V.F.11 Ionomer Dispersion Impact on Advanced Fuel Cell and Electrolyzer Performance and Durability

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Los Alamos National Laboratory (LANL), Los Alamos, NM

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Project End Date: March 8, 2015

Overall Objectives

- Validate the scalability and processability (roll to roll production) of membrane and electrode assembly (MEA) fabrication using LANL's ionomer dispersions
- Integrate Giner dimensionally-stabilized membrane (DSM) supports with LANL ionomer dispersion to make mechanically and chemically stable MEAs
- Explore commercial applications of LANL ionomer dispersions in fuel cell or electrolyzer markets

Fiscal Year (FY) 2015 Objectives

The FY 2015 objects are the same as the overall objectives since this is a nine-month Small Business Innovation Research Phase I project.

Technical Barriers

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

(A) Durability

Technical Targets

The targets of this project are to apply LANL ionomer dispersion technology and Giner DSM technology to make durable fuel cell MEAs that may meet the DOE targets listed in Table 1.

TABLE 1. DOE PEM Fuel Cell MEA Durability Targets

	Units	2020 Target
Platinum group metal (PGM) total content (both electrodes)	g/kW	<0.125
PGM total loading (both electrodes)	mg/cm^2	<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

Accomplishments

- Integrated LANL low equivalent weight (EW) ionomer dispersion into Giner DSM platform and created hybrid membranes that exhibit high proton conductivity and good mechanical properties
- Successfully developed DSM-based MEAs that demonstrate both chemical and mechanical stability over extensive voltage and relative humidity (RH) cycling tests
  - One MEA after 30,000 cycles (voltage cycling 0.6 V to 1.0 V) showed 10% to 15% electrochemical surface area (ECSA) loss and minimal performance loss
  - One MEA after 5,000 cycles (RH cycling from dry to fully saturated) showed less than 0.5 mA/cm^2 increase in hydrogen crossover
- Successfully applied ionomer dispersion to PEM and demonstrated high electrolyzer MEA durability in extensive voltage cycling
  - One MEA after 10,000 cycles (voltage cycling 1.4 V to 1.8 V) without any performance loss

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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 (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 a great potential to significantly improve the lifetime of PEM fuel cells [2–4]. However, the ionomer dispersion used was Nafion® 1100 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 dimensionally-stable membrane (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 dispersion from LANL in the acid form and utilizing Giner's DSM technology, this Phase I program validated this technology 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 AST protocols.

RESULTS

The DSM fabrication process [5] is described in Figure 2a. First, the dispersed Nafion® 1100 EW or 3M 825 EW solution was cast onto two pieces of Teflon™ film and then dried at the appropriate temperature (varying by solvent). The porous Kapton® film (DSM substrate) was sandwiched between two cast ionomer films and hot pressed at the appropriate pressure for transfer. The resultant ionomer film was then peeled off from the two Teflon™ substrates. All membranes were dried in a vacuum oven after fabrication at 120°C overnight to ensure complete solvent evaporation. The DSMs fabricated are shown in Figure 2b. These membranes can be placed into two categories (1100 EW and 825 EW) and vary in their thickness from 22 µm to 41 µm. Some of these DSMs were used for subsequent MEA fabrication and testing.

The MEA using Tanaka Pt/C catalyst (46.6 wt%), 3M 825 EW ionomer in dimethylacetamide, and DSM (865-32-1 in Figure 2b) was subjected to voltage cycling followed by AST recommended by DOE's Fuel Cell Technical Team (FCTT). The MEA was cycled from 0.6 V to 1.0 V at 50 mV/s for 30,000 cycles. Cyclic voltammograms (CVs) were obtained at different intervals to examine the ECSA change (see Figure 3a). The ECSA first increased until

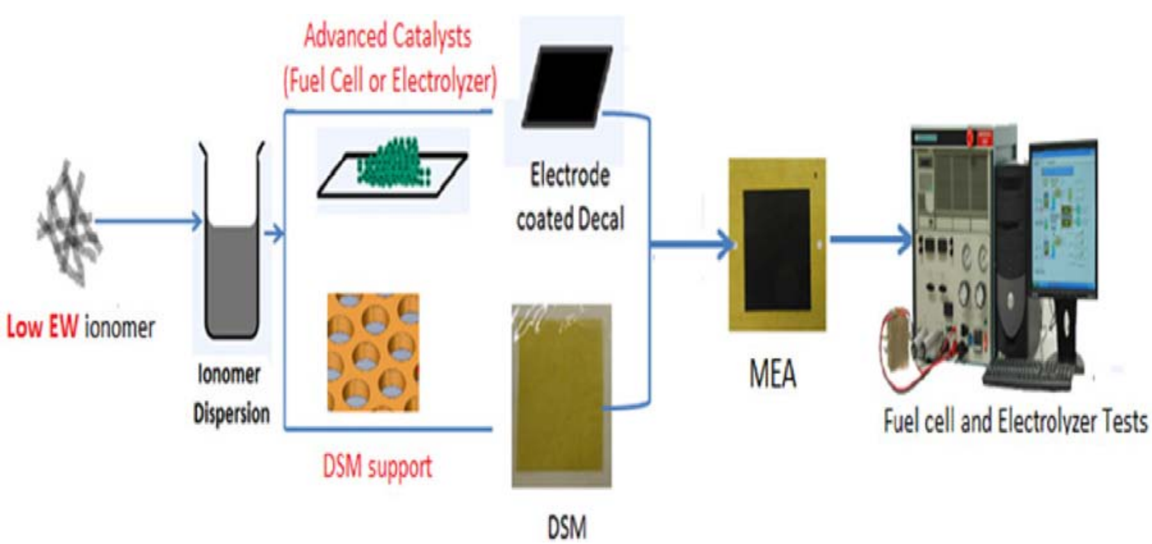
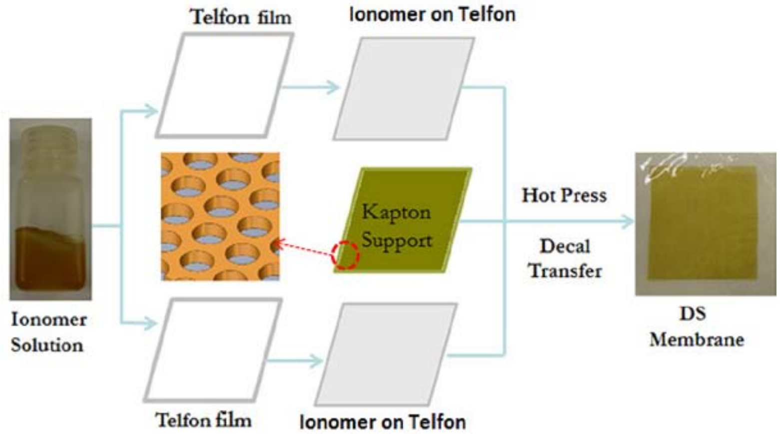


FIGURE 1. Technical approaches for PEM fuel cell and electrolyzer durability tests based on LANL's ionomer dispersion

(a)



(b)

Membrane ID	865-15-1	865-18-1 865-29-1 865-30-1	865-17-1	865-32-1
Ionomer	5% N1100EW	5% N1100EW	2.5% 3M 825EW	2.5% 3M 825EW
Solvent	1, 2 Pentanediol	NMP	1, 2 Pentanediol	DMAc
Thickness	35 µm	22 µm	24 µm	41 µm
Color	Dark yellowish	Yellow	Yellow	Yellow

FIGURE 2. Fabrication of DSMs using Giner porous supports and LANL's ionomer dispersion: (a) illustration of DSM fabrication; (b) a list of fabricated DSMs and corresponding compositions

10,000 cycles; it was likely due to the MEA being not fully conditioned at the beginning of voltage cycling. The DSM-based MEA demonstrated outstanding electrochemical stability: the ECSA loss was only 10% from 10,000 cycles to 30,000 cycles. A twin MEA with identical compositions was subject to RH cycling to evaluate its mechanical stability, again following FCTT AST protocol. During the RH-cycling durability testing, the MEA was cycled from dry to oversaturated conditions. Cyclic and linear-sweep voltammograms were performed at certain points during the test to calculate hydrogen crossover. As shown in Figure 3b, the MEA demonstrated excellent mechanical stability after nearly 5,000 cycles, with hydrogen crossover less than 0.5 mA/cm^2, far smaller than FCTT recommended 2 mA/cm^2.

The durability of PEM electrolyzer MEAs using LANL ionomer dispersion was also examined. The anode of these MEAs was made of an oxygen evolution reaction (OER) catalyst and LANL Nafion® 1100 EW ionomer in N-Methyl-2-pyrrolidone. Two categories of OER catalyst were evaluated; one was commercial iridium (Ir) black and the second was a Giner developmental Ir supported on tungsten doped titanium oxide ($Ir/W_xTi_{1-x}O_2$). The latter has higher ECSA and demonstrates much higher mass activity. Both MEAs were subject to a voltage cycling routine Giner developed for electrolyzer stability evaluation: cycling from 1.4 V to 1.8 V with 5 min hold for each voltage. Polarization curves were obtained at regular intervals in the cycling campaign (see Figure 4). Both MEAs demonstrated good durability after 1,500 cycles. In particular, the MEA using $Ir/W_xTi_{1-x}O_2$ catalyst was very stable over the entire course of 10,000 cycles. These data suggests two advantages of the LANL ionomer: good tolerance to high voltage and compatibility between ionomer and Giner's Ir/ $W_xTi_{1-x}O_2$. This is extremely meaningful because the durability and low PGM loading from LANL ionomer and the advanced catalyst will significantly reduce the cost of electrolyzer stacks. Giner has started a 1-MW stack/system development program in collaboration with our major partners and targeting the manufacture and sale of PEM stacks and systems globally. The LANL ionomer dispersion will play a big role for this initiative and will be further studied in our Phase II project.

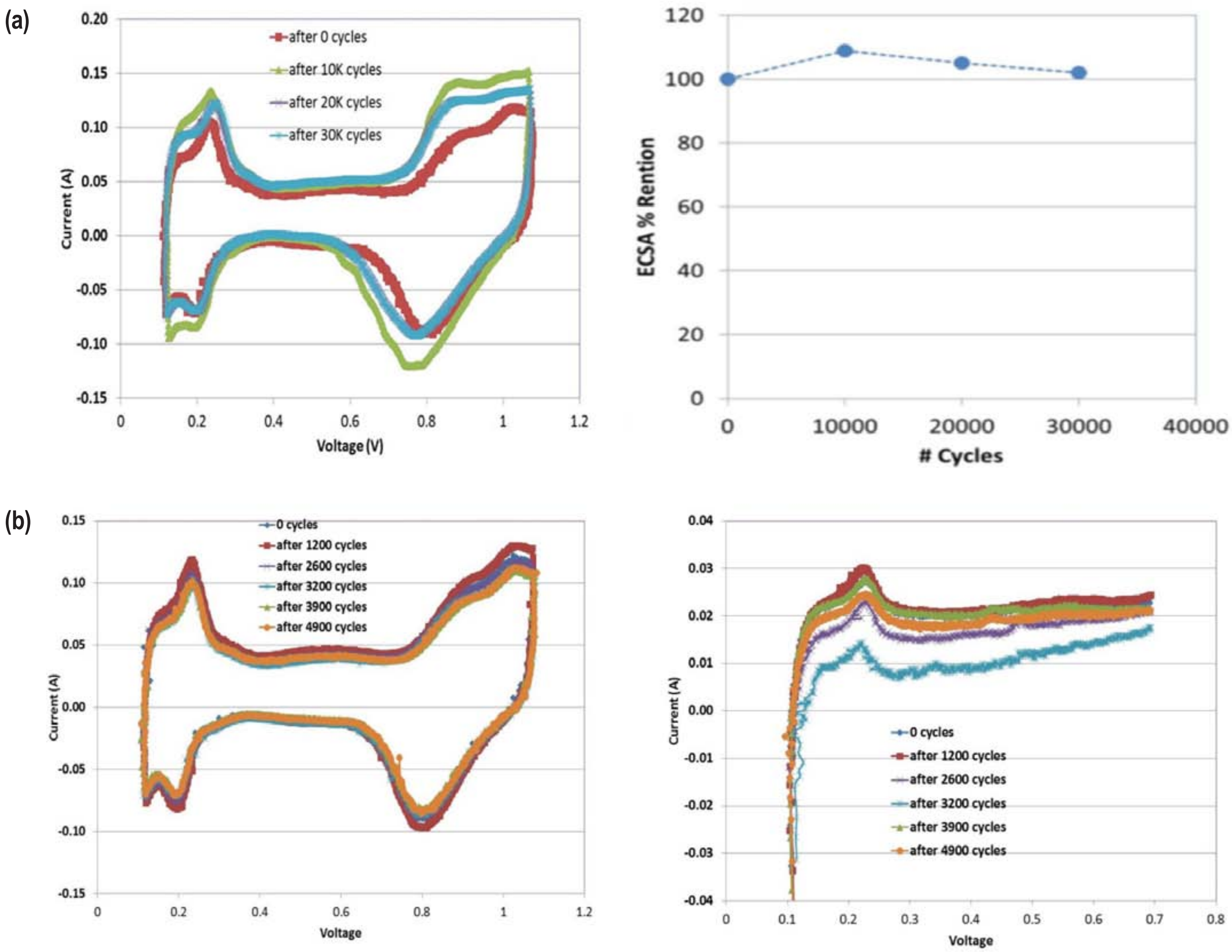


FIGURE 3. Chemical and mechanical durability of MEAs using DSM and LANL ionomer dispersion: (a) CVs and ECSA after voltage cycling: 0.6 V to 1.5 V, 50 mV/s; (b) CVs and hydrogen crossover after RH cycling from dry to saturated condition. Cell area: 50 cm^2; operating temperature: 80°C; cathode Pt loading: 0.4 mg/cm^2 from 46.6 wt% Tanaka Pt/C.

CONCLUSIONS AND FUTURE DIRECTIONS

Conclusions

- LANL non-aqueous ionomer dispersion technology has been validated at Giner in more scalable and processible conditions via DOE AST protocols.
- Hybrid membranes using Giner's DSM supports and LANL ionomer show good conductivity and improved mechanical properties.
- The combination of hybrid membrane and non-aqueous ionomer-based electrodes produces chemically and mechanically stable MEAs.
- The non-aqueous ionomer also demonstrates good compatibility with OER catalysts in electrolyzer, leading to excellent stability upon voltage cycling.

Future Direction

- Scale-up of non-aqueous ionomer dispersion production
- Scale-up of DSM-based MEA fabrication
  - Based on Giner's roll-to-roll DSM technology
- More durability tests in PEM electrolyzers
- Feasibility of licensing and commercializing LANL ionomer dispersion technology

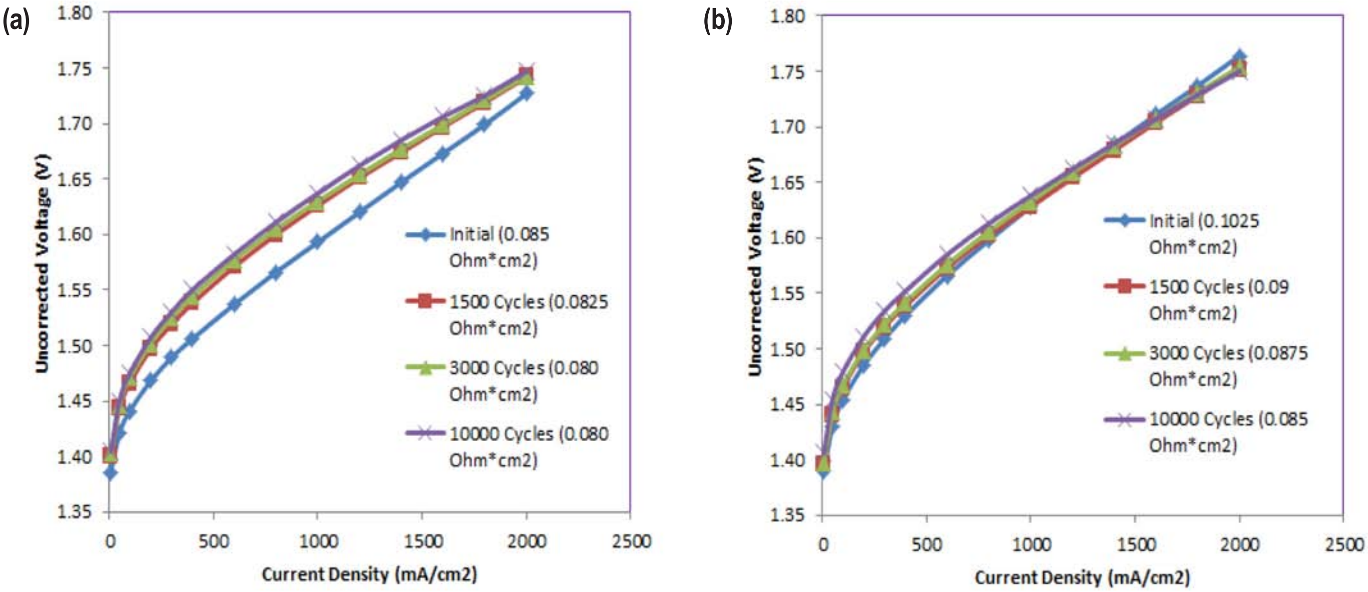


FIGURE 4. Durability of PEM water electrolyzer MEAs using LANL ionomer dispersion. Cell area: 50 cm^2; operating temperature: 80°C; anode catalyst: commercial Ir black or developmental Ir/$W_xTi_{1-x}O_2$, with Ir loading 0.4 mg/cm^2. Voltage cycling from 1.4 V to 1.8V.

FY 2015 PUBLICATIONS/PRESENTATIONS

1. Xu, H., J. Willey, T. McCallum, and Y.S. Kim, "Ionomer Dispersion Impact on Advanced PEM Fuel Cell Performance and Durability," STTR Phase I Final Report, U.S. Department of Energy Grant No. DE-SC0012049, March 2015.

2. Xu, H., "Ionomer Dispersion Impact on Advanced PEM Fuel Cell Performance and Durability," poster presentation in DOE Hydrogen and Fuel Cell Annual Merit Review meeting, Washington, D.C., June 2015.

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2. Kim, Y.S.; Lee, K.S.; Rockward T. U.S. Patent 7981319 B2, 2011.

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6. Welch, C., A. Labouriau, R. Hjelm, B. Orler, C. Johnston, and Y.S. Kim, "Nafion in Dilute Solvent Systems: Dispersion or Solution?" *ACS Macro Lett.*, 1, 1403−1407 (2012).