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# FY15 SBIR II Release 2: Ionomer Dispersion Impact on Fuel Cell and Electrolyzer Performance and Durability

Hui Xu (Primary Contact), Chao Lei,  
Magali Spinetta  
Giner, Inc.  
89 Rumford Ave  
Newton, MA 02466  
Phone: (781) 529-0573  
Email: [hxu@ginerinc.com](mailto:hxu@ginerinc.com)

DOE Manager: Donna Ho  
Phone: (202) 586-8000  
Email: [Donna.Ho@ee.doe.gov](mailto:Donna.Ho@ee.doe.gov)

Technical Advisor: John Kopasz  
Phone: (630) 252-7531  
Email: [kopasz@anl.gov](mailto:kopasz@anl.gov)

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#### Collaborators:

- Los Alamos National Laboratory, Los Alamos, NM
- Oak Ridge National Laboratory, Oak Ridge, TN
- University of Connecticut, Storrs, CT

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Project End Date: June 27, 2018

## Overall Objectives

- Further develop and commercialize Los Alamos National Laboratory's (LANL) nonaqueous solvent-based ionomer dispersion technology.
- Scale-up ionomer and dimensionally stable membrane (DSM) production to allow for continuous roll-to-roll production of low platinum-group metal (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) 2018 Objectives

- Characterize catalyst ink particle size and electrode layer structure using nonaqueous solvent based ionomer.
- Investigate the influence of the solvent on fuel cell performance and durability.
- Demonstrate the durability advantages of using nonaqueous ionomers in the electrode, and analyze reasons for improved durability.

## Technical Barriers

This project addresses the following technical barriers from the Fuel Cell Technologies Office Multi-Year Research, Development and Demonstration Plan<sup>1</sup>:

- PEM fuel cell durability
- PEM water electrolyzer durability and 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.

DOE has not set a target for PGM electrolyzers. Giner's targets are the following:

- Low PGM loading electrolyzer MEA demonstrates less than 20 mV loss (at 1.5 mA/cm<sup>2</sup>) 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/cm<sup>2</sup>.

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

### FY 2018 Accomplishments

- Catalyst ink particle size and rheology characterization were carried out to understand the impacts of solvent and various mixing processes on ink structure. The correlation between ink property and electrode morphology was established.
- Established MEA baseline using an nPA (1-propanol l)/water solvent system, which demonstrated a greatly improved, crack-free morphology; better performance; and more consistent test results than the 2-propanol (isopropanol, IPA) baseline MEA.
- Compared a series of nonaqueous solvents for their impact on ionomer dispersion and fuel cell durability and determined causes for improved fuel cell performance.
- Applied nonaqueous ionomer dispersions to low-Pt (platinum) loading PEM fuel cell MEAs and obtained high-resolution transmission electron microscopy (TEM) images of electrodes with Pt distribution and ionomer distribution. The electrode morphology/structures were correlated to cell performance and durability.

**Table 1. Progress Toward Meeting Technical Targets for MEA Durability Targets**

| <b>Characteristic</b>                        | <b>Units</b>                          | <b>DOE 2020 Target</b> |
|--|---------------------------------------|------------------------|
| PGM total content (both electrodes)          | g/kW                                  | <0.125                 |
| PGM total loading (both electrodes)          | mg-PGM/cm <sup>2</sup> <sub>geo</sub> | <0.125                 |
| Loss in catalytic (mass) activity            | % loss                                | <40                    |
| Loss in performance at 0.8 A/cm <sup>2</sup> | mV                                    | <30                    |
| Loss in performance at 1.5 A/cm <sup>2</sup> | mV                                    | <30                    |
| Mass activity @ 900 mV <sub>iR-free</sub>    | A/mg-PGM                              | 0.44                   |

## 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 nonaqueous liquids to produce superior electrode performance, stability, and durability during harsh fuel cell operating conditions [1–2]. The LANL-produced MEA has been evaluated and certified using an accelerated stress test 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 (EW); there has been a strong push in the industry towards lower-EW membranes that can increase proton conductivity. Low-EW 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 for 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 to reduce manufacturing costs and extend the lifetime of the electrochemical devices. In FY 2018, we focused on improving fuel cell durability using nonaqueous solvent-dispersed ionomer. Our approach to obtain good fuel cell durability is to (i) understand ionomer particle morphology in dispersion; (ii) investigate the electrode morphology, catalyst, and ionomer binder distributions in the electrodes; and (iii) evaluate the electrode performance using various electrodes prepared from different dispersing agents. Electrodes were made from different dispersions and tested both at Giner and LANL. Oak Ridge National Laboratory and the University of Connecticut characterized the electrode morphology including polymer electrolyte and catalyst distribution to correlate the beginning of life performance with electrode morphology.

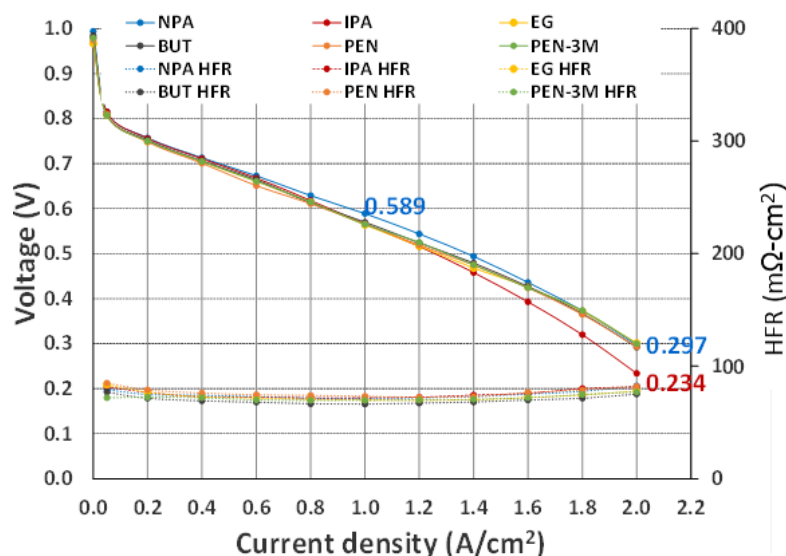
Table 2 summarizes the list of MEAs made at Giner using various ionomer dispersions; these are Nafion 1100 EW dispersed in ethylene glycol (EG), butanediol (BUT), pentanediol (PEN), and 3M low-EW ionomer dispersed in PEN (PEN-3M). Two baselines—IPA/water and nPA/water—also were compared. From our preliminary ionomer to carbon (I/C) ratio study, an I/C of 0.6 was found to provide the best performance when using TKK Pt/C (46.7 wt% Pt on carbon) catalyst. Pt loading for all MEAs was targeted around 0.2 mg/cm<sup>2</sup> and below and verified by X-ray fluorescence. The Pt loading of five spots on the electrode was measured, with the average value reported as the actual Pt loading.

**Table 1. List of Membrane Electrode Assemblies Made at Giner Using Various Dispersing Agents**

| Sample Abbreviation | Description                | I/C | Pt Loading (mg/cm <sup>2</sup> ) |
|---------------------|----------------------------|-----|----------------------------------|
| IPA                 | Nafion in 2-propanol/water | 0.6 | 0.19                             |
| nPA                 | Nafion in 1-propanol/water | 0.6 | 0.175                            |
| EG                  | Nafion in ethylene glycol  | 0.6 | 0.21                             |
| BUT                 | Nafion in butanediol       | 0.6 | 0.19                             |
| PEN                 | Nafion in pentanediol      | 0.6 | 0.18                             |
| PEN-3M              | 3M 825 EW in pentanediol   | 0.6 | 0.17                             |

## RESULTS

MEAs were fabricated by a decal transfer process onto Nafion NR-212 membrane. The MEAs were assembled with carbon paper gas diffusion layers (Toray H030). The prepared MEAs were placed in single-cell hardware with triple serpentine flow fields and a 25 cm<sup>2</sup> active area. The cell was conditioned by alternating between potential holds at 0.2 V (10 minutes) and 0.6 V (10 minutes) until constant currents were obtained at each voltage. The cell was heated to 80°C with humidity bottle temperatures of 80°C for the anode and 75°C for the cathode. The slightly lower cathode humidification temperature was employed to minimize the flooding at the cathode side. Figure 1 shows the dispersing solvent effect on fuel cell performance. The four dispersing agents using nonaqueous ionomers, EG, BUT, PEN, and PEN-3M, are similar in terms of initial performance. The nPA baseline MEA exhibits slightly better performance than all the others, while the IPA baseline displays significantly lower performance, especially in the high-current region. The initial performance ranks as illustrated below are nPA > EG ≈ BUT ≈ PEN ≈ PEN-3M > IPA.



**Figure 1. Effect of dispersing agents on initial fuel cell performance. Hydrogen/air fuel cell performance was measured at 80°C and ambient pressure. Membrane: Nafion 212; anode 50 wt% Pt/C (0.25 mg/cm<sup>2</sup>); cathode 50 wt% Pt/C catalyst; catalyst ink dispersing agent: varied.**

Figure 2 shows the electrode durability upon voltage cycling tests up to 30,000 cycles. The voltage loss at 1A/cm<sup>2</sup> is up to 65–80 mV for the nPA and IPA baselines based on two replicated durability tests for each cathode. On the other hand, both the EG and BUT cathodes demonstrate only 35 mV voltage loss, which is nearly half of those for the two baselines. The good durability in cathodes using nonaqueous solvents EG and BUT could be due to improved electrode morphology and structures that may help to reduce the catalyst degradation.

After durability testing (0.6 V to 1.2 V, 30,000 cycles) under H<sub>2</sub>/air, all tested cathodes were subject to particle-size measurements. Figure 3 summarizes the average particle size of Pt in all samples before and after the durability test. All beginning of life samples had comparable Pt particle sizes, 3.0–3.5 nm. After 30,000 voltage cycles, the average Pt particle size increased to 12 nm for both the IPA and nPA baselines, with particle size distribution (PSD) ranging from 5 nm to 30 nm. The BUT and EG cathodes showed a much smaller increase in Pt particle sizes (8–10 nm), with PSD ranging from 3 nm to 20 nm. Nonaqueous solvent-based MEAs demonstrated the least particle size increase. This is consistent with the durability data upon voltage cycling.

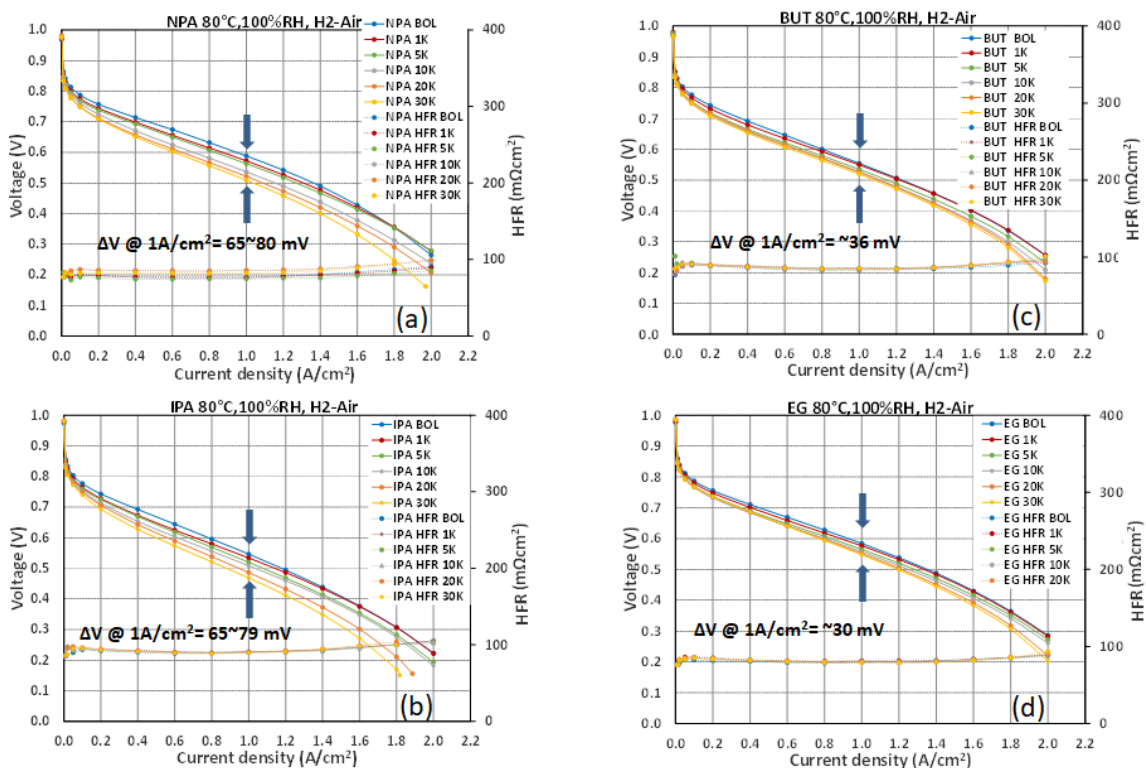


Figure 2. Electrode durability upon voltage cycling test: voltage cycling between 0.6 and 1.0 V. At 80 °C, 100% RH, 0.2 SLPM H<sub>2</sub> / 0.075 SLPM N<sub>2</sub> (a) nPA-based MEA; (b) IPA-based MEA; (c) BUT-based MEA; (d) EG-based MEA

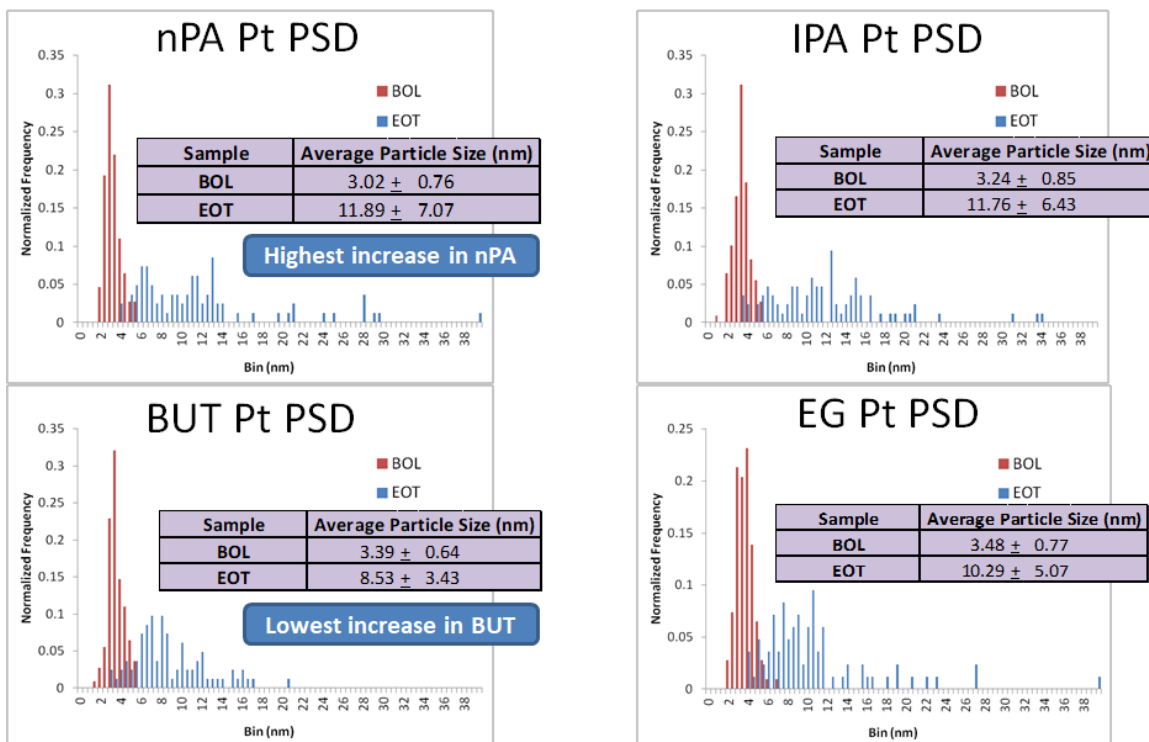


Figure 3. Particle-size measurements of fresh and tested MEAs using ionomers in various solvents

The high-resolution TEM–energy-dispersive X-ray spectroscopy images of the end of testing cathodes are shown in Figure 4. It is shown that there are significantly fewer Pt agglomerations in the BUT and EG samples than in the nPA and IPA baseline. Additionally, in the case of IPA, the electrode almost lost the majority of Pt particles. The loss of catalyst could be due to Pt dissolution and migration. It is also seen that BUT and EG samples have better ionomer distribution than the baseline. The durability benefit of using nonaqueous solvents may result from changed ionomer morphology in these solvents, which can help to prevent catalyst particle agglomeration and migration.

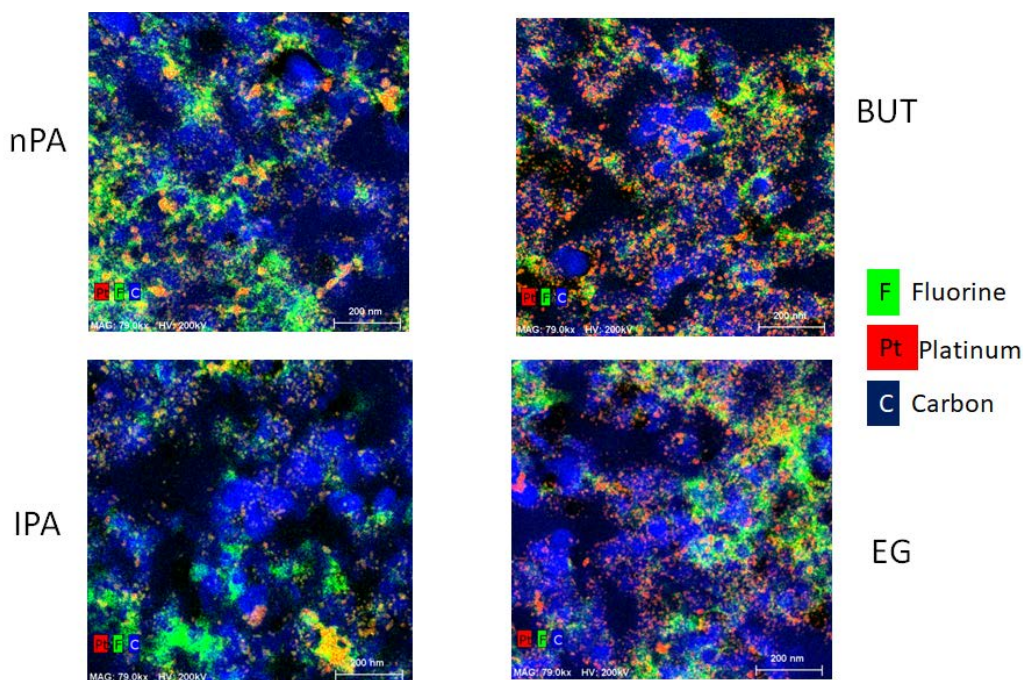


Figure 4. High-resolution TEM- energy-dispersive X-ray spectroscopy images of end-of-testing cathodes prepared from nPA, IPA, BUT, and EG

## CONCLUSIONS AND UPCOMING ACTIVITIES

### Conclusions

- Nonaqueous solvents affect ionomer morphology and platinum particle size distribution in catalyst inks.
- Nonaqueous solvent–based ionomer dispersions impact the electrode structures by changing the ionomer distribution and pore size distribution.
- Ionomer dispersions influence fuel cell electrode durability, and EG- and BUT-dispersed Nafion ionomers demonstrate the best fuel cell durability.
- The improved fuel cell durability is linked to reduced Pt particle agglomeration and migration, verified by TEM imaging and catalyst particle size distribution measurement.

### Upcoming Activities

- Quantitatively characterize catalyst inks and correlate these characteristics to cell performance and durability.
- Investigate interactions between nonaqueous ionomer dispersion/catalysts to develop scalable MEA manufacturing for Giner’s water electrolyzer business.



## FY 2018 PUBLICATIONS/PRESENTATIONS

1. H. Xu, “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 2018).

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2. Y.S. Kim, K.S. Lee, T. Rockward, U.S. Patent 7981319 B2 (2011).
3. Y.S. Kim, K.S. Lee, T. Rockward, U.S. Patent 8236207 B2 (2012).
4. C. Welch, A. Labouriau, R. Hjelm, B. Orlor, C. Johnston, and Y.S. Kim, “Nafion in Dilute Solvent Systems: Dispersion or Solution?” *ACS Macro Lett.* 1 (2012): 1403–1407.