Ionomer Dispersion Impact on PEM Fuel Cell and Electrolyzer Durability

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**Project #
FC 117**

Project Overview

Timeline

- Project Start Date: 7/28/2015
  Project End Date: 7/27/2017

Budget

- Total Project Value
  - Phase II: $1 million
  - Spent: $353,362

Barriers Addressed

- PEM fuel cell and electrolyzer durability

Giner Researchers

Brian Rasimick, Zach Green and Tom McCallum

Partners

- LANL: Dr. Yu-Seung Kim

Technical Targets

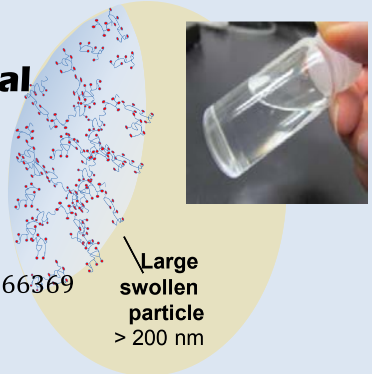
- Integrate Giner dimension-stabilized membrane (DSM) with non-aqueous ionomer dispersions
- Create fuel cell MEAs that are mechanically and chemically stable (DOE 5000 hrs target)
- Develop processible and scalable membranes and MEAs fabrication platforms using non-aqueous ionomer dispersion for water electrolyzers

Project Nature

- First DOE Technology Transfer Opportunity Project (SBIR-TTO)

LANL Ionomer Dispersion Technology

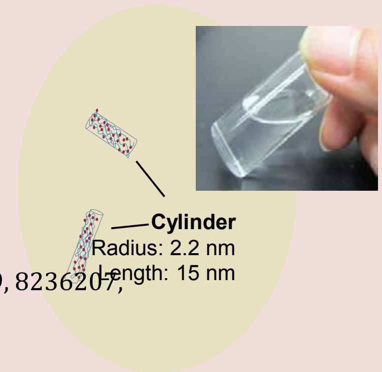
Conventional Ionomer Dispersion



Dupont
European Patent 0066369

- Water based **multiple** solvent system
- **Expensive** processing: required high temperature (> 200°C) & pressure (> 1000 psi)
- **Large** and **non-uniform** particle suspension: particle size (hydrodynamic radius: 200 – 400 nm)
- Produce **brittle** membrane: toughness ~ 0.001 MPa
- Produce **less stable** electrode: cell voltage loss after durability test: 40-90 mV

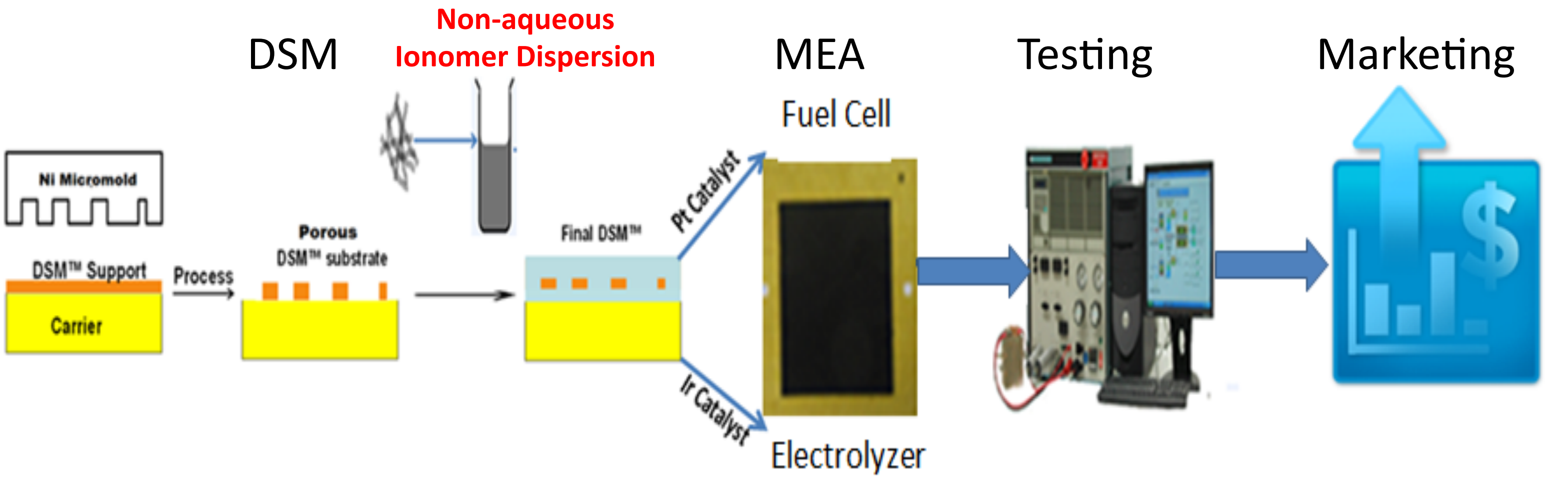
LANL Ionomer Dispersion



LANL
US Patent 7981319, 8236207, 8394298

- **Single** solvent system
- **Cost effective** processing: required lower temperature (< 120°C) & ambient pressure
- **Small** and uniform particle suspension: particle size (2.2 x 15 nm cylinder)
- Produce **tough** membrane: toughness 10 MPa (> 4 magnitude order difference!!)
- Produce **stable** electrode: cell voltage loss after durability test: 0 mV

Technical Approach



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

Processibility
- Roll-to-roll production of DSM
- Ultra 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

LANL: investigating low Pt loading electrodes using non-aqueous ionomer dispersion for *PEM Fuel cells*

Giner: developing scalable and processible membrane and MEA fabrication platforms for *PEM electrolyzers: membrane cast and electrode fabrication*

Accomplishment 1: Producing Non-aqueous Ionomer Dispersions and Membranes

- **Two Categories of Ionomers**
  - Nafion® 1100 EW
  - 3M 825 EW
- **Two Categories of Solvents**
  - Protic: glycerol, n-butanol, 1,2-pentanediol
  - Aprotic: N-Methyl-2-pyrrolidone (NMP)
    Dimethylacetamide (DMAc)
- **Processing**
  - Place membrane pieces in individual solvent
  - Heat up to optimized T to obtain ionomer dispersion
- **Ionomer/Solvent Interactions**
- **Membrane: conductivity and mechanical properties**

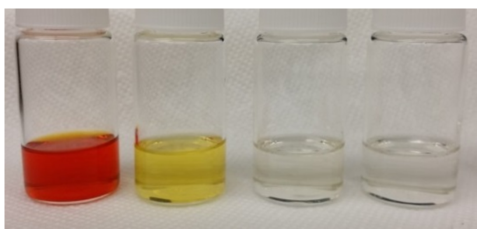
3M PFSA in Ketone and Ester

- **Ketone**

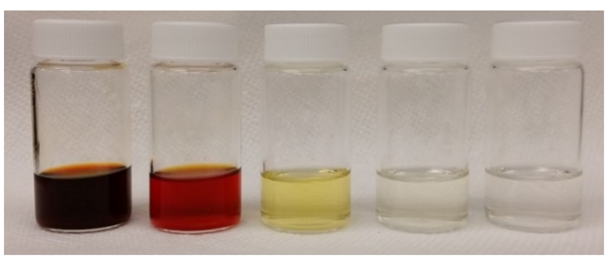
  10 wt% ionomer in acetone containing various amounts of water, aged at 37 °C

Wt (%)	0.2	0.5	1	2	5
λ	0.9	2.3	4.6	9.3	23

6 hrs



20 hrs

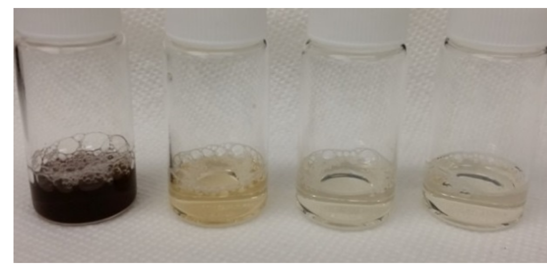


- **Ester**

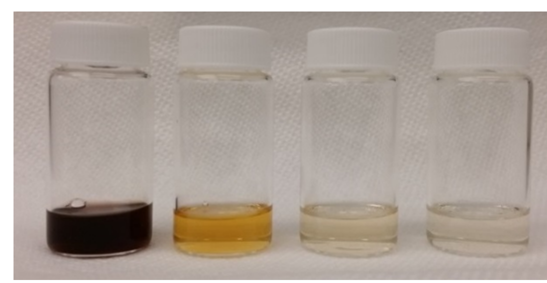
  20 wt% ionomer in γ-butyrolactone aged at 37 °C with various water content

Wt (%)	0.1	1	2	5
λ	0.2	2.3	4.6	12

2 hrs

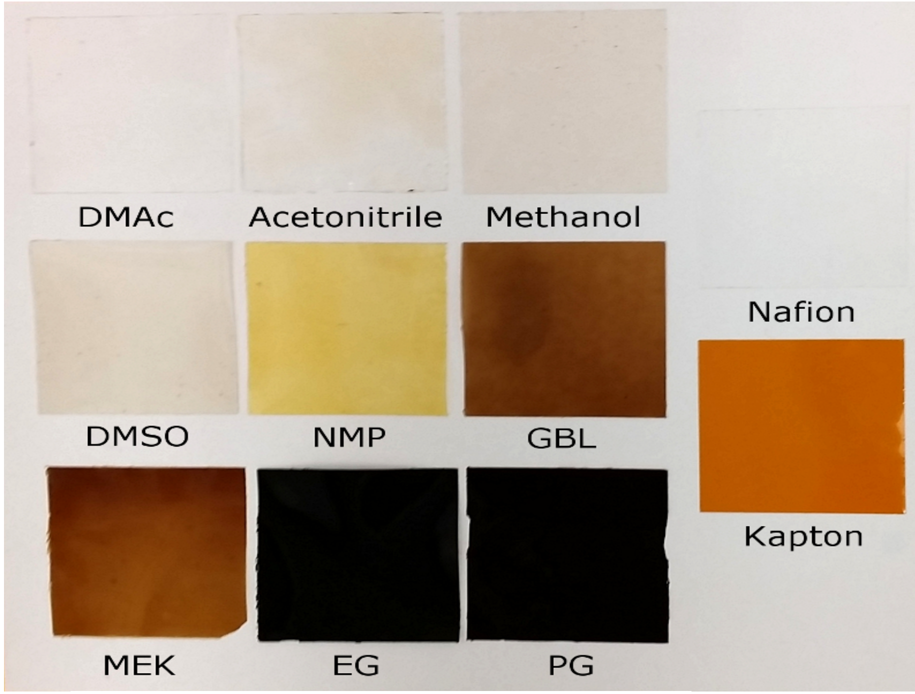


16 hrs



Dispersions containing 1 wt% water or less were unstable as indicated by color

Cast Membranes Using Different Solvents

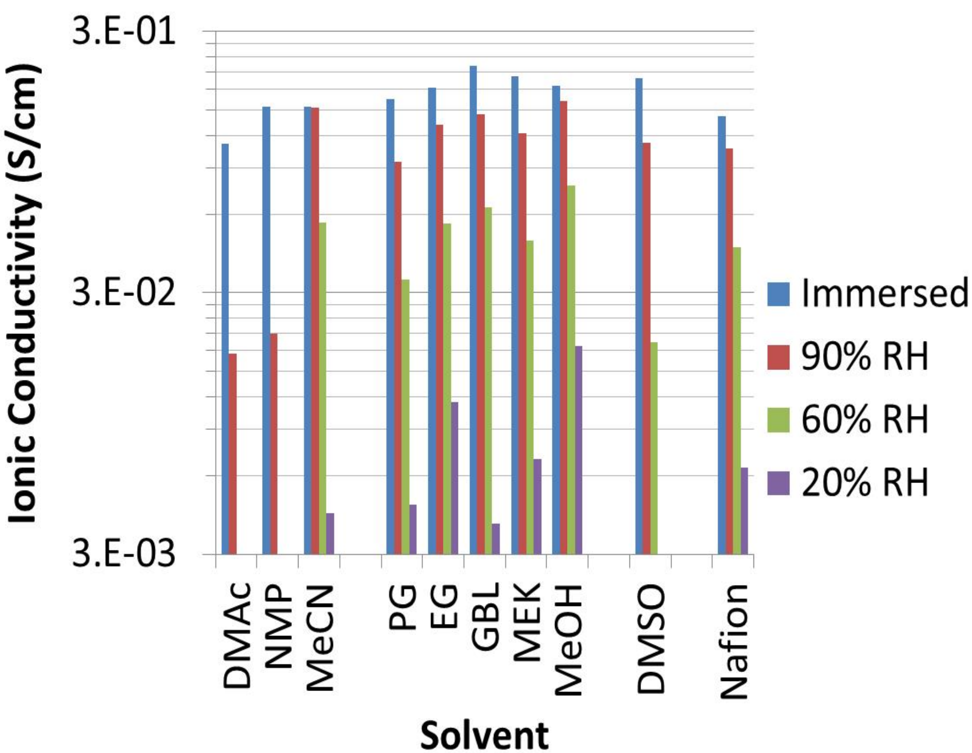


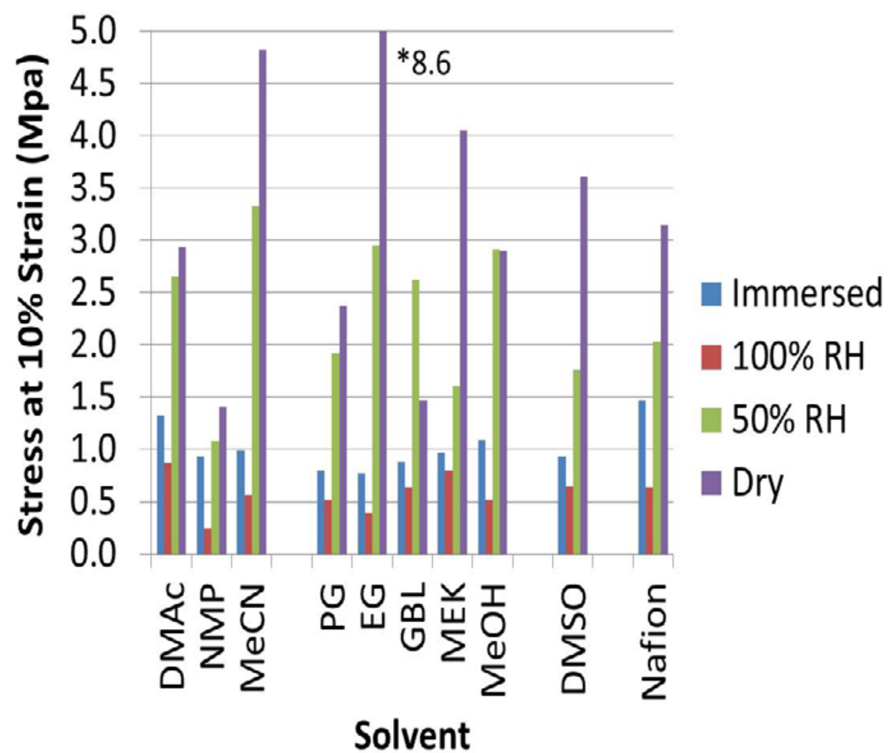
Casting Solvent	Casting Temperature (°C)	Casting Concentrati on (wt%)
Dimethylacetamide (DMAc)	110	30
N-methylpyrrolidone (NMP)	150	30
Acetonitrile (MeCN)	45	30
Propylene Glycol (PG)	150	30
Ethylene Glycol (EG)	150	30
g-butyrolactone (GBL)	150	20
Methylethylketone (MEK)	45	15
Methanol (MeOH)	45	20
Dimethylsulfoxide (DMSO)	150	20

2 mil Kapton and N115 are shown as a color controls.

- Further chemical reactions occur during the hot-casting and hot-pressing processes
  - Clear ethylene glycol solution turns light brown during hot-casting (150°C for 10 minutes) and darken to nearly black during hot-pressing (175°C for 15 minutes)
- Despite strong color changes and odors, solvent decomposition does not appear to be a major detriment to the performance of the cast membrane

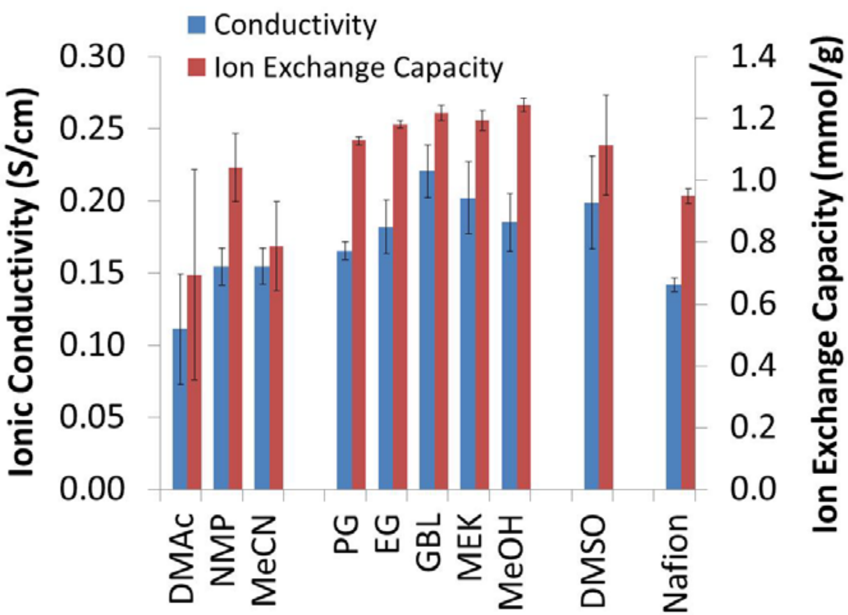
Membrane Conductivity and Mechanical Property at Various RH

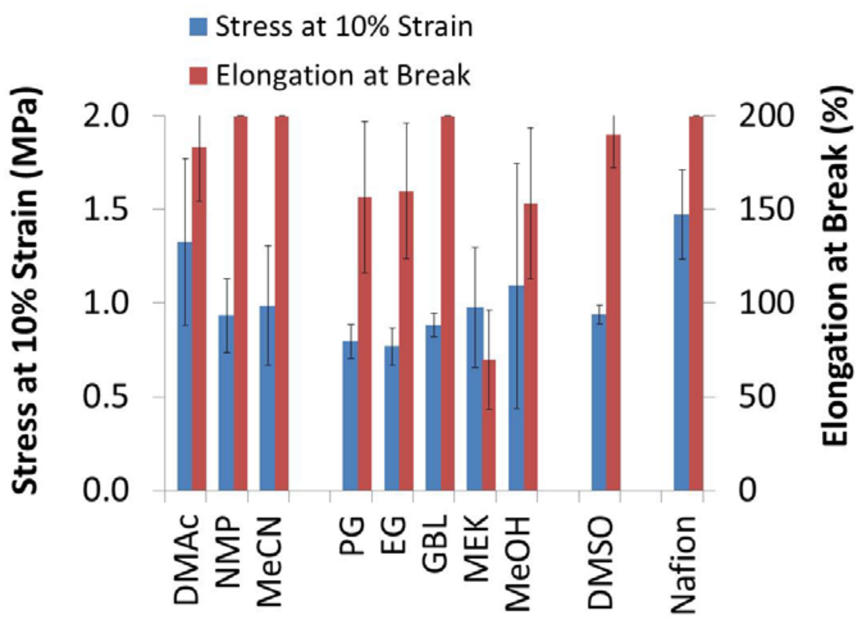




- Solvent impacts conductivity and mechanical properties, particularly at low RH
- MeOH, DMSO and GBL appear to be good solvents for ionomer dispersion based on simultaneously high ionic conductivity and good mechanical property
  - Wet condition typically for electrolyzer application

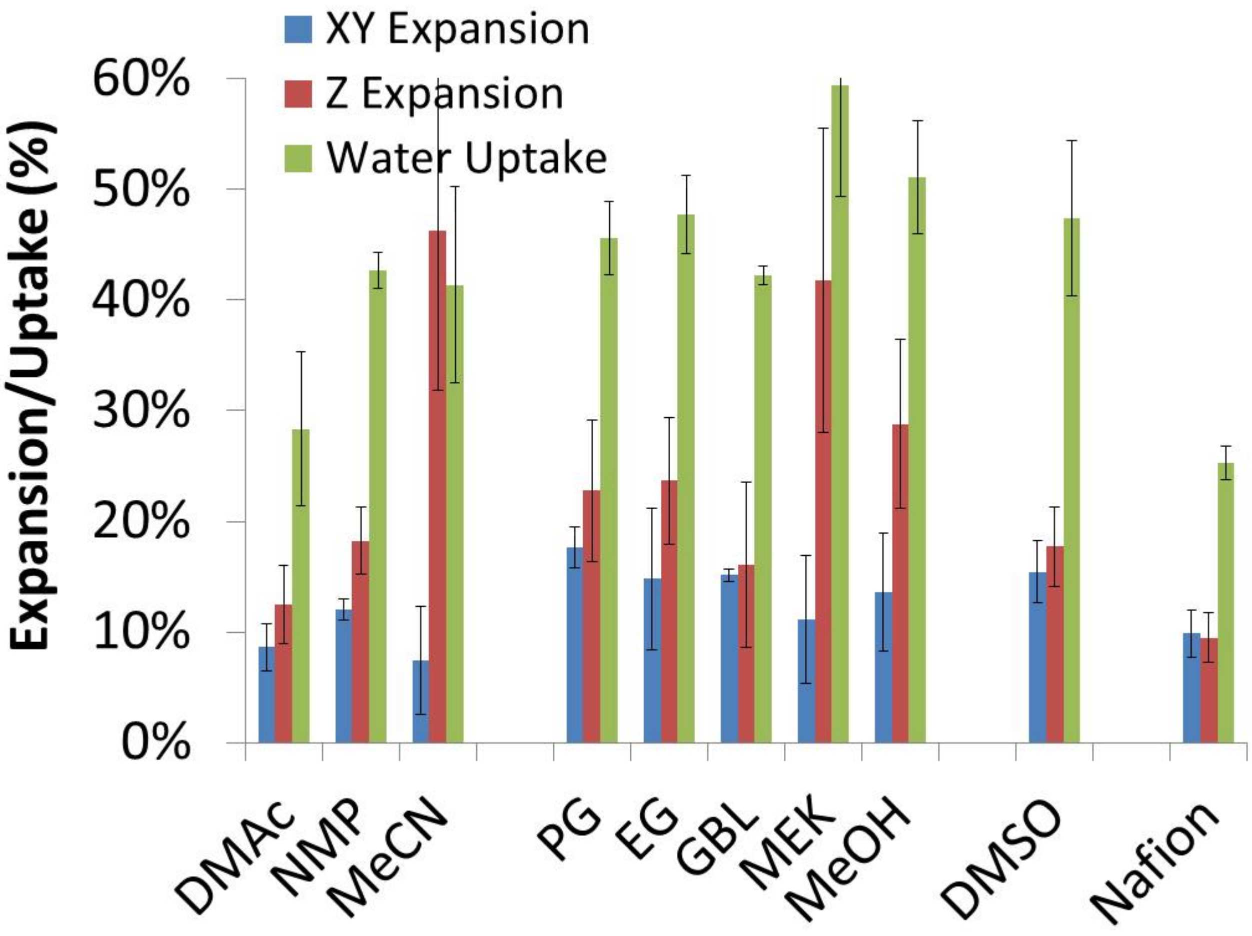
Conductivity and Mechanical Properties at Immersed Condition





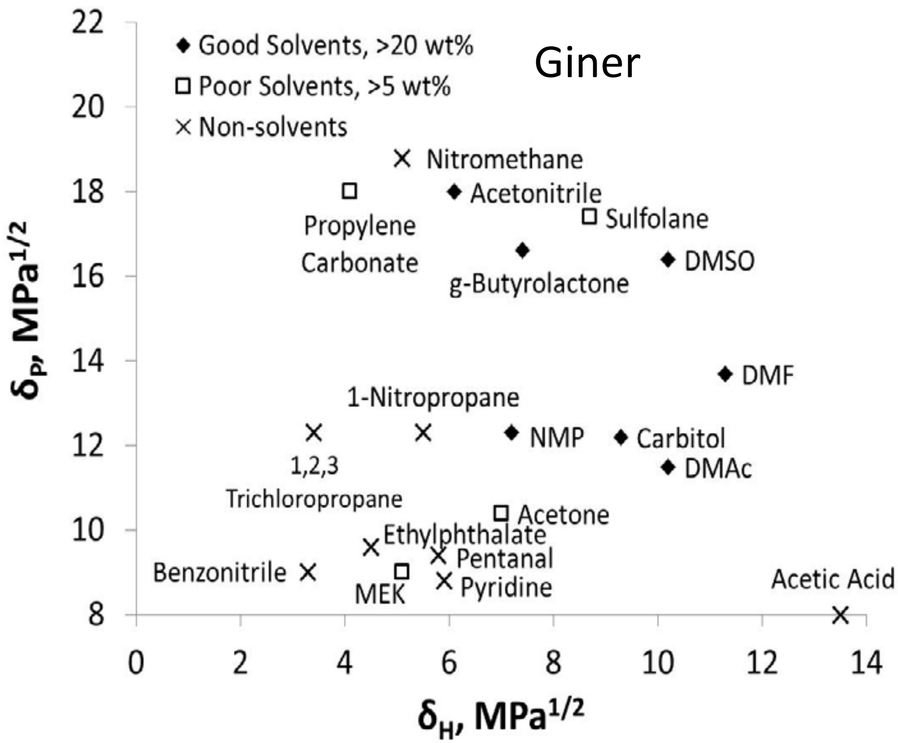
- Immersed condition mimics water electrolyzer operation
- DMSO, MeOH and GBL appear to be good solvents in terms of high membrane conductivity and good mechanical properties at immersed conditions

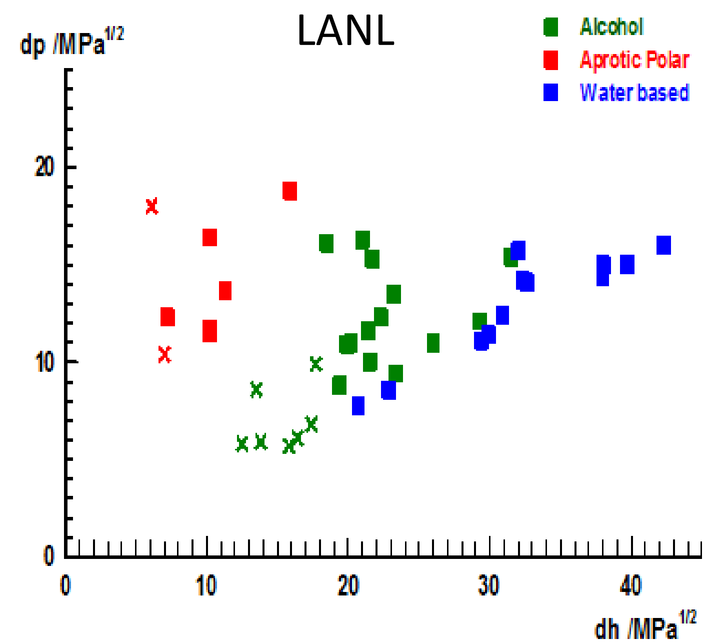
Membrane Expansion



- DMSO, GBL and MeOH solvent-based membranes show less expansion

Hansen Solubility Plot



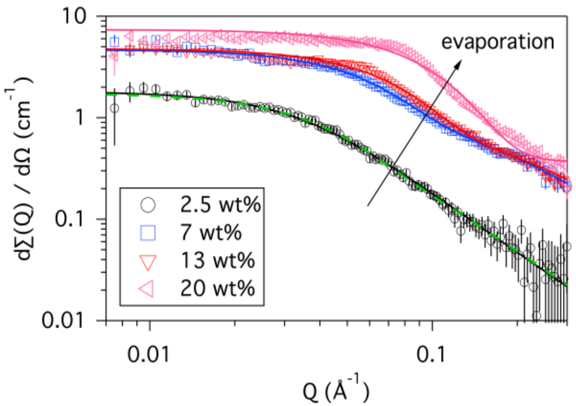


- DMSO, DMF, NMP, GBL tend to disperse ionomer at high concentration (> 20 wt%)
- Unusual wide Hansen solubility parameter range is achieved at LANL

Ionomer 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. Particle morphology of NMP dispersion is different from what we know.

SANS of Nafion dispersion in NMP



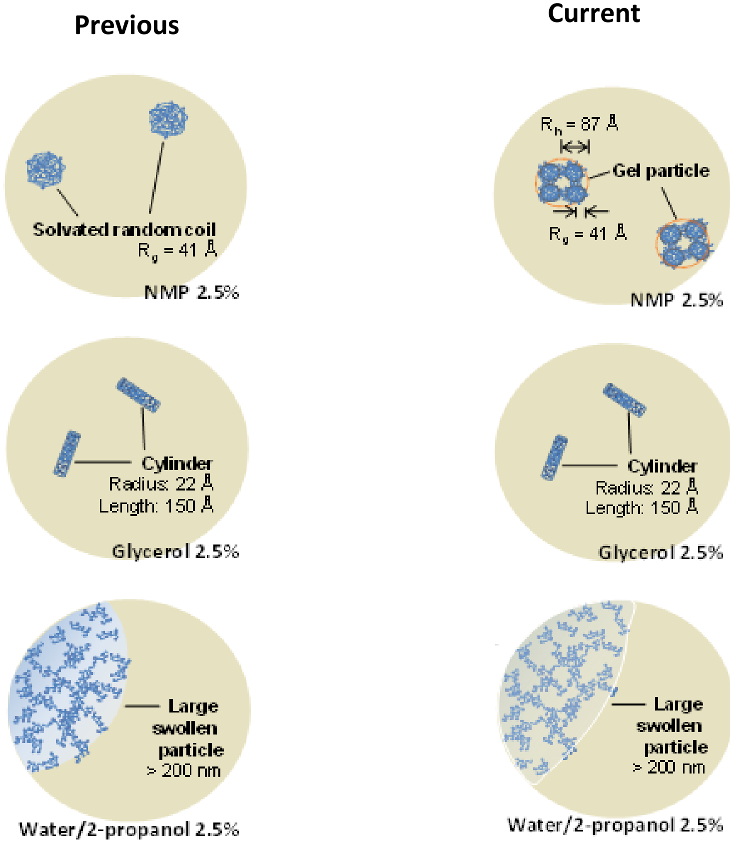
Black line: Random walk modeling

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

Green line: Gel particle modeling

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

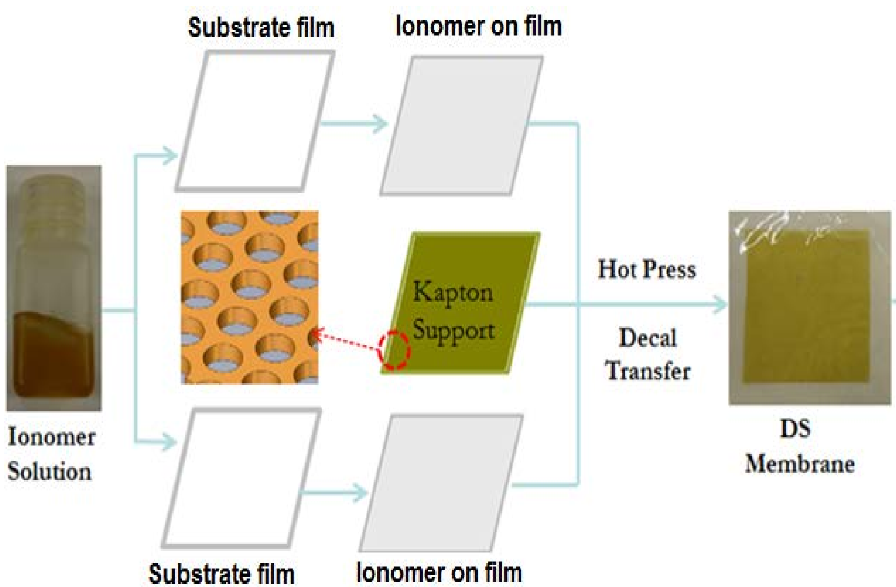
Particle size from DLS: RH = 8.7 nm



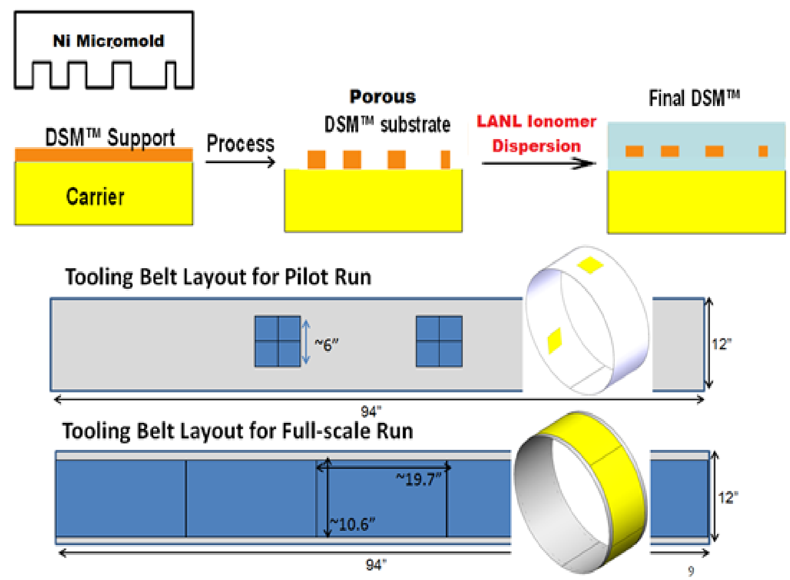
Y.S. Kim et al. *Macromolecules*, 48, 2161-2172 (2015)

Accomplishment 2: Develop DSM Using Non-aqueous Ionomer Dispersions

Batch Process



Continuous Process



Hybrid membranes obtained using Giner's high throughput continuous DSM fabrication platform

DSM Based Membranes

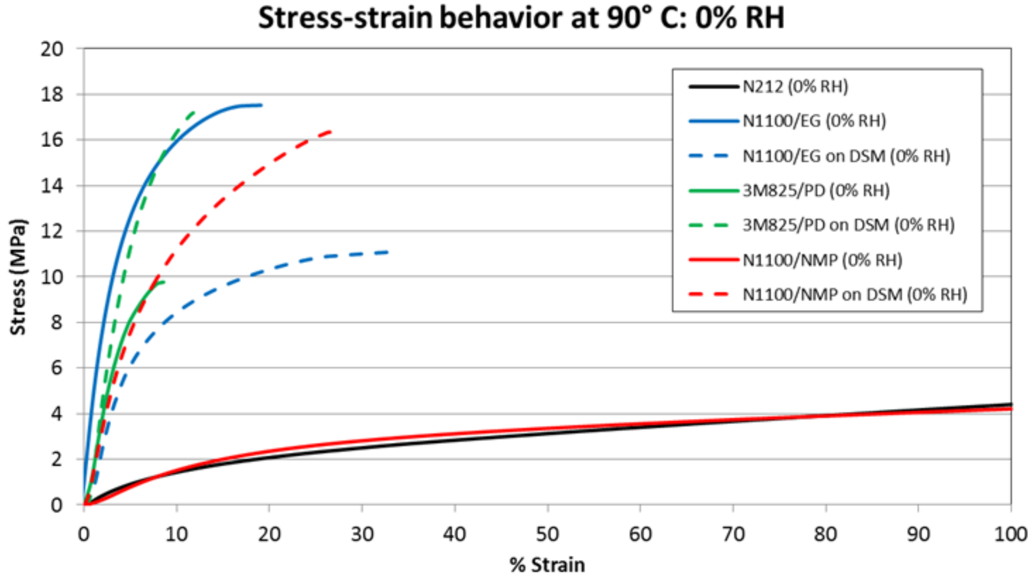
Phase I Project

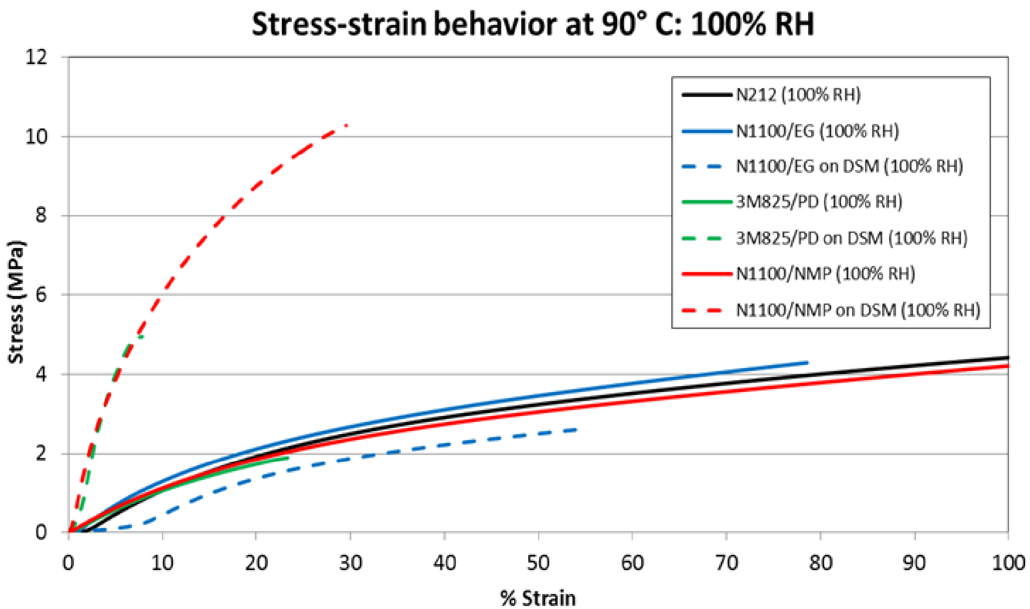
Membrane ID	865-15-1	865-18-1 865-29-1 865-30-1	865-17-1	865-32-1
Ionomer	5% N1100EW	5% N1100EW	2.5% 3M 825EW	2.5% 3M 825EW
Solvent	1, 2 Pentanediol	NMP	1, 2 Pentanediol	DMAc
Thickness	35 µm	22 µm	24 µm	41 µm
Color	Dark yellowish	Yellow	Yellow	Yellow
Dark color due to high heating temperature during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

Phase II Project

#	Ionomer Dispersion	DSM
1	N1100 in NMP	Yes
2	N1100 in NMP	No
3	N1100 in EG	Yes
4	N1100 in EG	No
5	3M 825 in DMAc	Yes
6	3M 825 in DMAc	No
7	3M 825 in PTD	Yes
8	3M 825 in PTD	No

Mechanical Tests and Conductivity



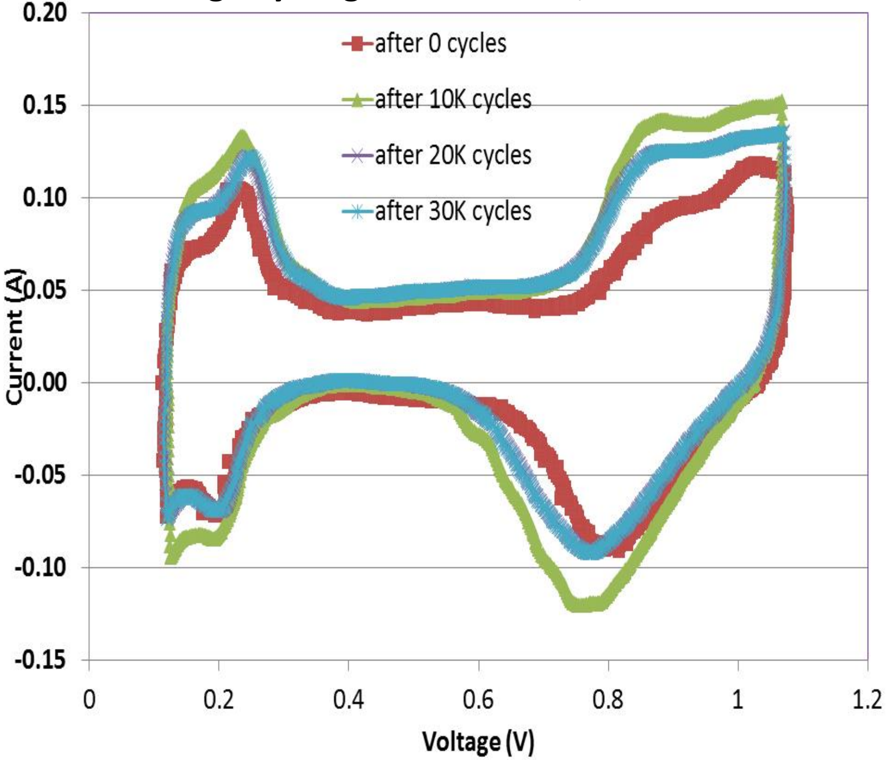


- The integration of ionomer with DSM improves the membrane mechanical properties;
- The stress at fixed strain varies from solvent to solvent even with DSM
  - PD comparable to EG
  - EG better than NMP
- EG-dispersed N1100EW performed well even without DSM

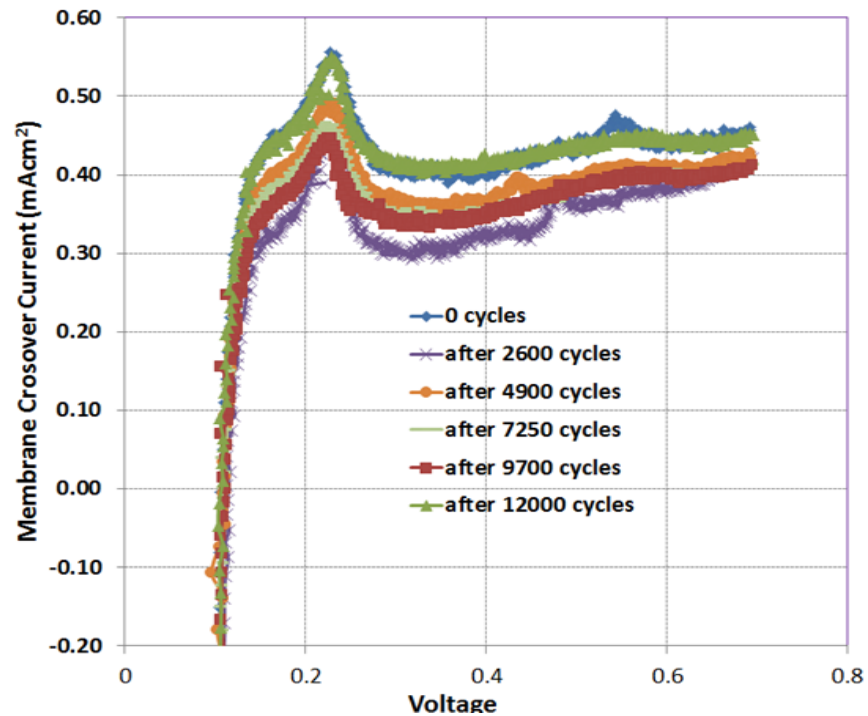
Voltage and RH Cycling

Cell conditions: EG based N1100 EW in DSM (30 μm) and cathode; anode and cathode: 0.2 mg/cm2 Pt (from Tanaka 46.7% Pt/C), 50cm^2 FCT hardware

Voltage Cycling: 0.6 V to 1.2 V, 50mV/sec



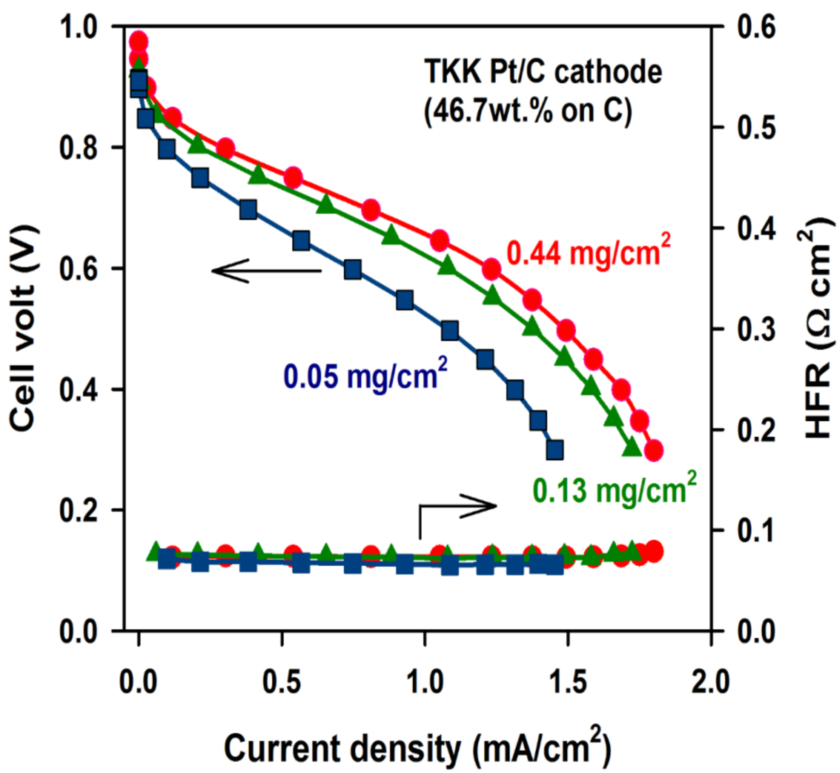
RH Cycling: dry and 105% RH



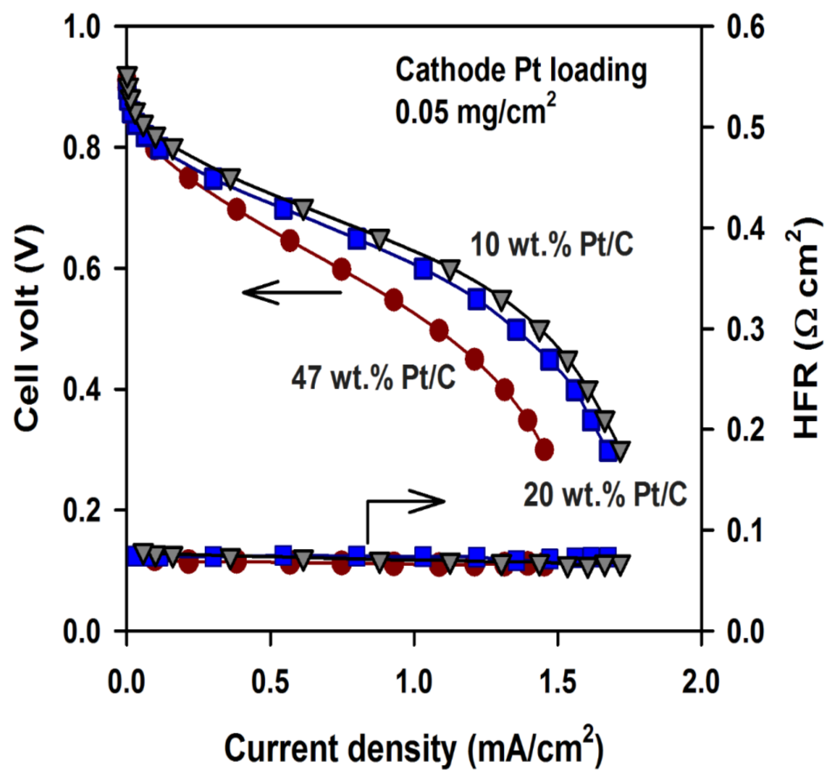
- ECSA calculated by H2 adsorption/desorption decreased by 12% from 10k to 30K, upon voltage cycling (no change from 0 to 30k cycles)
- Extremely low H_2 crossover: 0.4 mA/cm^2 upon 12K RH cycling

Accomplishment 3: Fuel Cell Performance and Durability

H_2/air fuel cell performance at 80 °C at 30 psig backpressure; Membrane: Nafion 212; Anode: 20 wt.% Pt/C (0.2 mg/cm²); Cathode: 46.7 wt.% TKK Pt/C catalyst; Catalyst ink dispersing agent: water/2-propanol



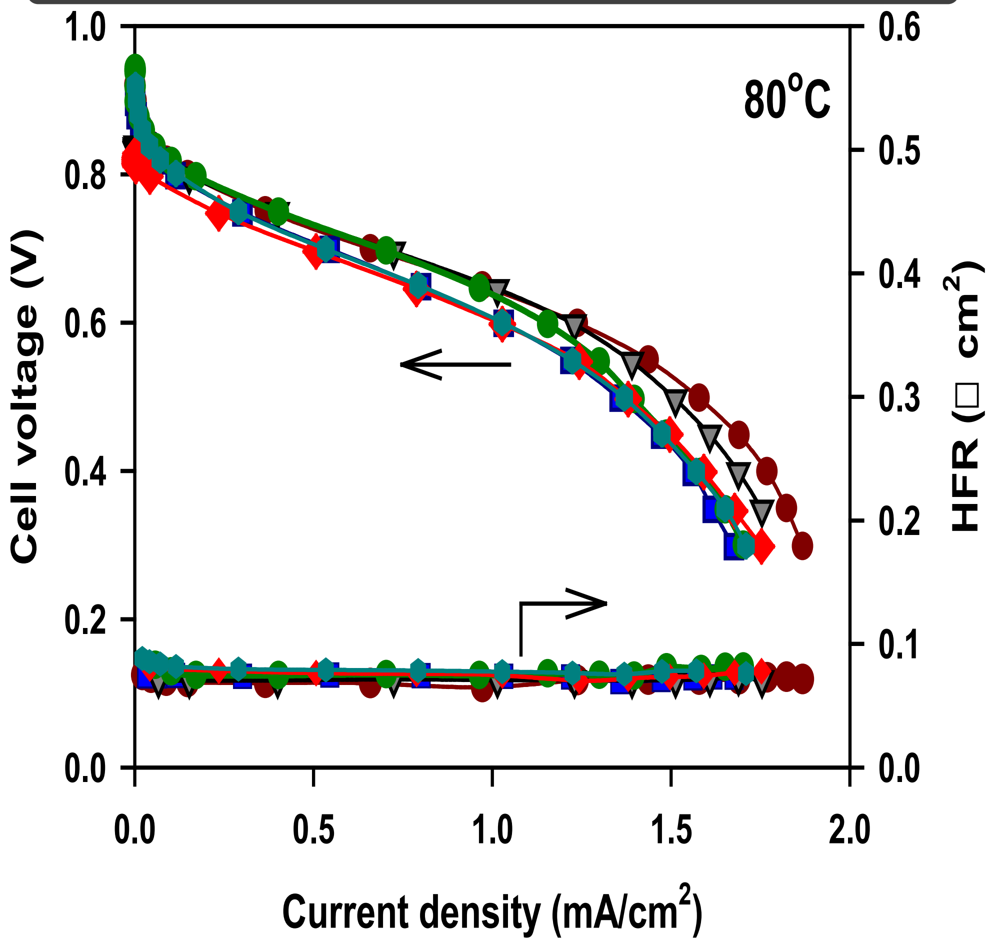
H_2/air fuel cell performance at 80°C at 30 psig backpressure; Membrane: Nafion 212; Anode: 20 wt.% Pt/C (0.2 mg/cm²); Cathode: 46.7 wt.% TKK Pt/C; 20 and 10 wt.% ETEK Pt/X catalyst; Catalyst ink dispersing agent: water/2-propanol



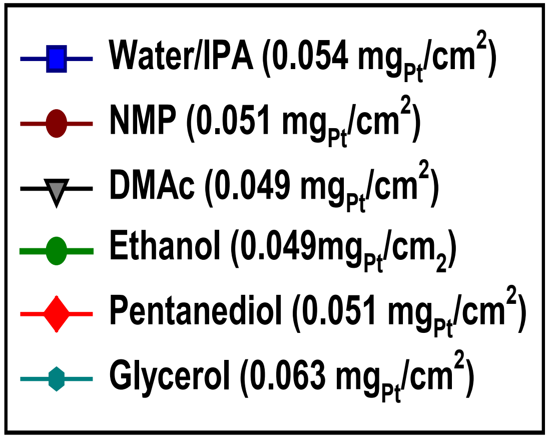
- **More significant performance loss when Pt loading decreased from 0.13 to 0.05 mg_{Pt}/cm^2.**
- **Catalyst with low Pt to C ratio showed better performance for low loading cathode.**

Solvent Impact on Low Pt loading Fuel Cell Performance

H_2/air fuel cell performance at 80°C at 30 psig backpressure; Membrane: Nafion 212; Anode: 20 wt.% Pt/C (0.2 mg/cm²); Cathode: 20 wt.% wt.% Pt/C catalyst; Catalyst ink dispersing agent: varied



Cathode dispersing agent (cathode Pt loading)

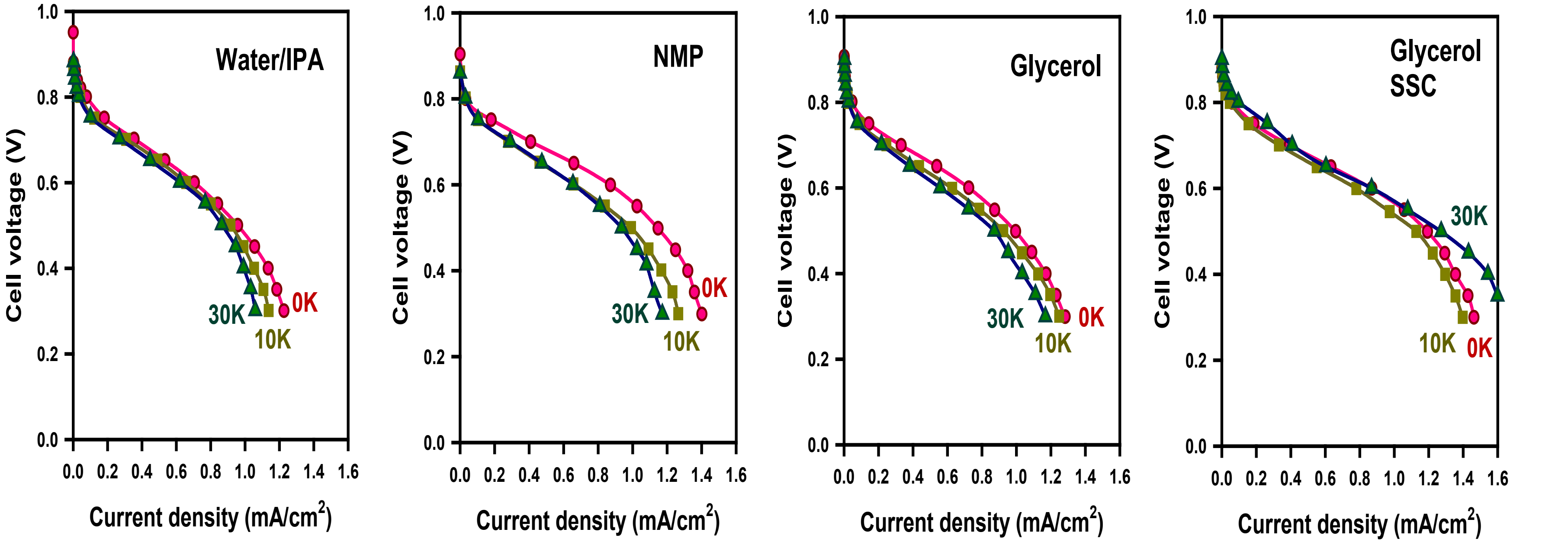


* Low loading Pt cathode needs longer break-in time (see complementary slide 2)

- **Similar H_2/air fuel cell performance was obtained using different cathode dispersing agent after full break-in.***
- **NMP and DMAc dispersing agents produced little better performance.**

Solvent Impact on Low Pt loading Fuel Cell Durability

Cathode dispersing Solvent: *varied;* ***ionomer****: Nafion or aquivion;* ***ionomer to pt/C composition****: 30wt.%;* ***Anode:*** *0.2 mg_{Pt} cm^{-2} (20 wt.% Pt/C, BASF),* ***Cathode:*** *0.05-0.25 $mg_{Pt}cm^{-2}$ (20 wt.% Pt/C, BASF);* ***Membrane****: Nafion® 212;* ***Operating conditions:*** *cell temperature: 80°C, backpressure: 10 psi, Potential cycling: 0.6 – 1.0 V under H_2/N_2 at 80°C, Break-in: 12 h at 0.6 V H_2/air & 2 polarization curves at initial, 3, 10 and 30K potential cycles*

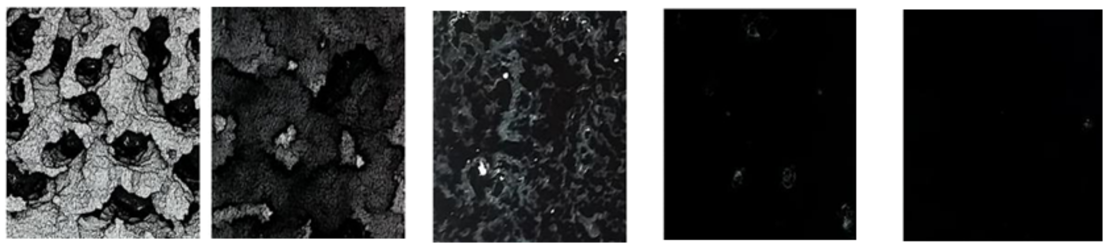


- **Cathode catalyst inks were prepared from 7 different dispersing agents and tested** (for other dispersing agents see Supplemental Slide)**.**
- **MEAs prepared from glycerol based cathode catalyst ink showed superior durability.**

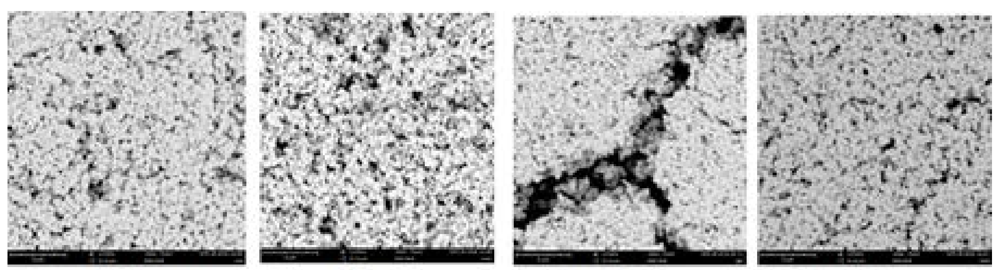
Highlight: **Short-side-chain Aquivion® ionomer prepared from glycerol based ink showed excellent performance and durability**

Accomplishment 4: Electrolyzer Performance and Durability

- Apply non-aqueous ionomer dispersion to water electrolyzers to develop a scalable, durable, and high-performance MEA
  - Ir black + 15% ionomer in various solvents



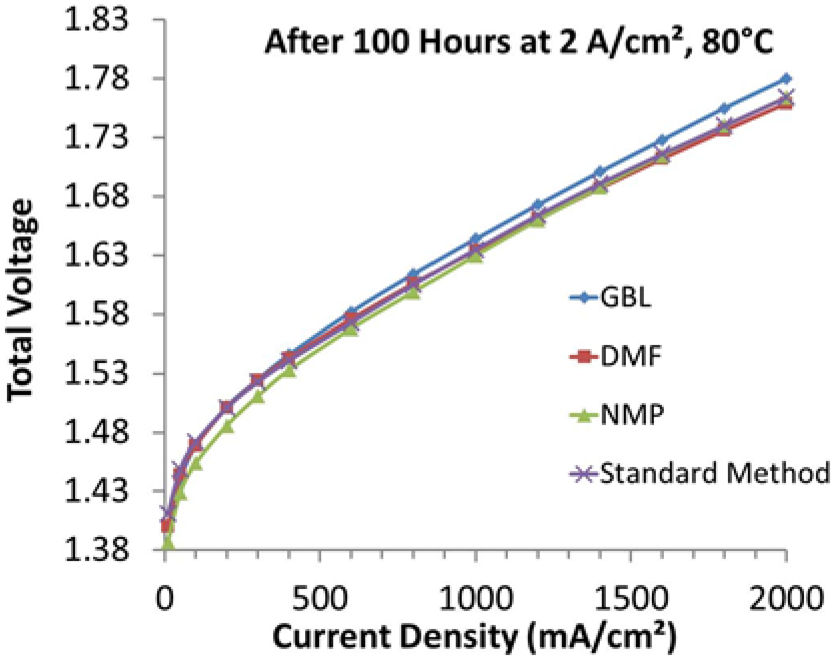
Acetonitrile (MeCN) | Acetone (ACT) | g-butyrolactone (GBL) | n-methylpyrrolidone (NMP) | Dimethylformamide (DMF)

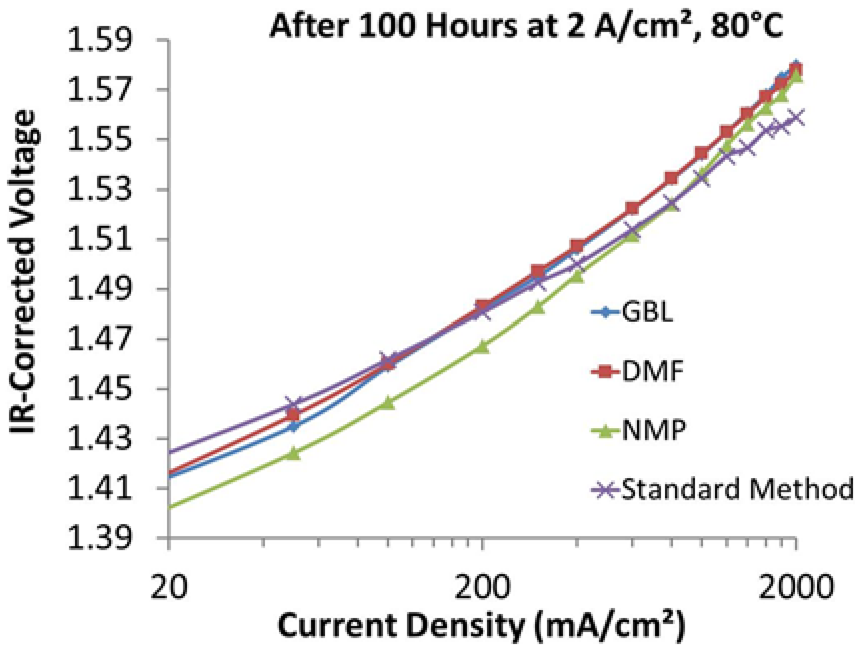


Aqueous solvent | NMP | GBL | DMF

- Decals using GBL, NMP and DMF shows best morphology: uniform and little cracking
- Scalable for electrode mass production

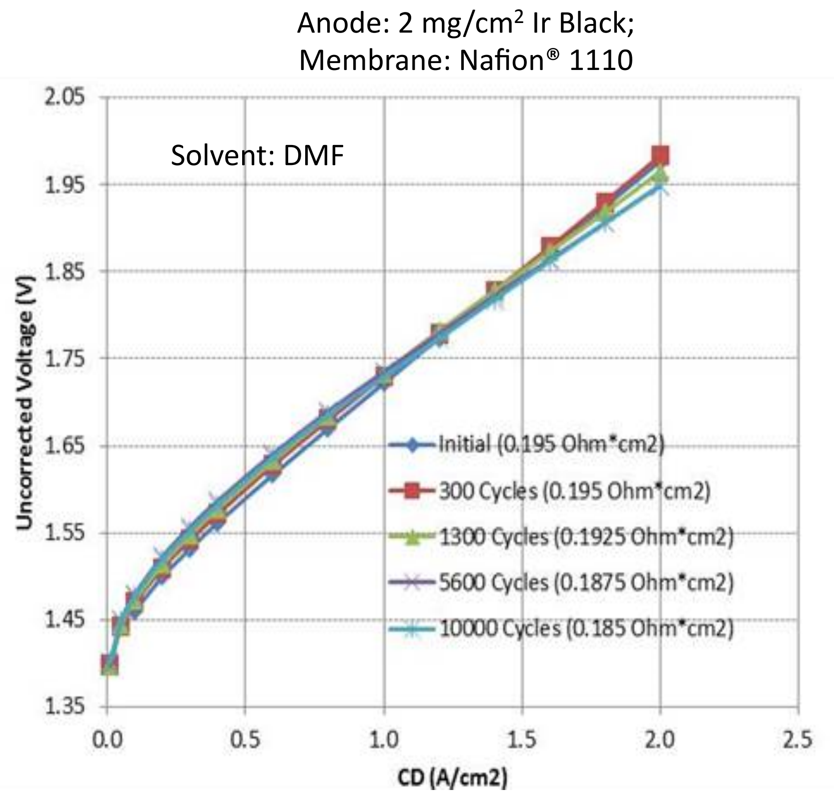
Performance of Cast Anode Decals

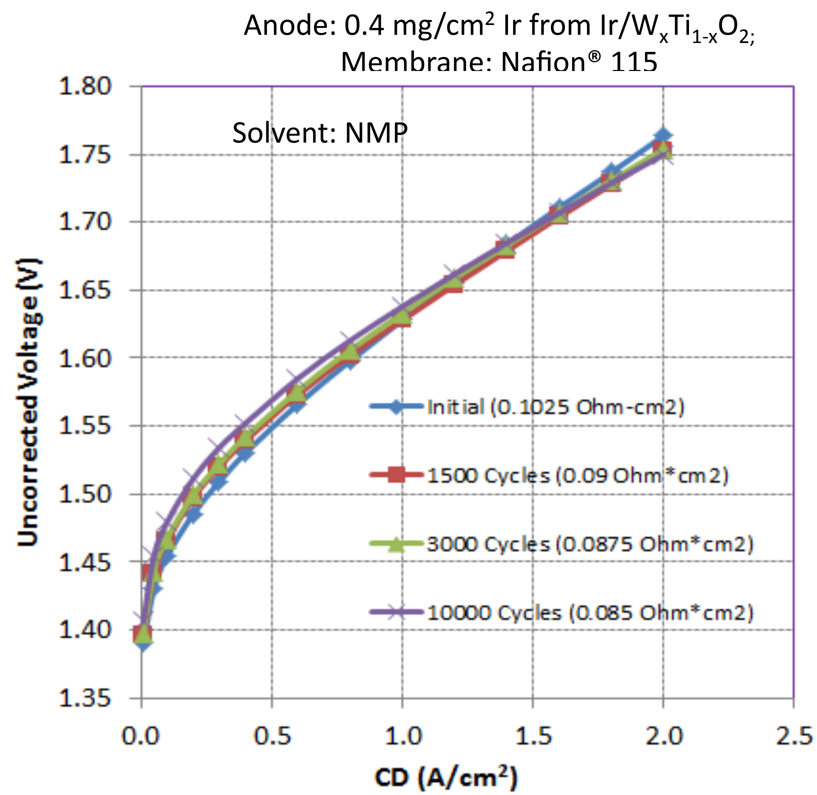




- All anodes using GBL, DMF and NMP-based ionomer performed as well as standard one using aqueous ionomer
- Using GBL, DMF or NMP enables the fabrication of electrodes in a processable and scalable level

Stability of Electrolyzer MEAs





Voltage cycling from 1.4 V to 2.0 V, square wave, 30 second at each voltage

- Good compatibility between catalyst and ionomer
- Excellent MEA durability demonstrated upon voltage cycling (1.4 V to 2.0 V)

Summary

- 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 includes DMSO, GBL, NMP and MeOH

- Selected non-aqueous ionomer dispersions were impregnated in the DSM substrate and used in the fuel cell cathode, leading to mechanical and chemically stable MEAs

- 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 Plans

- 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 business

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