at 80°C, 100% relative humidity (RH), and 0.2 standard liters per minute (SLPM) H₂/0.075 SLPM N₂ (shown in Figure 4). The voltage loss at 1 A/cm² from BOL to end of test is about 20 mV. Further in situ electrochemical characterization, including hydrogen crossover, cycling voltammetry, electrochemical impedance spectroscopy and high frequency resistance (HFR), etc., was carried out to understand the degradation mechanism in this sample. The cycling voltammetry plots show that electrochemical surface area (ECSA) gradually decreases during durability test, which is very common in the AST and related to catalyst particle degradation. HFR stays nearly the same after the AST. It is indicated that the main losses during the AST are in the ECSA and enhanced charge transfer resistance.

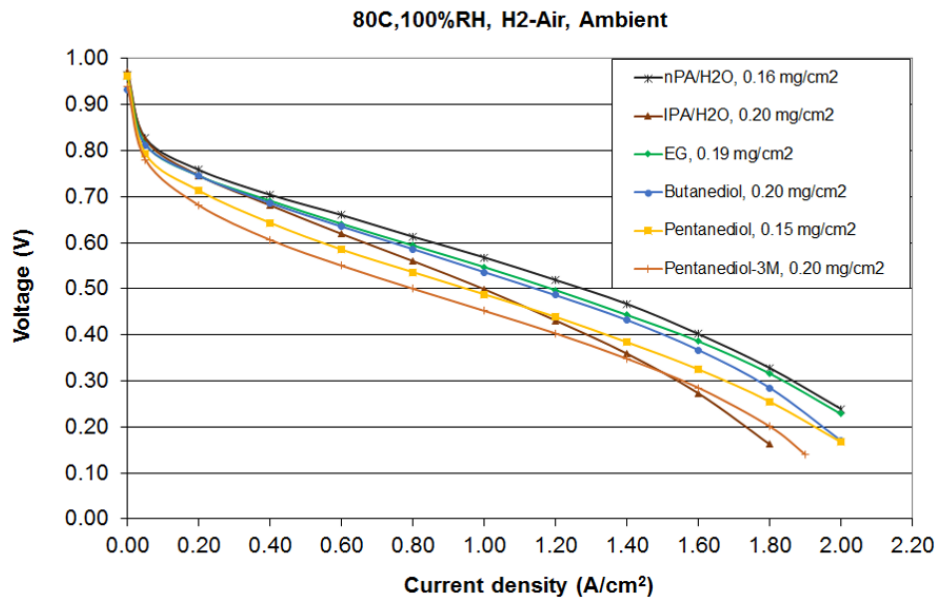


FIGURE 3. Solvent effect of the ionomer dispersion in cathode layer on H₂-air fuel cell performance: 80°C, 100% RH, ambient, H₂: 1.5 SLMP, air: 3 SLMP

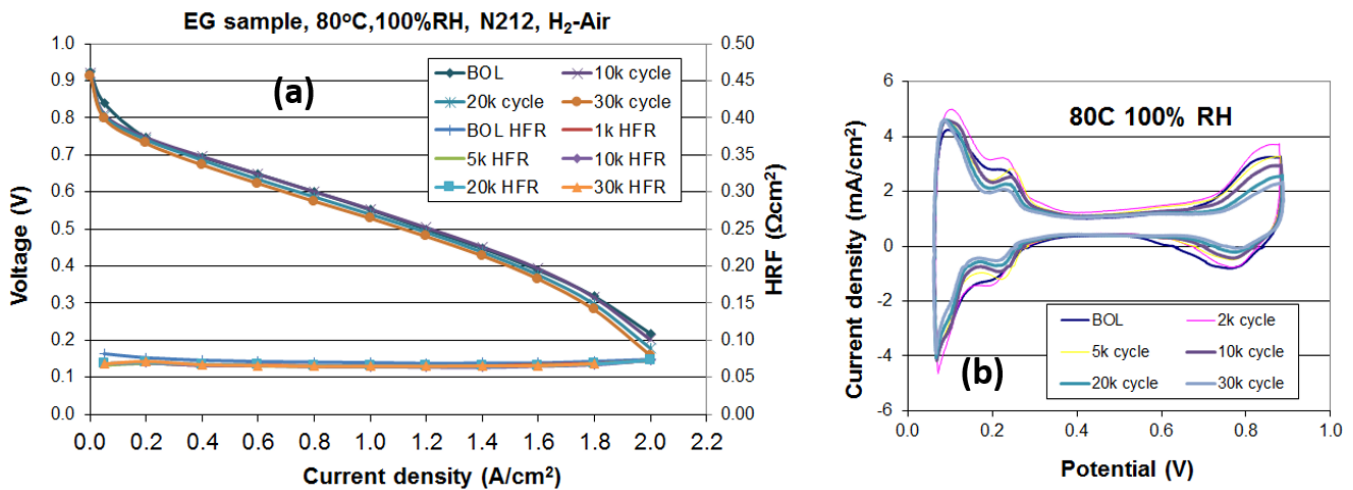


FIGURE 4. Durability test of EG-based sample for up to 30,000 voltage cycling: voltage cycles between 0.6 V and 1.0 V, at 80°C, 100% RH, 0.2 SLPM H₂ / 0.075 SLPM N₂. (a) H₂-air fuel cell performance as a function of voltage cycling. (b) Cycling voltammetry as a function of voltage cycling.

CONCLUSIONS AND UPCOMING ACTIVITIES

Conclusions

- LANL’s non-aqueous solvent-based ionomer dispersion technology in a variety of solvents has been investigated; the solvent affects ionomer morphology and ink particle size distribution.
- Ionomer dispersions impact the electrode structures by affecting the ionomer distribution and pore size

distribution. Ionomer distribution seems to be improved with hydrophilicity of the solvent.

- Ionomer dispersions influence fuel cell electrode performance. nPA- and EG-dispersed Nafion ionomers demonstrate the best fuel cell performance.

Upcoming Activities

- Further investigate the mechanism of solvent influence on fuel cell performance and durability via in situ and ex situ characterizations.

- Further investigate interactions between non-aqueous ionomer dispersions and catalysts to develop scalable MEA manufacturing for Giner’s water electrolyzer business.
- Develop large-scale DSM/non-aqueous ionomer dispersion based fuel cell MEA manufacturing processes and perform techno-economic analysis.

FY 2017 PUBLICATIONS/PRESENTATIONS

1. Xu, H., “Ionomer Dispersion Impact on Advanced PEM Fuel Cell Performance and Durability,” Oral Presentation. DOE Hydrogen and Fuel Cell Annual Merit Review Meeting, Washington, DC. June 2017.

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