V.C.4 Ionomer Dispersion Impact on Fuel Cell and Electrolyzer Performance and Durability

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Overall Objectives

- Further develop and commercialize LANL's non-aqueous 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 membrane electrode assemblies (MEAs) for fuel cells and electrolyzers.
- Demonstrate the durability of proton exchange membrane (PEM) fuel cell and electrolyzer MEAs at more extensive cycling and operating conditions.

Fiscal Year (FY) 2016 Objectives

- Prepare ionomer dispersions on a large scale to produce 1–2 kg.
- Fabricate DSM using ionomer dispersions from LANL in a more scalable continuous roll-to-roll process.
- Fabricate scaled-up, low-platinum-group-metal-loading MEAs for fuel cells (overall PGM loading less than 0.25 mg/cm^2) and electrolyzers (PGM loading less than 0.4 mg/cm^2 for anode plus cathode).

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Multi-Year Research, Development, and Demonstration Plan of the DOE Fuel Cell Technologies Office.

(A) Durability

(B) Cost

Technical Targets

The target of this project is 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. Progress towards Meeting Technical Targets for 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$_{iR\text{-}free}$	A/mg$_{PGM}$	0.44

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

- Low-PGM-loading electrolyzer MEAs demonstrate less than 20 mV loss (at 1.5 mA/cm^2) after 50,000 cycles from 1.4 V to 1.9 V.
- Low-PGM-loading electrolyzer MEAs demonstrate less than 20 mV performance loss after 1,000-hour test at 1.5 A/cm^2.

FY 2016 Accomplishments

- Various ionomer dispersions were produced in batch sizes up to over 1 kg. More than 40 non-aqueous solvents were evaluated.
- Significant progress was made to transition manufacturing to a roll-to-roll process. Electrode layer manufacturing was changed from batch spraying to an ink-casting process. DSM-based MEAs were fabricated from selected ionomer dispersions.

- MEAs produced by the new process were evaluated as fuel cells and electrolyzers. Short-term durability was evaluated.

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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 [1–6]. 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 a great potential to significantly improve the lifetime of PEM fuel cells [2–4]. However, the ionomer dispersion used was Nafion® 1,100 equivalent weight (EW); there has been a strong push in the industry towards membranes with lower EW 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 project will validate these technologies towards viable commercial applications in advanced fuel cell and electrolyzer systems.

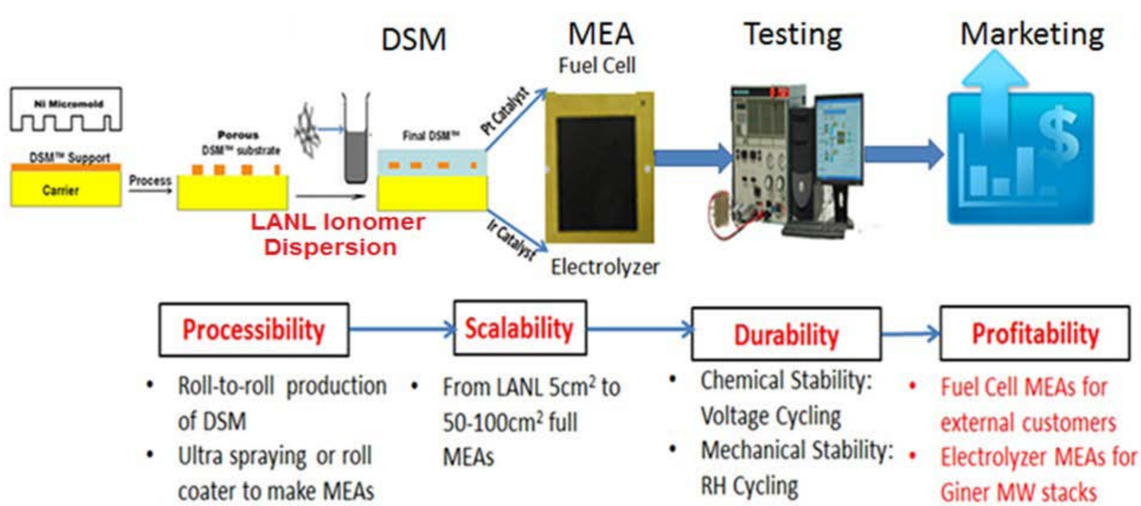
APPROACH

The approach used for this project is shown in Figure 1. First, the ionomer dispersion technology invented by LANL was applied in the platforms of the DSM™ developed at Giner; the impregnation of the novel low-EW ionomer dispersion into porous DSM supports has created more durable membranes with excellent proton conductivity for PEM fuel cells. Second, Giner will extend the ionomer dispersion studies to state-of-the-art PEM fuel cell catalysts. Most experiments performed at LANL were based on ETEK 20 wt% Pt supported on VULCAN 72 (20% Pt/C). Giner will examine the ionomer dispersion technology paired with more advanced catalysts (e.g., Tanaka catalyst). Finally, the project will also investigate the impact of ionomer dispersion on PEM electrolyzer MEAs that generally use unsupported iridium (Ir) catalysts. Giner will perform MEA durability tests following the DOE accelerated stress test protocols.

RESULTS

Giner and LANL have formed a wide range of ionomer dispersions starting from either Nafion 1100 EW or 3M's 825 EW perfluorosulfonic acid (PFSA). More than 40 non-aqueous solvents were investigated. The selected ionomer dispersions were used to fabricate membranes, DSM-reinforced membranes, and catalyst layers.

Membranes were made using 3M low-EW PFSA solutions and evaluated according to the following performance criteria: ionic conductivity, mechanical strength, and dimensional change on hydration. The materials were evaluated at 80°C when immersed in liquid water or equilibrated at various humidity levels. The ionic conductivity of the materials is shown in Figure 2a. Ionic conductivity was typically measured using a four-



RH - Relative humidity

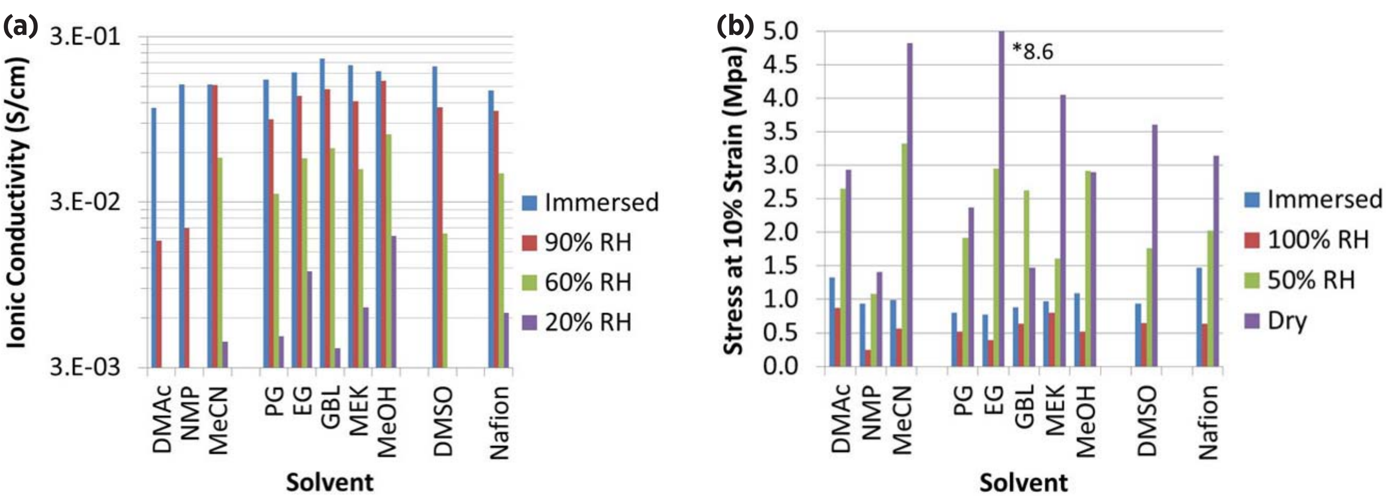
FIGURE 1. Technical approaches for PEM fuel cell and electrolyzer durability tests based on LANL's ionomer dispersion

point probe with platinum wires attached to a sine wave generator at 1 kHz. When immersed in liquid water, the ionic conductivity of all materials was on the same order of magnitude. Many of the solvent-cast materials had conductivity higher than that of Nafion; this is expected as the 3M PFSA has a lower EW than Nafion and is known to be more conductive. Certain solvent-cast membranes, namely dimethylacetamide (DMAc) and N-methylpyrrolidone (NMP), showed lower-than-normal conductivity when immersed in water and extremely low conductivity when only exposed to humid air. It is possible that DMAc or NMP were hydrolyzing during fabrication and form amines that might poison the membrane by ion exchange. If poisoning were occurring, one would expect a strong reduction in conductivity under humid conditions but a much weaker reduction when immersed in water, which allows contaminants to diffuse away. The results of dynamic mechanical testing upon the membranes are shown in Figure 2b. The solvent-cast materials had a lower stress at 10% strain (roughly equivalent to modulus) compared to Nafion. All materials other than methyl ethyl ketone (MEK) had a strain at break of greater than 150%.

We prepared cathodes with catalysts having different Pt loading on the carbon. At a fixed Pt loading, as the Pt weight percent decreases, the electrode thickness increases since the density of the carbon is more than 20 times lower than the density of the platinum. Figure 3a shows the polarization curves of 5-cm^2 standard MEAs having different Pt weight percent in the cathode. The Pt loading was fixed to ~0.05 mg/cm^2 for these MEAs. As expected, the fuel cell performance is improved as Pt weight percent decreases. No notable high frequency resolution (HFR) difference between the MEAs was observed. Currently LANL is investigating the durability of low Pt/C cathodes during potential cycling from 0.6 to 1.0 V. The performance and durability data will be used as the baseline for our further study using LANL ionomer dispersions.

The effect of the dispersing agents of low-Pt-loading cathodes on initial fuel cell performance was investigated. In this experiment, five LANL dispersing agents were used and compared with water/isopropyl alcohol (IPA) dispersing agents. All MEAs had a Pt loading of ~0.05 mg_{Pt}/cm^2. The initial fuel cell performance is shown in Figure 3b. All cathodes prepared from LANL dispersing agents showed at least comparable performance to the water/IPA dispersing agent processed cathode. There was a slight difference between cathodes using different dispersing agents. The cathodes processed from NMP, DMAc, and ethanol showed relatively better kinetic performance than the cathodes processed from pentanediol, glycerol, and water/IPA. The cathodes processed from NMP and DMAc showed relatively better mass transfer performance than the other cathodes. The improved mass transport performance using NMP and DMAc is in good agreement with higher-Pt-loading cathodes, i.e., 0.2–0.5 mg/cm^2.

The 3M PFSA ionomer solutions were evaluated for use in casting electrolyzer anode decals via a blade-casting method. The three most promising decals were tested in electrolyzer cells. The resulting performance after 100 hours of operation at 2 A/cm^2 is given in Figure 4a. The blade-cast decals performed just as well as Giner's standard spray-cast decal method. Tafel slope analysis indicated that the blade-cast decals displayed some curvature at high current densities. Based on prior experience, this indicates that the ionomer content in the anode decal layer may be too high, and decreasing it could lead to performance gains. Cells were also built to evaluate durability via accelerated stress testing. Figure 4b shows the performance change for a cell built using an anode cast from a dimethylformamide (DMF)-based solution on Nafion 1110 membrane. Little to



MeCN – Acetonitrile; PG – Propylene glycol; EG – Ethylene glycol; GBL – γ-butyrolactone; MeOH – Methanol; DMSO – Dimethyl sulfoxide

FIGURE 2. Selected properties of membranes cast from various solvent dispersions: ionic conductivity (a) and stress at 10% strain (b)

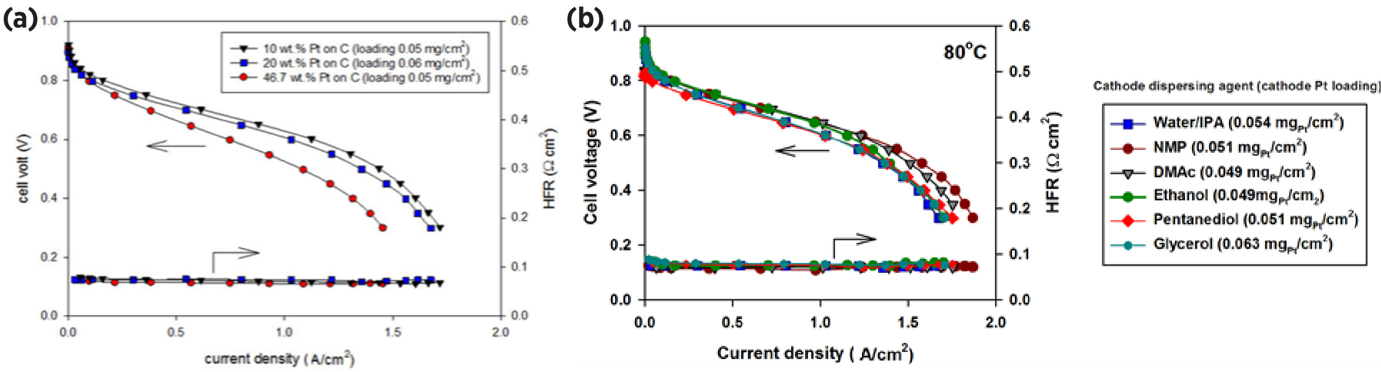


FIGURE 3. H_2/air fuel cell performance: 80°C, 100% relative humidity, 30 psi back pressure, stoic number: H_2:3, air:2: (a) effect of cathode Pt wt% in the catalyst; (b) effect of the solvent for the ionomer dispersion

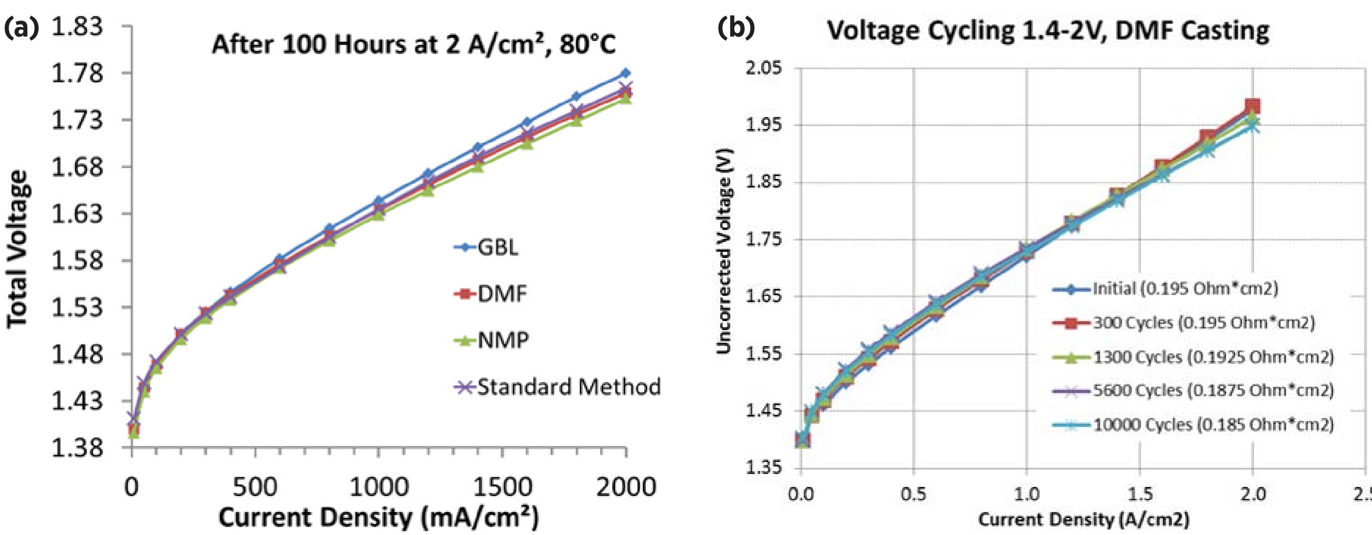


FIGURE 4. Electrolyzer cell performance at 80°C using the blade-cast electrodes: constant current operation (a) and accelerated stress testing via voltage cycling (b)

no signs of degradation were observed. In fact, performance below 1.2 A/cm^2 improved as the result of decreasing high-frequency resistance. The other solvent systems produced similar results.

CONCLUSIONS

- A variety of non-aqueous ionomer dispersions were evaluated in terms of ionomer concentration, conductivity, dimensional expansion, and mechanical properties of cast membranes.
- Selected solvents include DMSO, GBL, and MeOH.
- Low-Pt-loading fuel cell electrodes using non-aqueous ionomer dispersions were developed; glycerol-based electrodes demonstrated a good trade-off between performance and durability.
- Water electrolyzer electrodes using non-aqueous ionomer dispersions were investigated. GBL-, NMP-, and DMF-based ionomer dispersions led to uniform electrodes with good performance and durability.

FUTURE DIRECTIONS

- Further investigate the transport properties of fuel cell electrodes using low-Pt-loading and non-aqueous ionomer dispersions.
- Use non-aqueous ionomer dispersions to develop fully scalable and processible electrode and MEA manufacturing platforms for Giner's water electrolyzer.

FY 2016 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 2016.

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