Ionomer Dispersion Impact on PEM Fuel Cell and Electrolyzer Durability

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Giner Inc.
Newton, MA

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Project ID# FC117

Project Overview

Timeline

- Project Start Date: 6/9/2014
  Project End Date: 3/8/2015

Budget

- Total Project Value:
  $149, 949
- Total Funding Spent:
  $149, 949

Barriers Addressed

- PEM fuel cell and electrolyzer durability

Technical Targets

- Validate the scalability and processibility of MEAs
- Integrate Giner dimension-stabilized membrane (DSM) with LANL ionomer dispersion to create MEAs mechanically and chemically stable

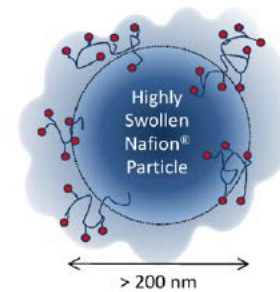
Partners

- LANL: Dr. Yu-Seung Kim

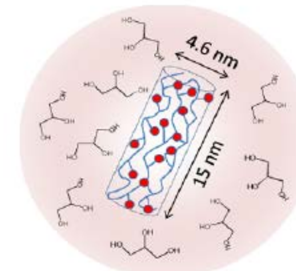
Relevance: LANL Non-aqueous Ionomer Dispersion Technology Transfer and Commercialization

DOE Fuel Cell Catalyst Technical Targets

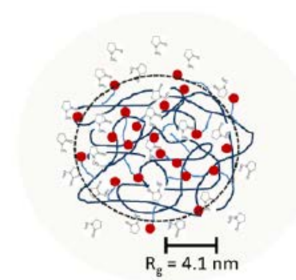
	Units	2020 Target
Platinum group metal (PGM) total content (both electrodes)	g/kW	<0.125
PGM total loading (both electrodes)	mg/cm^2	<0.125
Loss in catalytic (mass) activity[a,b]	% loss	<40
Loss in performance at 0.8 A/cm^2 [a]	mV	30
Loss in performance at 1.5 A/cm^2 [b]	mV	30
Mass activity @ 900 $mV_{iR\text{-}free}$ [c]	A/mg_{PGM}	0.44



In water/2-propanol

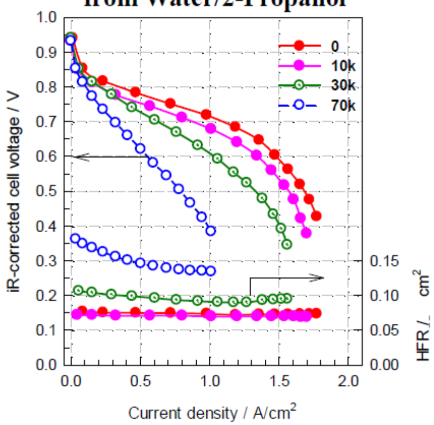


In glycerol



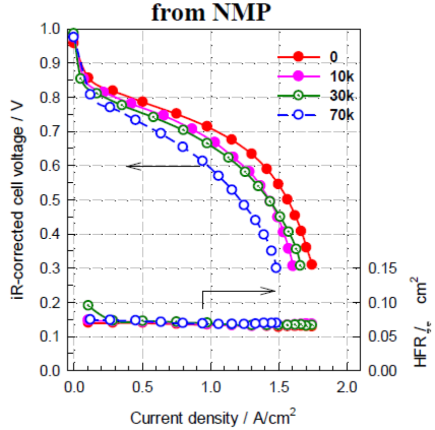
In NMP

Nafion® from Water/2-Propanol



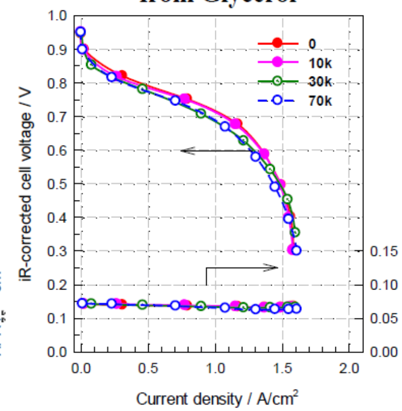
Premature electrode & electrode-membrane interface failure

Nafion® from NMP



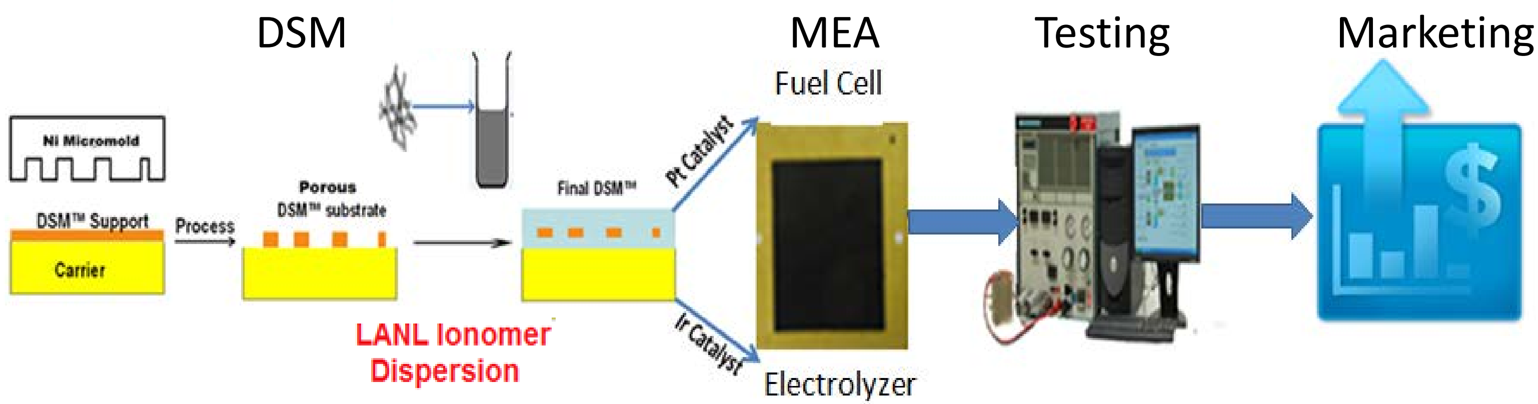
Performance decrease due to Pt nano-catalyst agglomeration

Nafion® from Glycerol



Performance decrease was compensated with time dependent structural change

Approach



Processibility → **Scalability** → **Durability** → **Profitability**

Processibility
- Roll-to-roll production of DSM
- Spraying or roll coater to make MEAs

Scalability
- From LANL 5cm^2 to 50-100cm^2 full MEAs

Durability
- Chemical Stability: Voltage Cycling
- Mechanical Stability: RH Cycling

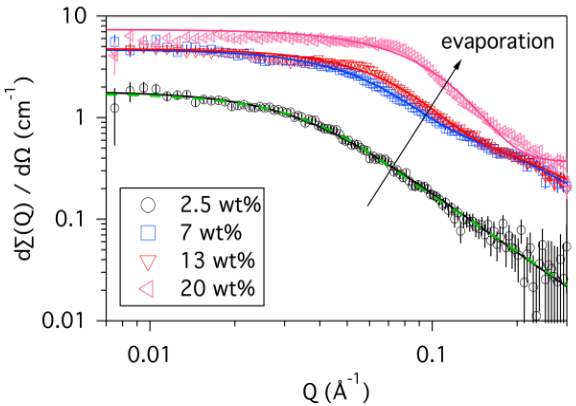
Profitability
- Fuel Cell MEAs for external customers
- Electrolyzer MEAs for Giner MW stacks

Combining Giner's DSM technology with LANL's ionomer dispersion technology may deliver lower-cost MEAs that are mechanically and chemically stable.

Accomplishment: Nafion Particle Morphology

Particle morphology in dispersion is critical for membrane and electrode properties. LANL performed SANS and dynamic light scattering to investigate the particle morphology. Recently we found that the particle morphology of NMP dispersion is different from what we know.

SANS of Nafion dispersion in NMP



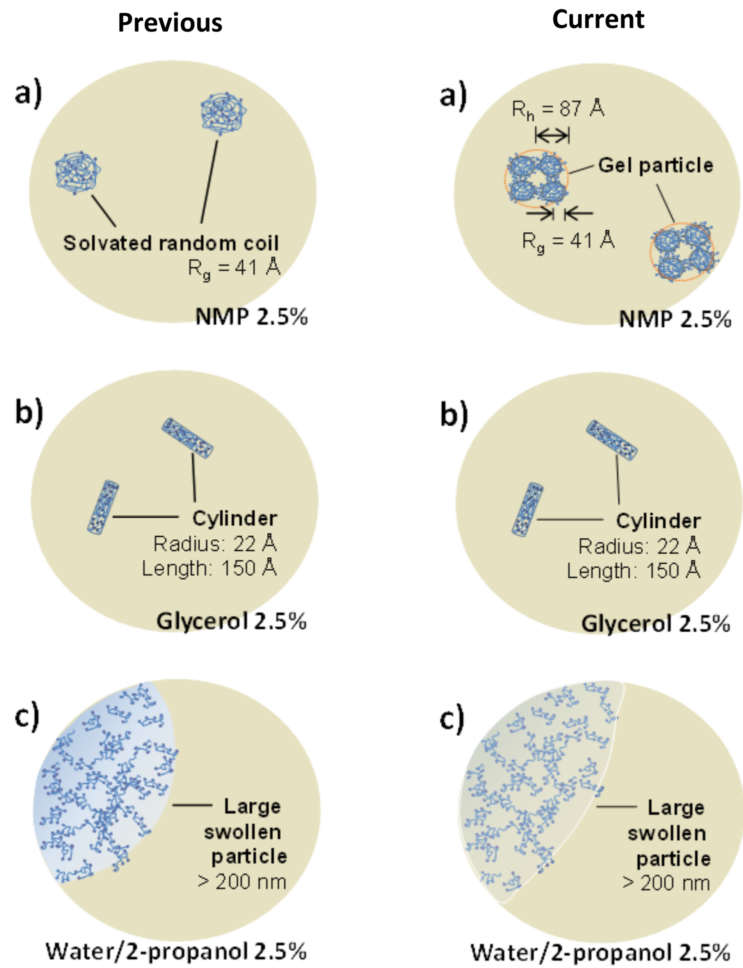
Black line: Random walk modeling

$I(Q) \propto \Delta\rho <P(Q)S(Q)>$

Green line: Gel particle modeling

$$I(Q) = I_G(0)\exp[-Q^2\Xi^2/2] + I_L(0)/(1+Q^2\xi^2) + B$$

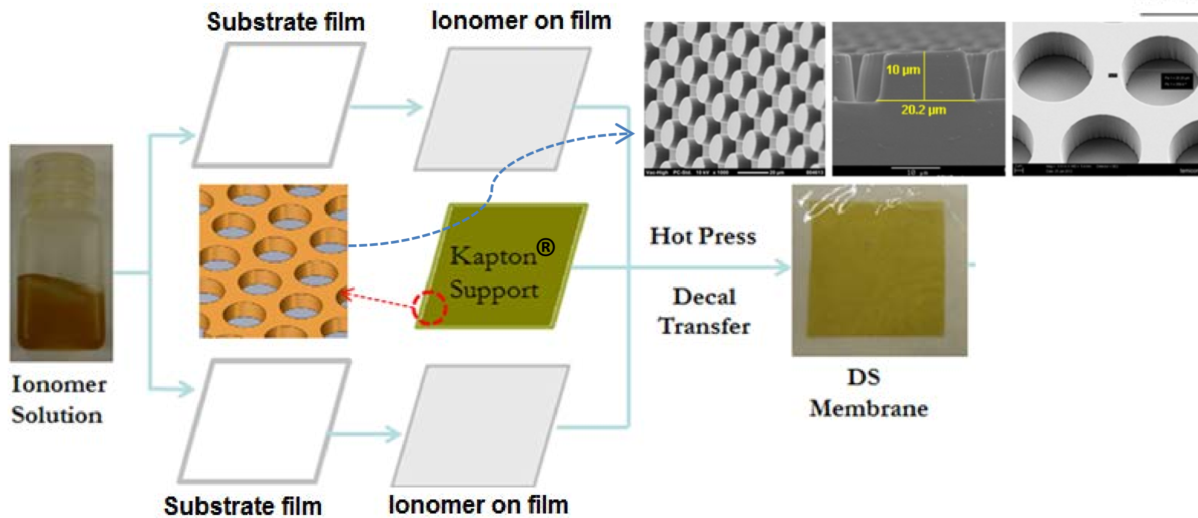
Particle size from DLS: RH = 8.7 nm



Current morphology is more consistent with electrode porosity and fuel cell mass transfer behavior

Y.S. Kim et al. *Macromolecules*, 48, 2161-2172 (2015)

Accomplishment: DSMs Using LANL Ionomer

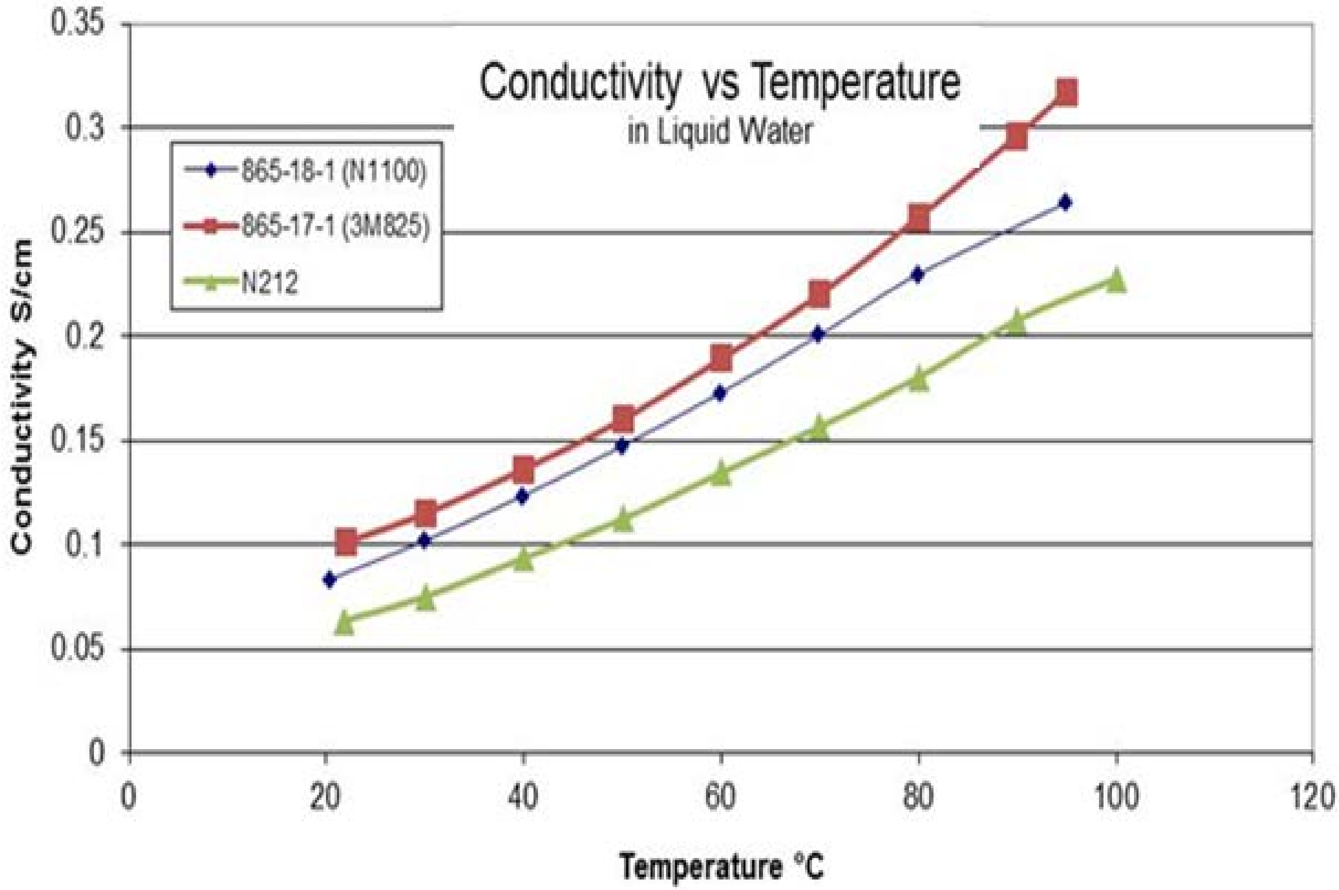


Membrane ID	865-15-1	865-18-1 865-29-1 865-30-1	865-17-1	865-32-1
Ionomer	5% N1100EW	5% N1100EW	2.5% 3M 825EW	2.5% 3M 825EW
Solvent	1, 2 Pentanediol	NMP	1, 2 Pentanediol	DMAc
Thickness	35 µm	22 µm	24 µm	41 µm
Color	Dark yellowish	Yellow	Yellow	Yellow

Dark color due to high heating temperature during membrane casting

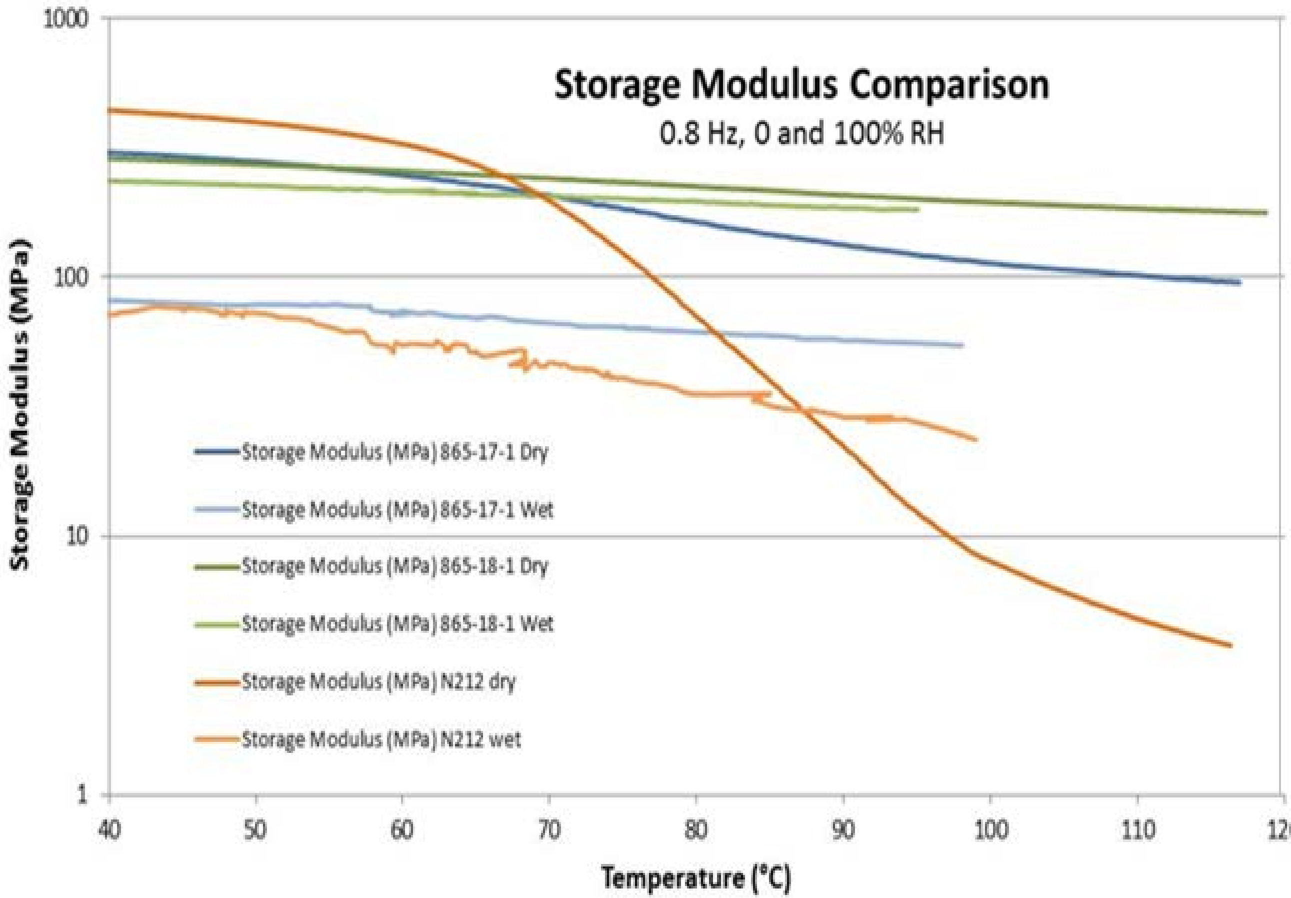
Hybrid membranes obtained using Giner's high throughput DSM platform

DSM Conductivities



- Conductivity of the DSMs was measured in liquid water at various temperatures and compared to Nafion®212 (N212).
- Conductivity was as expected for the lower equivalent weight DSM, and higher than expected for the N1100 based DSM.

DSM Mechanical Characteristics

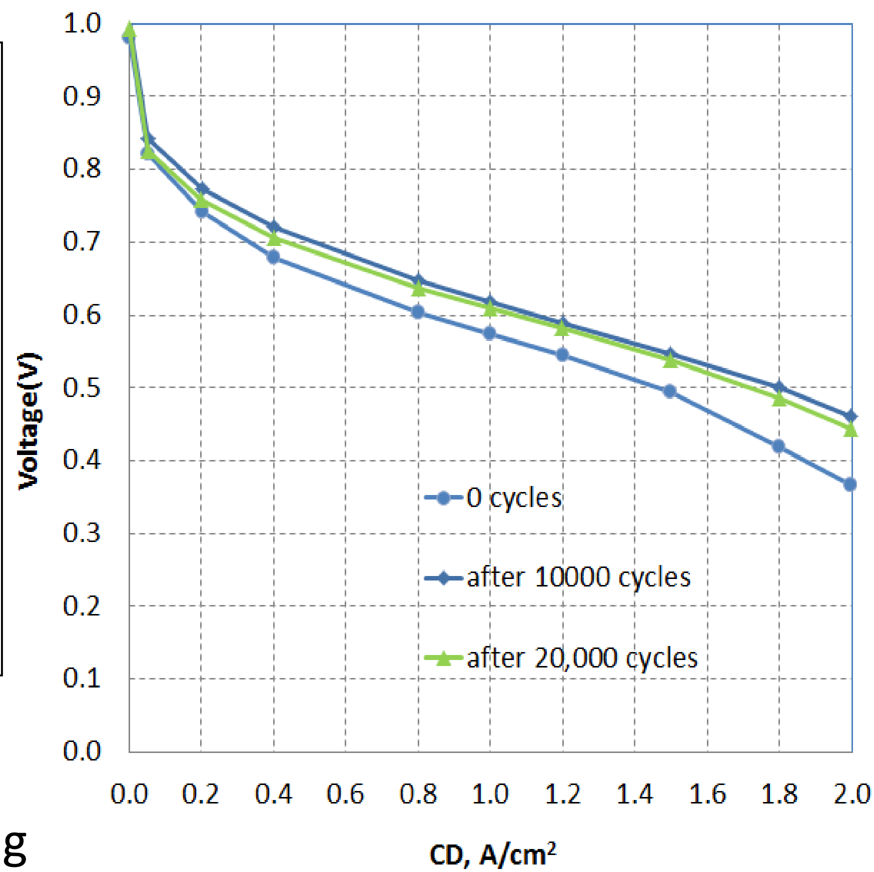


- DSMs show higher stiffness than unsupported N212
- Low EW DSM (865-17-1) shows some loss of stiffness under high RH conditions, but is still higher than N212 at all temperatures

Accomplishment: MEA Stability via Voltage Cycling

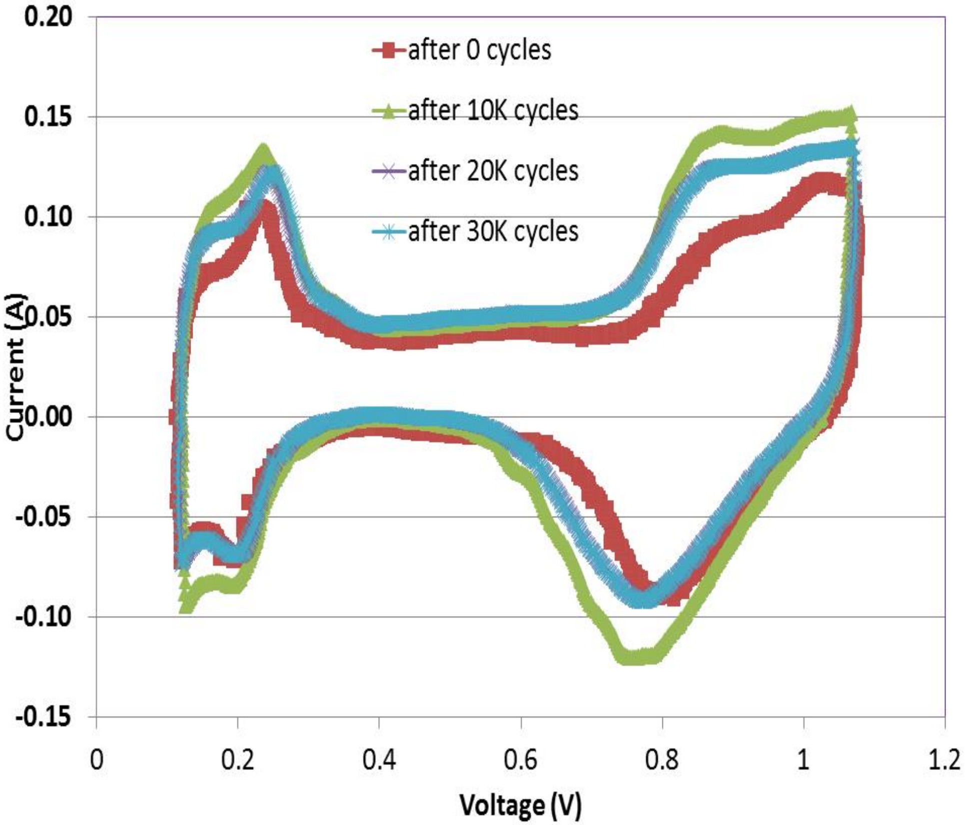
Ionomer: Nafion® in DMAc; T=80 °C; RH=100%; ambient pressure; 50 cm^2 MEA; Voltage cycling from 0.6 to 1.0 V; H_2 flow: 1 L/min; O_2 flow rate 2 L/min

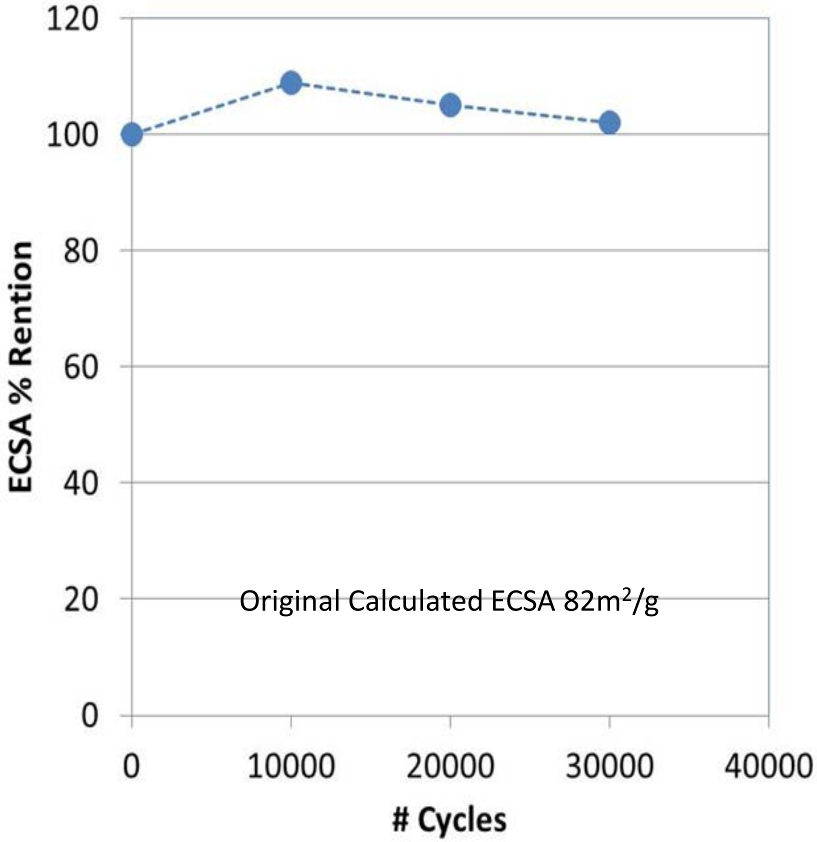
Cycle	Triangle sweep cycle: 50 mV/s between 0.6 V and 1.0 V. Single cell 25 cm^2	
Number	30,000 cycles	
Cycle time	16 seconds	
Temperature	80°C	
Relative humidity	Anode/cathode 100/100%	
Fuel/oxidant	Hydrogen/N_2 (H_2 at 100 sccm and N_2 at 50 sccm for a 25 cm^2 cell)	
Pressure	Atmospheric pressure	
Metric	**Frequency**	**Target**
Catalytic mass activity*	At beginning and end of test minimum	≤40% loss of initial catalytic activity
Polarization curve from 0 to ≥1.5 A/cm^2**	After 0, 5k, 10k, 20k, and 30k cycles	≤30 mV loss at 0.8 A/cm^2
ECSA/cyclic voltammetry***	After 0, 5k, 10k, 20k, and 30k cycles	≤40% loss of initial area



No MEA voltage loss after voltage cycling

ECSA of MEA Upon Voltage Cycling



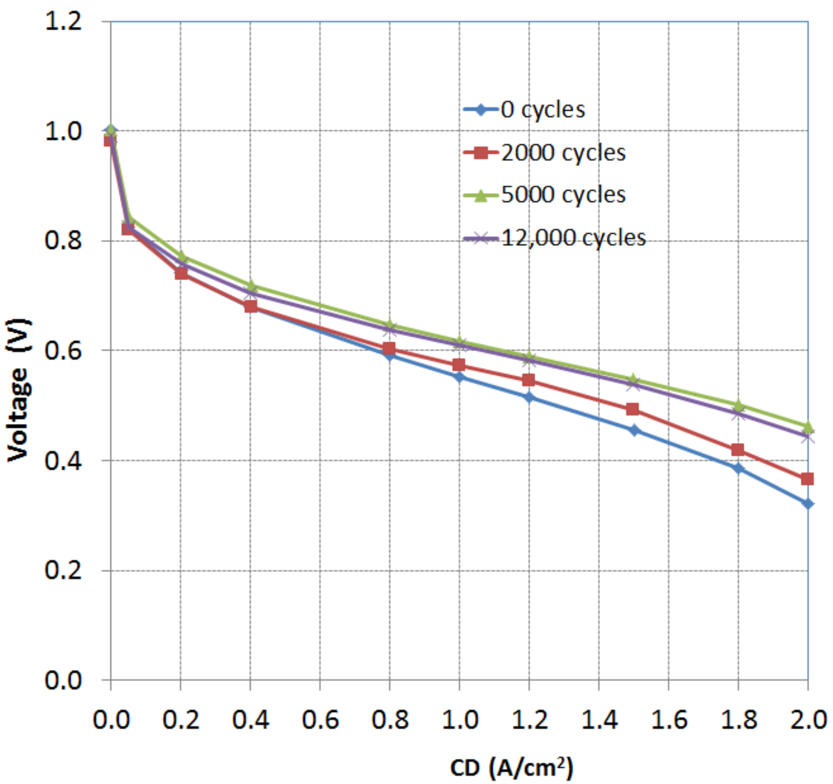


- Cyclic voltammogram (CV) profile is very stable upon voltage cycling;
- Negligible ECSA change after 30, 000 cycles

MEA Stability upon RH Cycling

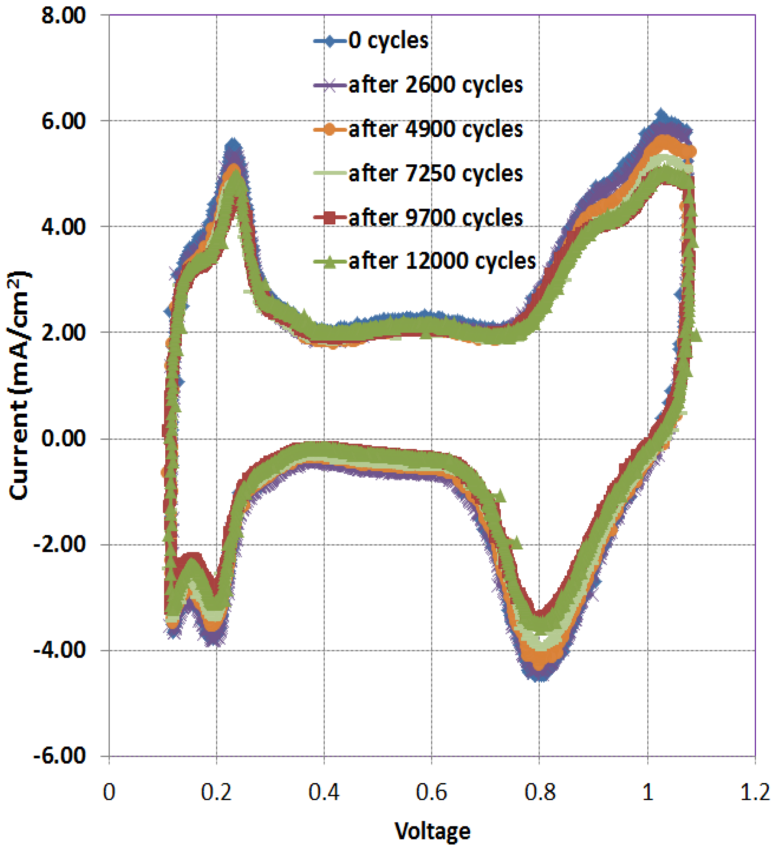
Ionomer: Nafion® in DMAc; T=80 °C; ambient pressure; 50 cm^2 MEA;
RH cycling from dry to 100%; H_2 flow: 1 L/min; O_2 flow rate 2 L/min

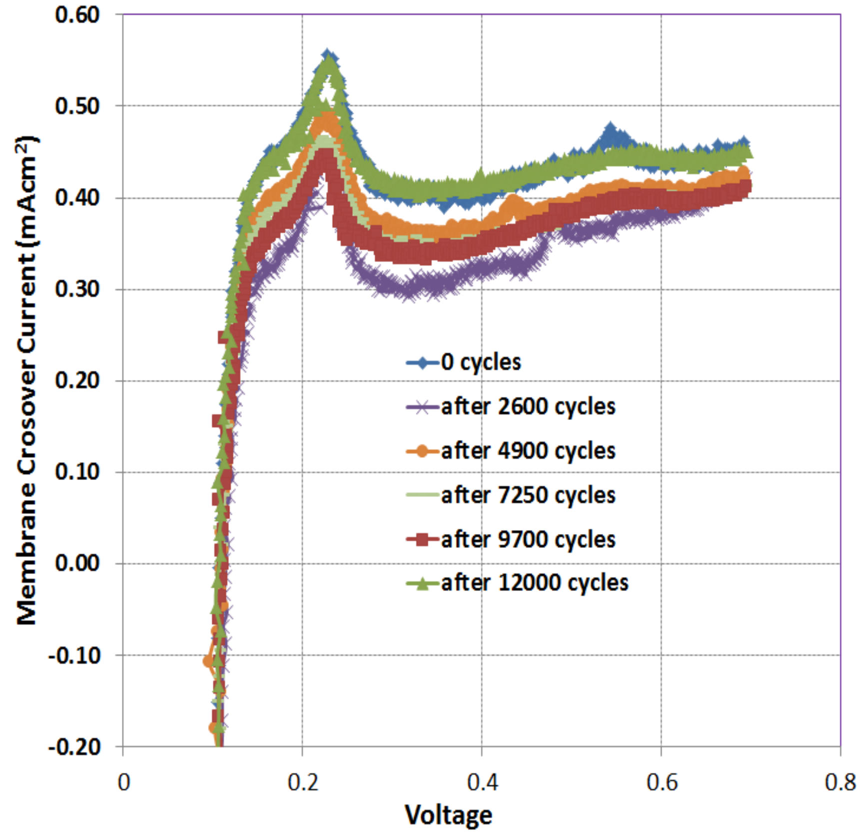
Cycle	Cycle 0% RH (2 min) to 90°C dewpoint (2 min), single cell 25–50 cm^2	
Total time	Until crossover >2 mA/cm^2 or 20,000 cycles	
Temperature	80°C	
Relative humidity	Cycle from 0% RH (2 min) to 90°C dewpoint (2 min)	
Fuel/oxidant	Air/air at 2 SLPM on both sides	
Pressure	Ambient or no back-pressure	
Metric	**Frequency**	**Target**
Crossover*	Every 24 hours	≤2 mA/cm^2
Shorting resistance**	Every 24 hours	>1,000 ohm cm^2



MEA performance is well retained after 12,000 cycles

MEA Crossover after RH Cycling

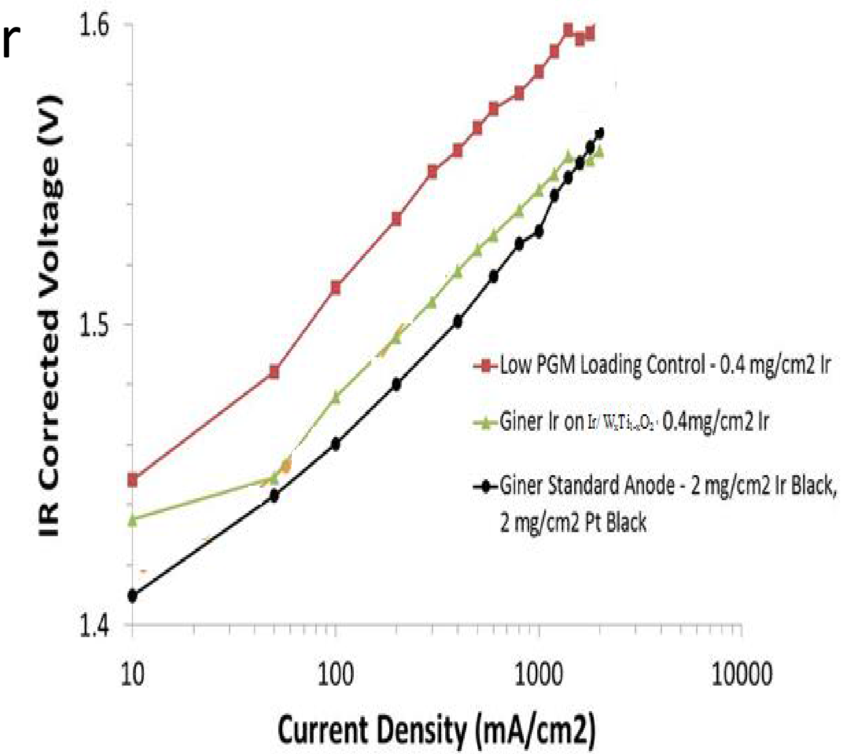




- Stable CV and no ECSA change upon RH cycling
- Extremely low H_2 crossover: 0.4 mA/cm^2, no electrical shorting

Accomplishment: Electrolyzer MEA Stability

- Giner Protocol: 1.4 V to 1.8 V voltage cycling; 30 seconds for each voltage
- Two Categories of Anode Catalysts
  - Baseline: 2 mg/cm^2 Ir black
  - 0.4 mg/cm^2 $Ir/W_xTi_{1-x}O_2$, demonstrating comparable performance to baseline
- LANL Ionomer Dispersion
  - 5 wt% Nafion in NMP

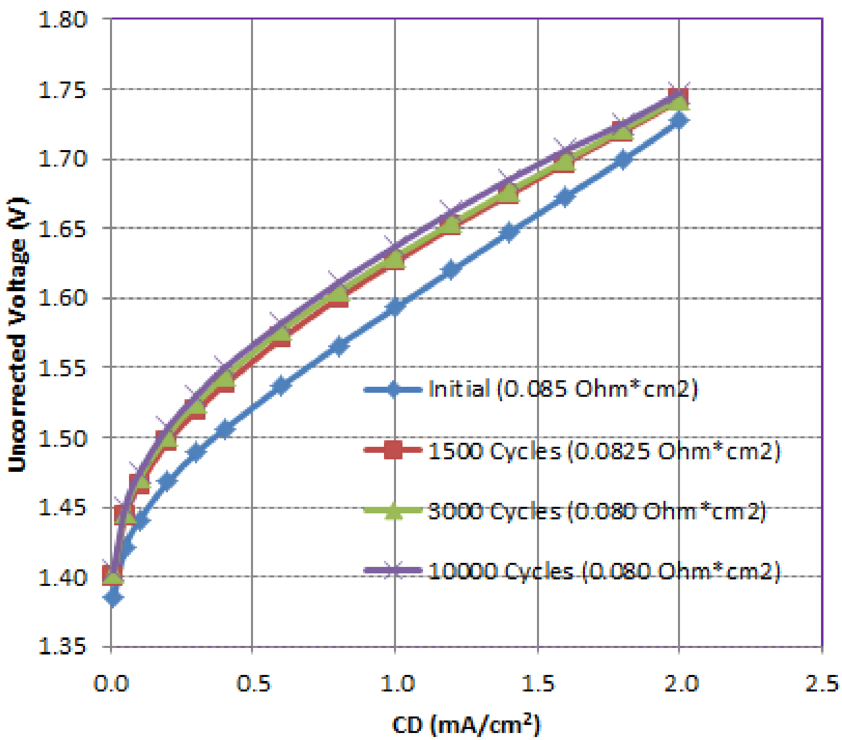


Electrolyzer MEA Stability Test

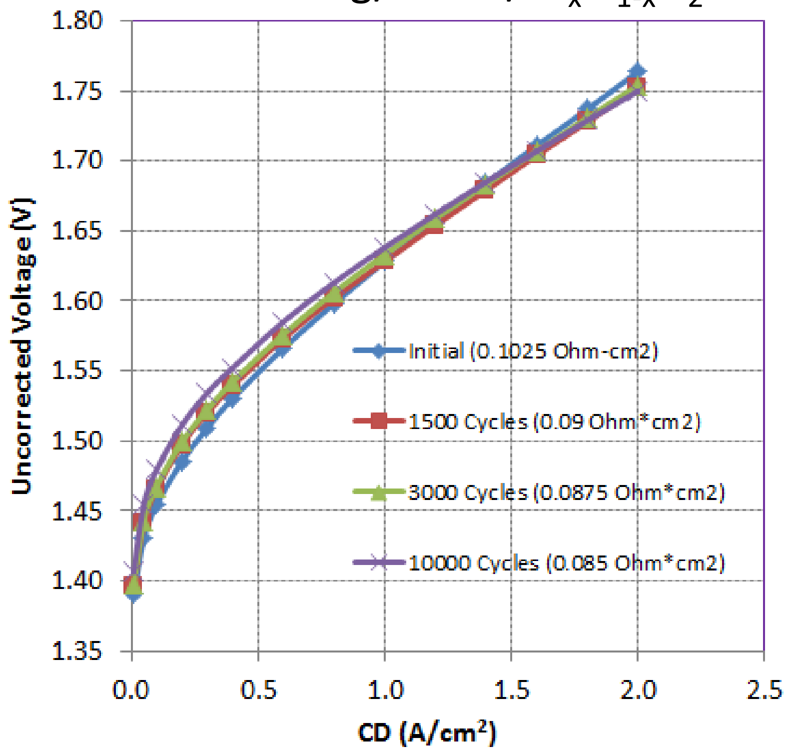
GINER

Los Alamos NATIONAL LABORATORY EST. 1943

2 mg/cm^2 Ir Black



0.4 mg/cm^2 Ir/$W_xTi_{1-x}O_2$



- Good compatibility between catalyst and ionomer
- Excellent MEA durability demonstrated

Performance Schedule

Task	% Time	Month								
		1	2	3	4	5	6	7	8	9
1. Prepare ionomer dispersions	15									
2. Make DSM using dispersed ionomer	15									
3. Characterize membrane properties	10									
4. Make fuel cell and electrolyzer MEAs	20									
5. Validate PEM fuel cell durability	20									
6. Evaluate PEM electrolyzer durability	15									
Report	5			X			**X**			**X**

Milestone #	Description	Scheduled Time	Completion
1	Obtain DSMs using LANL ionomer dispersions and Giner porous support	Month 3	100%
2	Achieve fuel cell MEA < 20 mV drop after 30,000 cycles 0.6 to 1.0 V.	Month 7	100%
3	Achieve electrolyzer MEA < 20 mV drop after 10,000 cycles 1.4 to 1.8 V.	Month 9	100%

Proposed Future Work

- Scale-up of non-aqueous ionomer dispersion
- Scale-up of DSM-based MEA fabrication
  - Based on Giner’s roll-to-roll DSM technology
- More applications in PEM electrolyzers
- Licensing and commercialization

Acknowledgments and Collaborations

- Financial support from DOE SBIR/STTR Program
- Subcontractor
  - Dr. Yu- Seung Kim and David Langlois at LANL
- Giner Personnel
  - Jason Willey
  - Tom McCallum
  - Brian Rasimick
  - Zach Green
  - Corky Mittelsteadt

Summary

- LANL non-aqueous ionomer dispersion technology has been further validated at Giner in more scalable and processible conditions via accelerated stress tests;
- 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