2017 DOE H_2 and Fuel Cell Annual Merit Review Meeting

Ionomer Dispersion Impact on PEM Fuel Cell and Electrolyzer Performance and Durability

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Giner, Inc.
Newton, MA

Project#
FC117

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This presentation does not contain any proprietary, confidential, or otherwise restricted information

Project Overview

Timeline

- Project Start Date: 7/28/2015
  Project End Date: 2/27/2018

Budget

- Total Project Value
  - Phase II: $1.0 million
  - Spent: $685 K (by 3/31/17)

Barriers Addressed

- PEM fuel cell and electrolyzer performance and durability

Partners

- LANL: Dr. Yu-Seung Kim
- ORNL: Dr. Karren More

Giner Researchers

Chao Lei, Jason Willey, Zach Green, and Tom McCallum

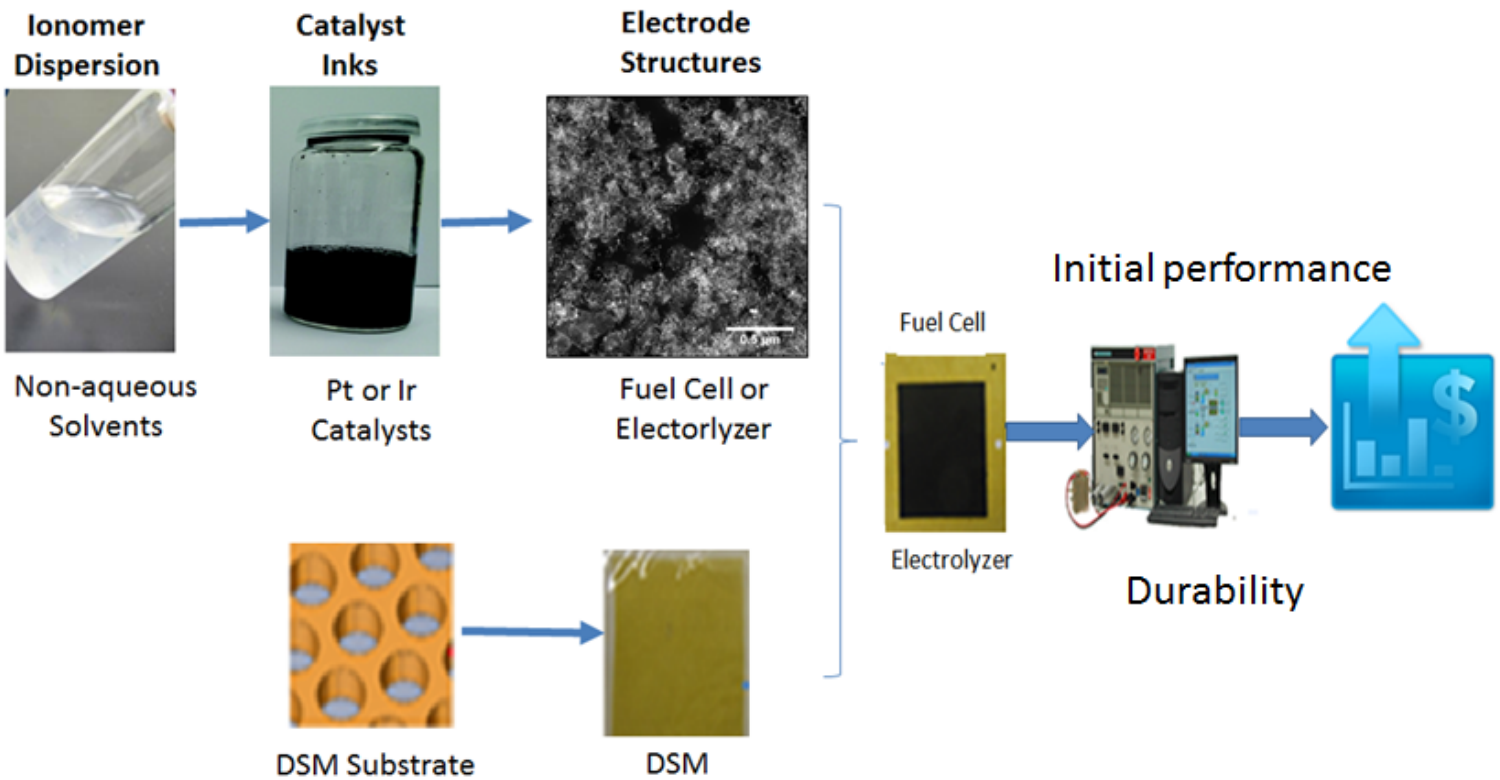
Technical Targets

- Elucidate how ionomer dispersions impact electrode structures and performance
- Create fuel cell MEAs that are mechanically and chemically stable (DOE 5000 hrs. target)
- Develop processable and scalable MEAs fabrication platforms using LANL ionomer dispersion and Giner DSMs

Project Nature

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

Technical Approaches



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

- Roll-to-roll production of DSM
- Ultra spraying or roll coater to make MEAs

- From LANL 5cm² to 50-100cm² full MEAs

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

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

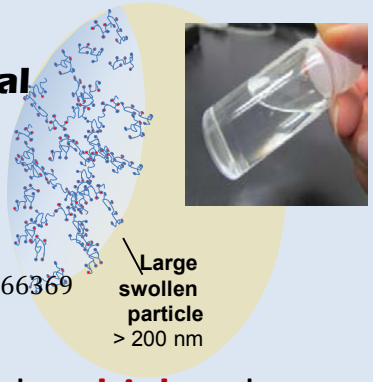
Task and Milestones

	Srat Date: July 28, 2017	Year 1						Year 2						Extension			Completion
ID	Task Name	M2	M4	M6	M8	M10	M12	M14	M16	M18	M20	M22	M24	M26	M28	M31	
	Task 1: Prepare Ionomer Dispersions in a Large Scale																100%
M1.1	LANL provides 1 kg of 10 wt% Nafion 1100 EW in NMP and 500g of 5 wt% 3M 825 EW ionomer in DMAc by Month 4																100%
	Task 2: Make DSM using ionomer dispersions																100%
M2.1	Giner produces 1 m^2 DSM using PSU support and LANL ionomer that demonstrates ionic conductivity >0.1 S/cm (liquid water) and 3x better mechanical property (via DMA) than Nafion 112 by Month 8																100%
	Task 3: Fabricate Large-sized Fuel Cell and Electrolyzer MEAs																70%
M3.1	LANL delivers low PGM loading (total Pt loading <0.25mg/cm^2) fuel cell MEA composition to Giner by Month 11																100%
M3.2	Giner completes low PGM loading (total Pt loading <0.4 mg/cm^2) electrolyzer MEA by Moth 12																100%
	Task 4. Evaluate the durability of PEM fuel cell MEAs																70%
	a. Voltage Cycling																100%
	b. RH Cycling																100%
M4.1	Low PGM loading Fuel Cell MEAs demonstrate less than 20mV voltage loss after 30,000 cycles by Month 16																100%
M4.2	Low PGM loading Fuel Cell MEAs demonstrate less than 2 mA/cm^2 membrane crossover 30,000 cycles by Month 20																100%
	Task 5. Evaluate the durability of PEM electrolyzer MEAs																70%
M5.1	Low PGM loading electrolyzer MEAs demonstrate less than 20 mV loss (at 1.5 mA/cm^2) after 50,000 cycles by Month 24																80%
M5.2	Low PGM loading electrolyzer MEAs demonstrate less than 20 mV performance loss after 1,000 hour test at 1.5mA/cm^2 by Month 28																50%
	Task 6. Develop Fuel Cell and Electrolyzer MEA Markets																40%
M6.1	Provide low-PGM loading MEAs for building 300 kW electrolyzer																5%

Ionomer Dispersion Technology

Conventional Ionomer Dispersion

Dupont
European Patent 0066369



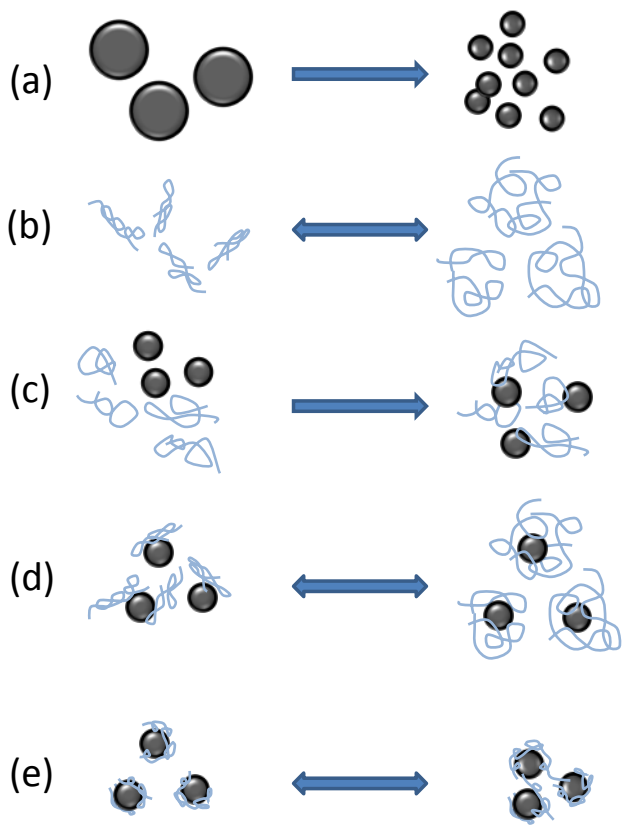
- Water based **multiple** solvent system
- **Expensive** processing: requires high temperature (> 200°C) & pressure (> 1000 psi)
- **Large** and **non-uniform** particle suspension: particle size (hydrodynamic radius: 200 – 400 nm)
- Produces **brittle** membrane: toughness ~ 0.001 MPa
- Produces **less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

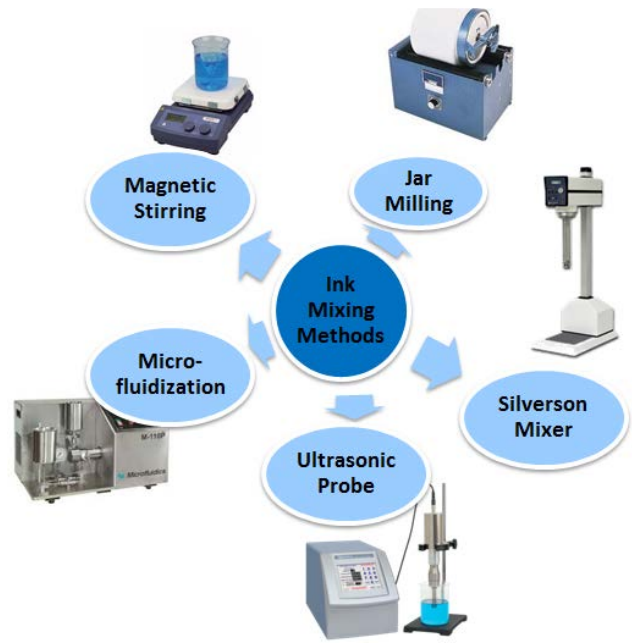
LANL Ionomer Dispersion

LANL
US Patent 7981319, 8236207, 8394298

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

Pt/C Ink and Ionomer Interaction



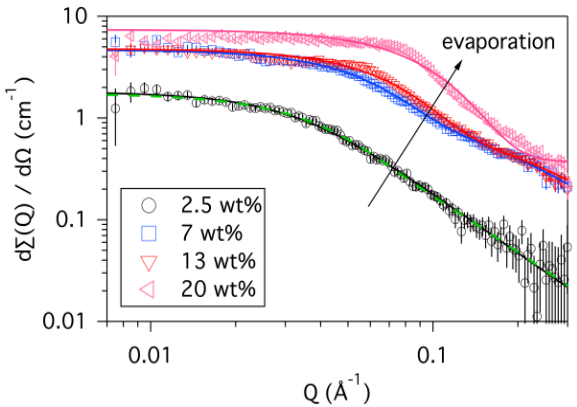


(a) Breakdown of core catalyst agglomeration
(b) Ionomer re-conformation in various solvent blend
(c) Ionomer adsorption onto catalyst particle surface
(d) Ionomer re-conformation on particle surface
(e) Formation and breaking-up of flocculation

Accomplishment: Ionomer Particle Morphology (LANL)

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



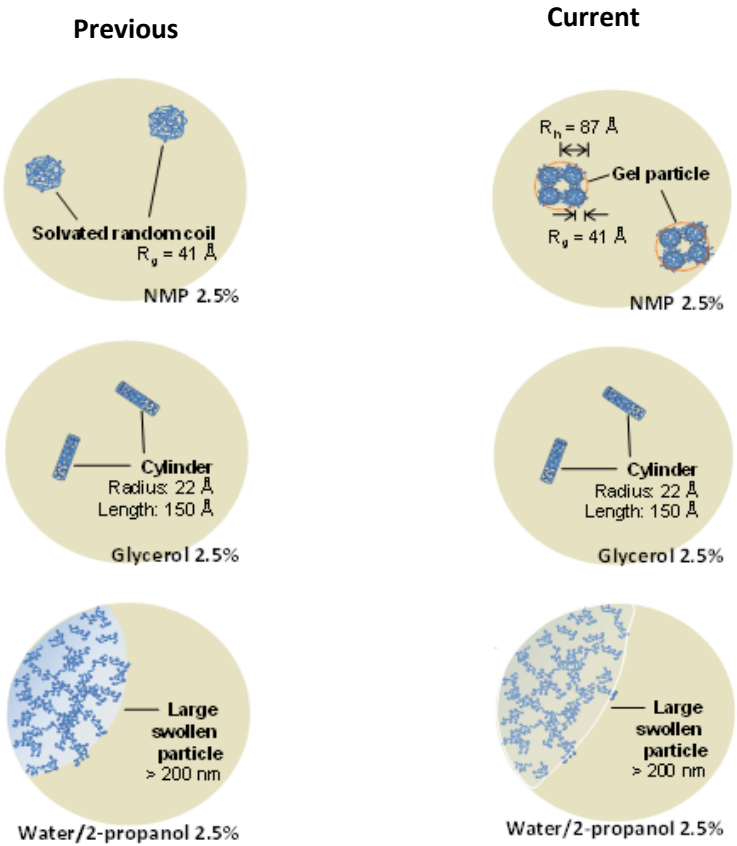
Black line: Random walk modeling

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

Green line: Gel particle modeling

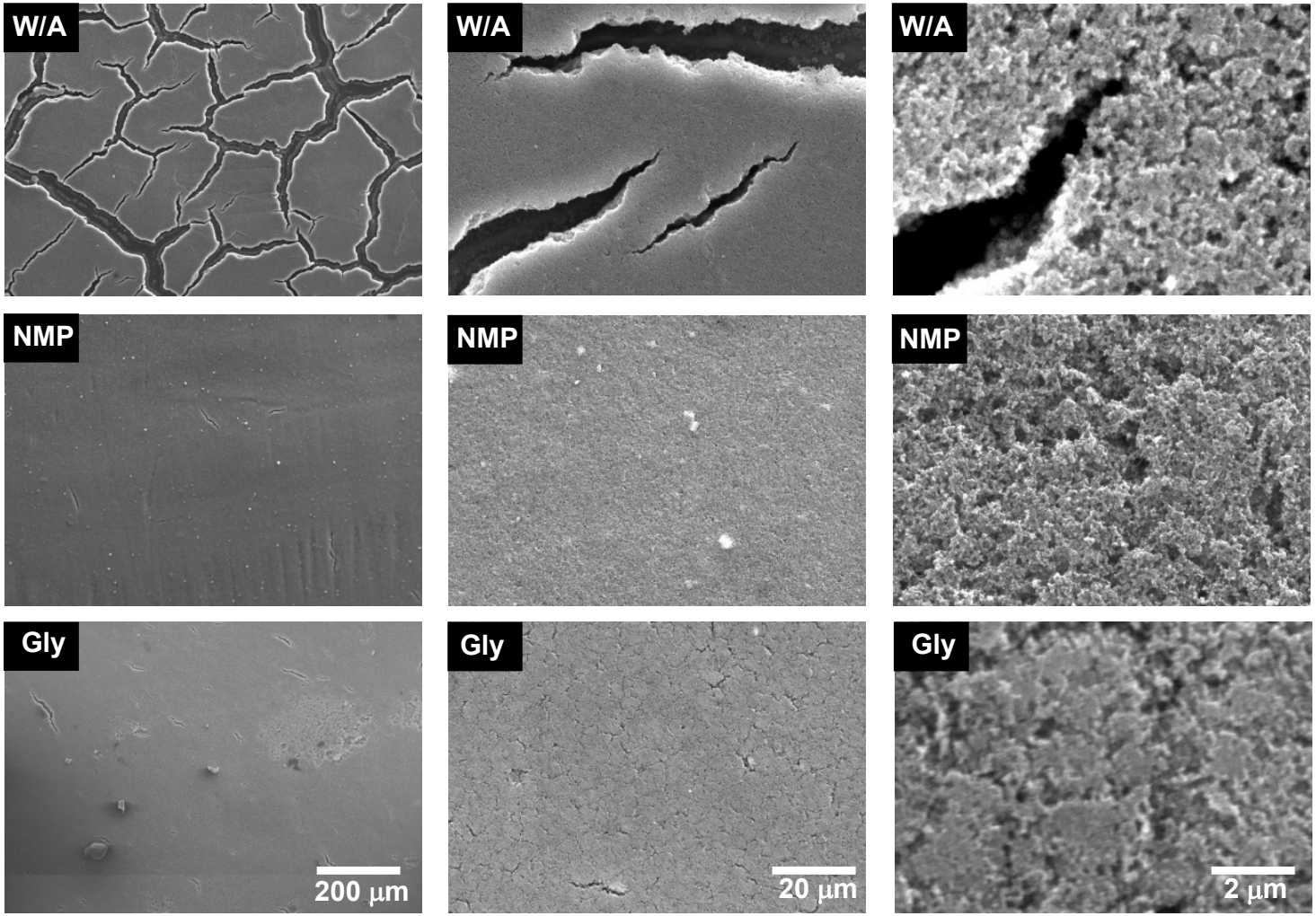
$$I(Q) = I_G(0)\exp[-Q^2\Xi^2/2] + I_L(0)/(1+Q^2\xi^2) + B$$

Particle size from DLS: RH = 8.7 nm



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

Impact of Dispersing Agents on Electrode Morphology



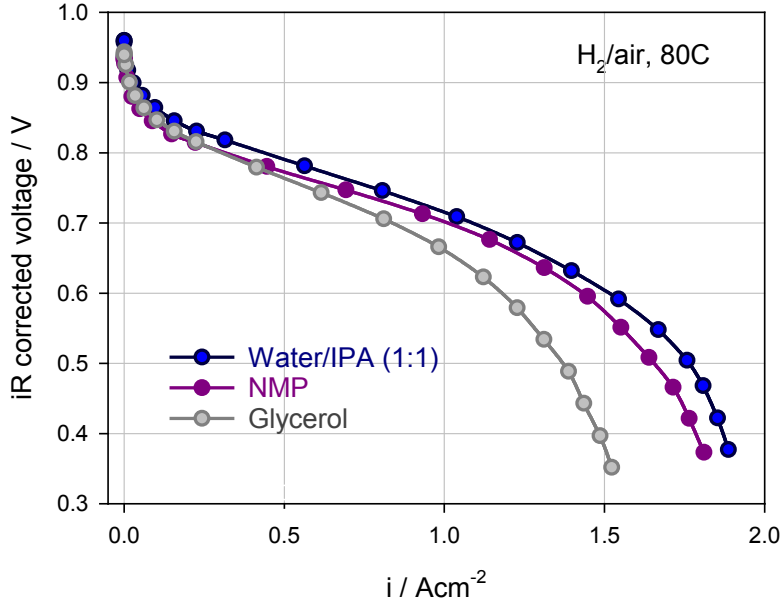
W/A : water/IPA (1:1)

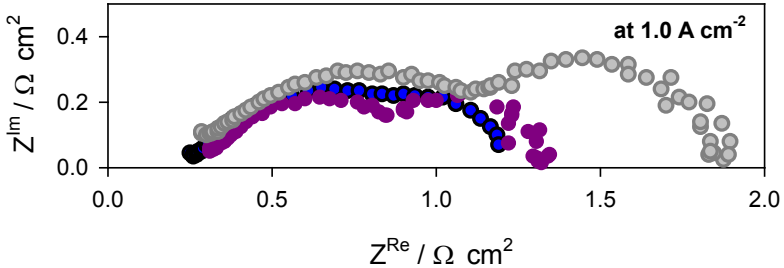
NMP : N-methyl-2 pyrrolidone

Gly : glycerol

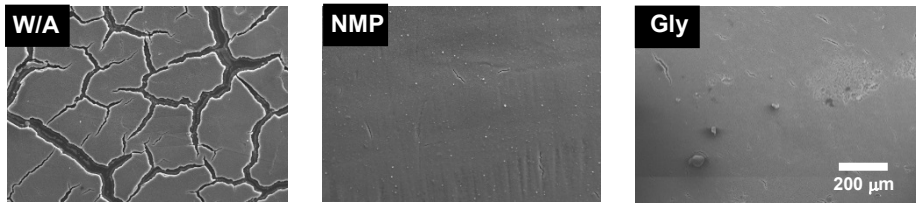
- Water/IPA electrode has large (~100 μm) cracks.
- NMP electrode is crack-free but microporous structure (sub micron size)
- The electrode prepared from glycerol has small cracks but forms dense microstructure.

Impact of Dispersing Agents on BOL H_2/air Fuel Cell Performance (LANL)





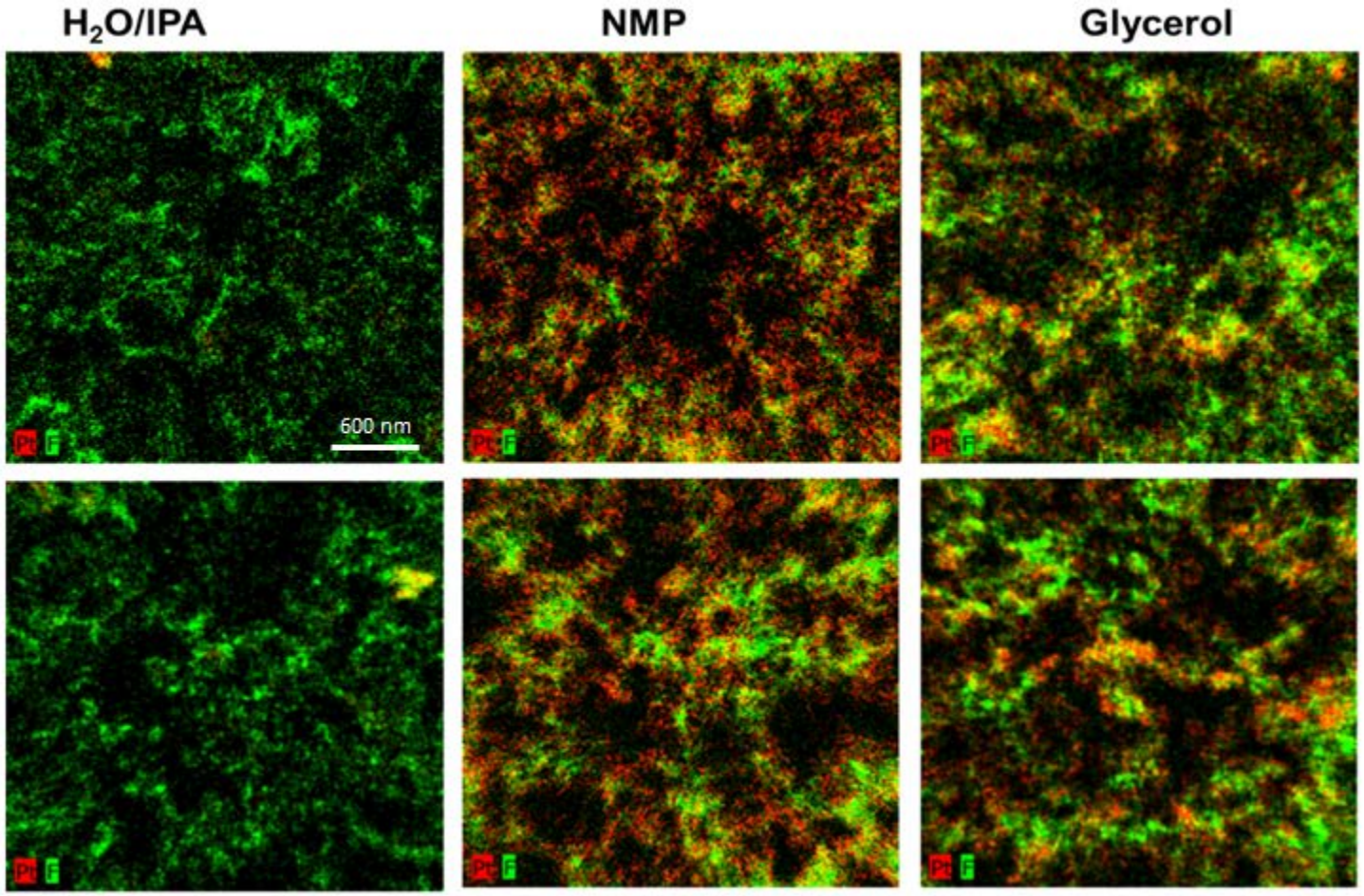
Test conditions: Operating temperature: 80°C; Humidification: Fully humidification; Backpressure: 30 psig; Break-in: > 15 hours at 0.6 V; Cathode Pt loading: 0.2 mg_{Pt}/cm^2



- Fuel Cell Performance: Water/IPA > NMP > Glycerol.
- Glycerol cathode has substantial catalyst mass transport limit.
- NMP cathode has comparable mass transport limit with water/IPA cathode, even though crack free structure; however, the performance at high cell voltage (> 0.8V) is relatively poor.
- Two key questions

1. What is the governing factor for BOL fuel cell performance?
2. Can we make water/IPA equivalent fuel cell performance with non-aqueous dispersing agent?

Impact of Dispersing Agent on Electrode Morphology – Catalyst Particle Distribution



Courtesy: Karren More (ORNL)

- Electrode from H_2O/IPA has poor catalyst particle distribution.
- Electrodes prepared from single dispersing agent have relatively good catalyst particle distribution.

Accomplishment: More Non-Aqueous Ionomer Dispersions (Giner)

Sample #	Abbreviation	Description
11	N-IPA	Nafion in 2-propanol/water
12	N-NPA	Nafion in 1-propanol/water
13	N-EG	Nafion in ethylene glycol
14	N-BD	Nafionin butanediol
15	N-PD	Nafion in pentanediol
16	LE-DMAc	3M 825 EW in DMAc
17	LE-PD	3M 825 EW in pentanediol

Pt/C Electrodes Fabrication

Magnetic Stirring- 2 days

Mayer Bar Coating

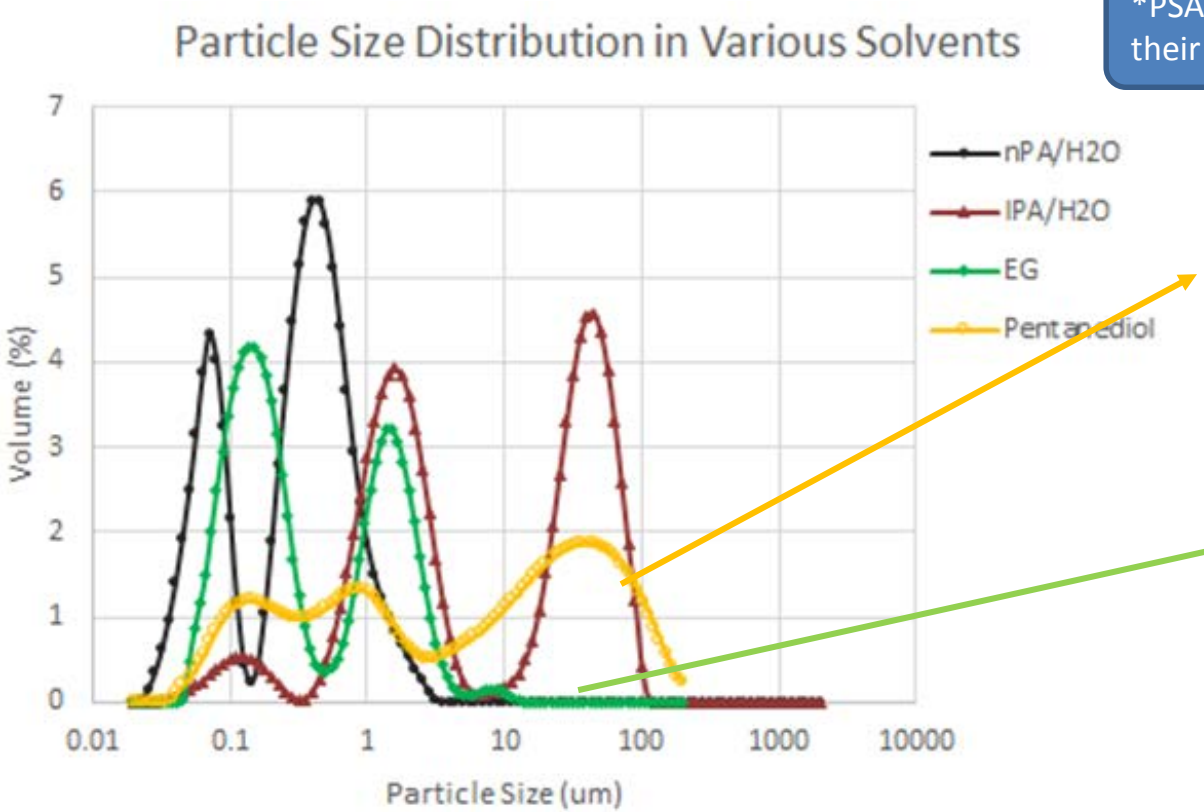
- Drying at 60°C for 30 min, then vacuum oven overnight @150°C
- Pt loading was verified by XRF
- Decal transfer is successful for all the electrode studied.

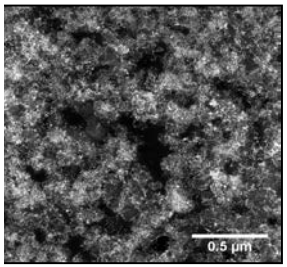
- Ionomer in the electrode and membrane are both in acid form so re-protonation is not required
- Both ink mixing and coating processes are easily scalable

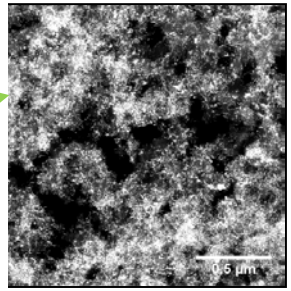
Pt/C Ink Particle Size Distribution

---by laser diffraction particle size analyzer

*PSA measurement was carried out in their own background solvent

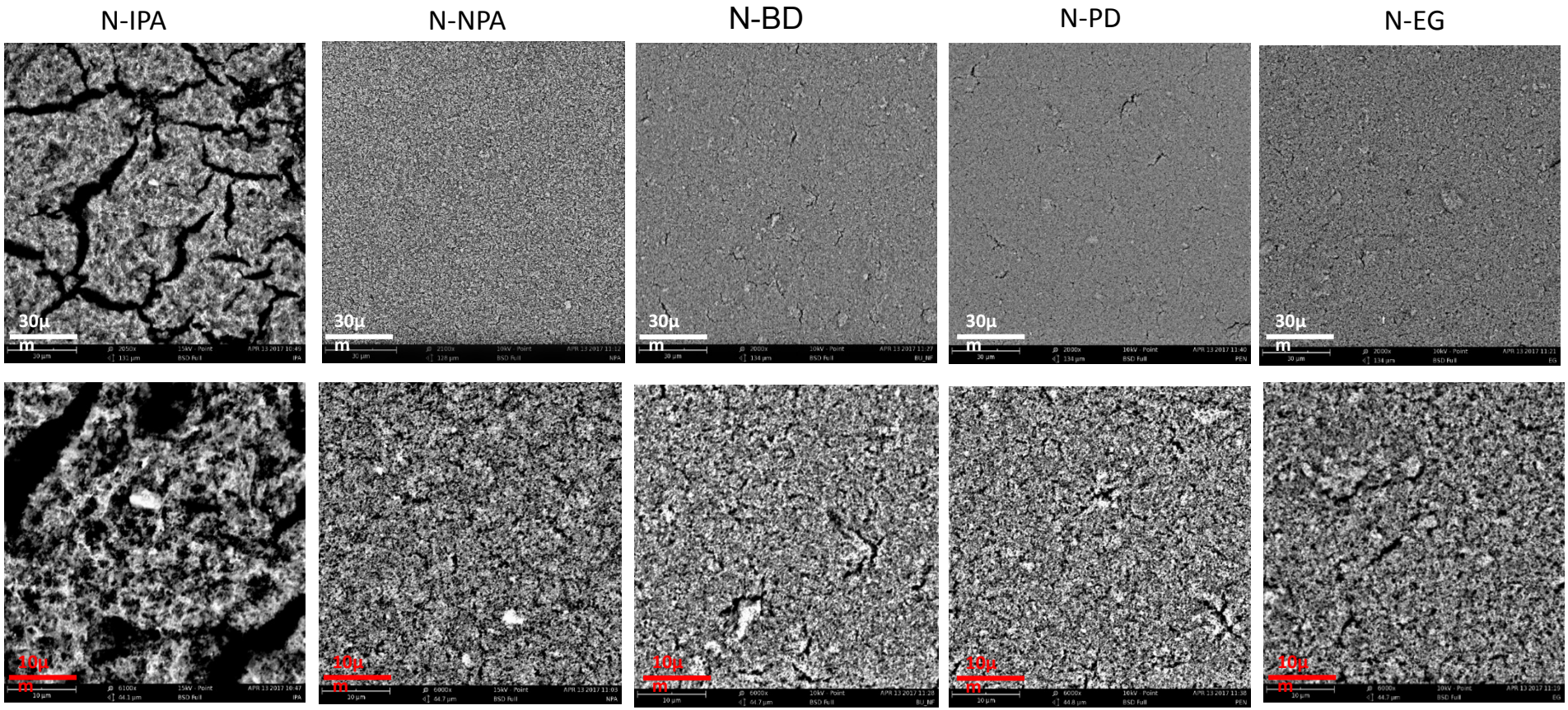






- ❑ The solvent has significant impact on ink particle size and distribution.
- ❑ EG and NPA based ink shows the smallest particle size, likely suggesting that they provide better catalyst-solvent interactions.
- ❑ Further study needed to understand the correlations between solvent effect on ink particle size distribution and electrode structure.

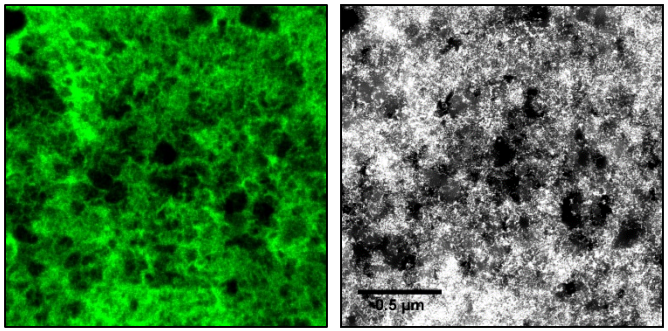
SEM Images of Electrodes

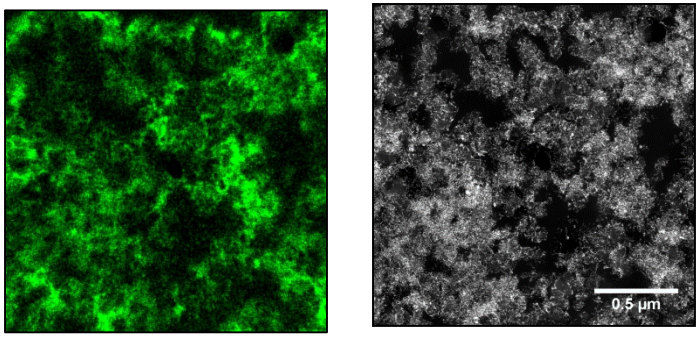


- ❑ Electrode made from IPA/H2O based ink exhibits large “mud cracks”.
- ❑ All the other electrodes demonstrate smooth coating surface and good quality.

TEM Images of Ionomer Distribution in Electrodes

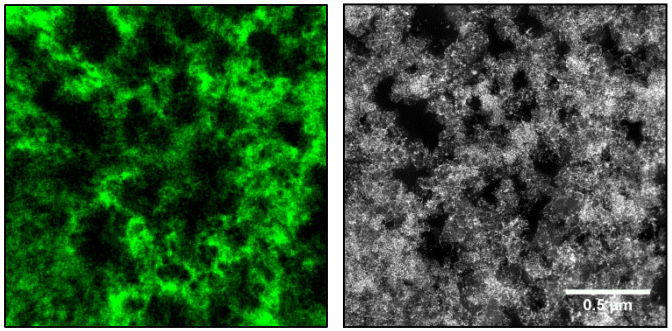
N-EG

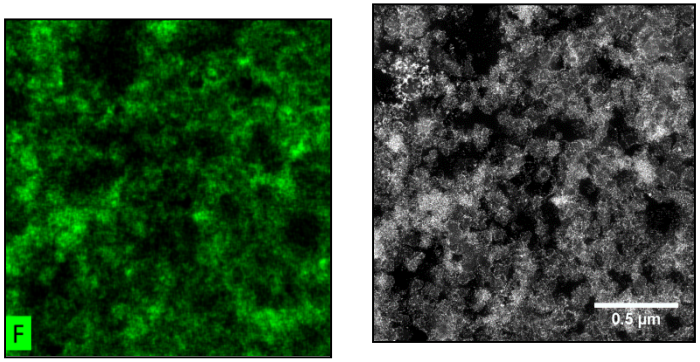




N-BD

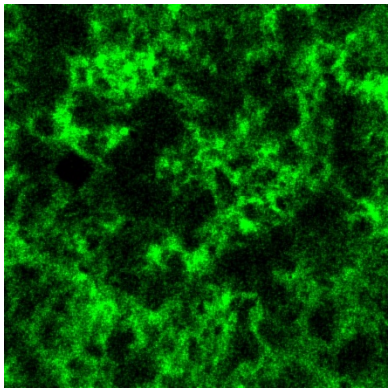
N-PD

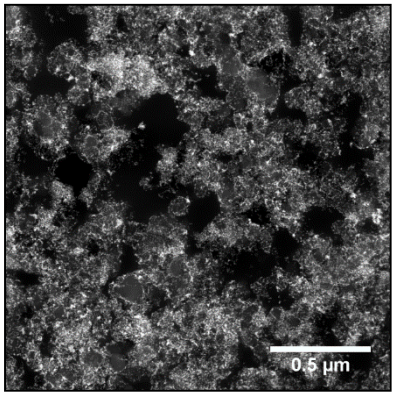




LE-DMAc

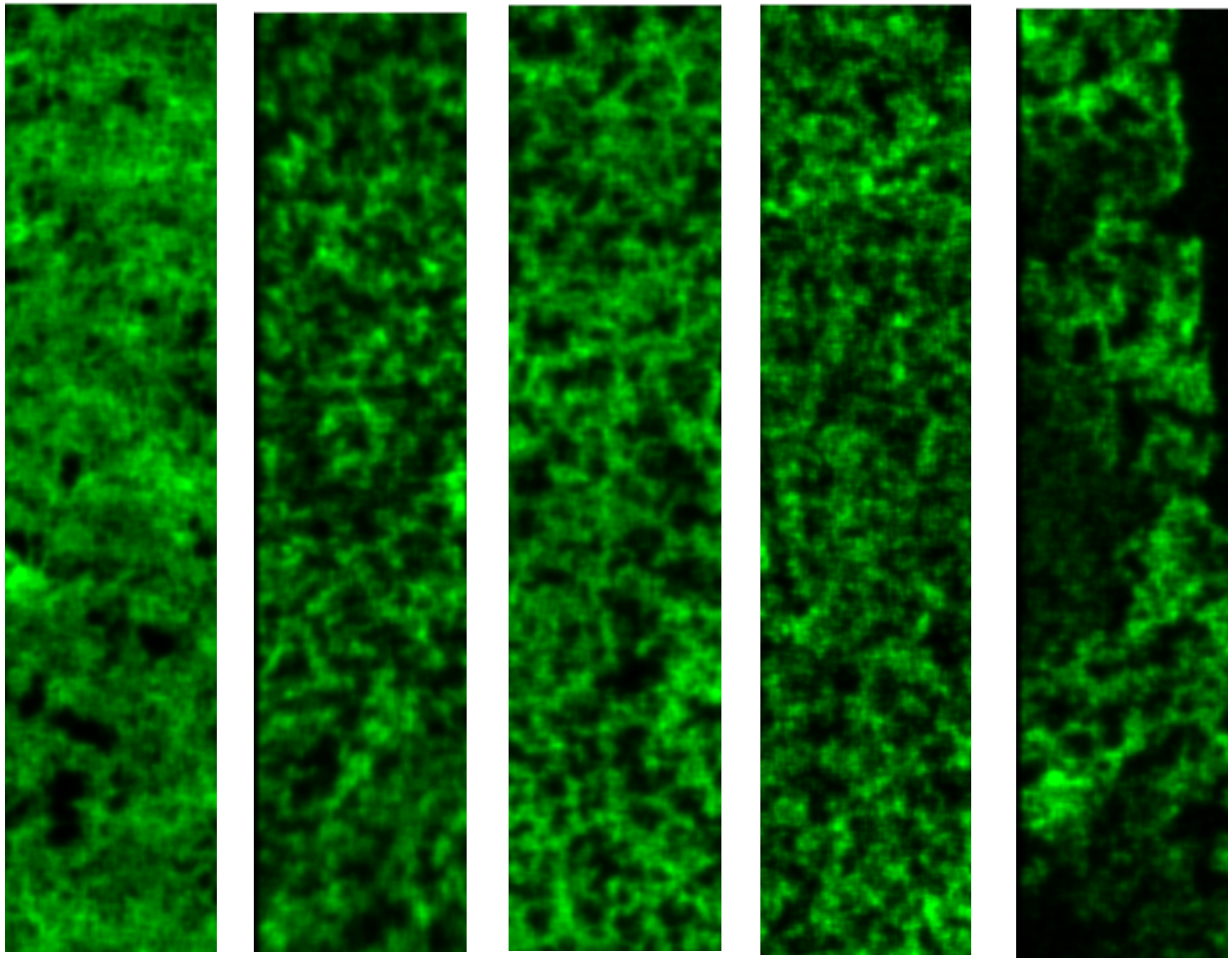
Green= Fluorine





LE-PD

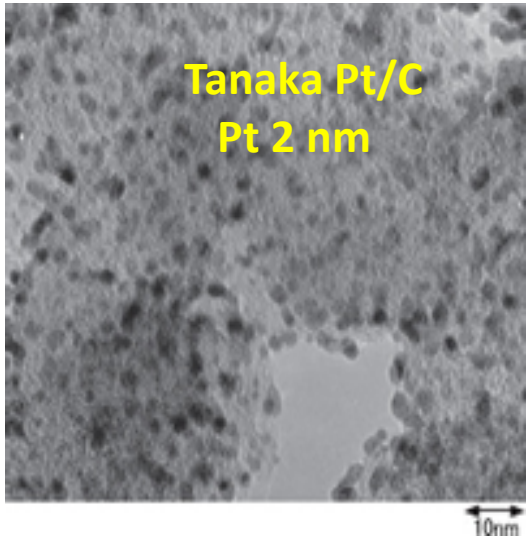
Impact of dispersing agent on electrode morphology – Ionomer distribution

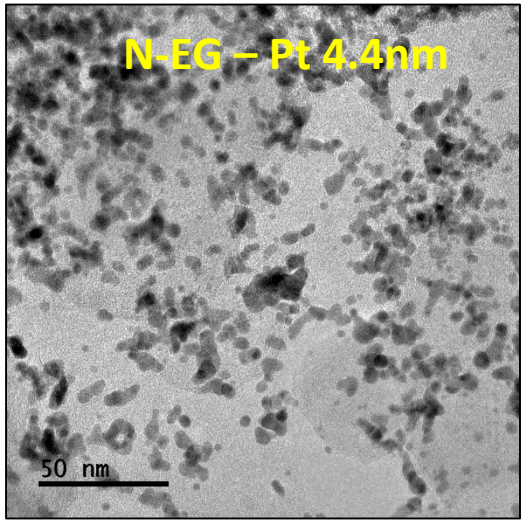


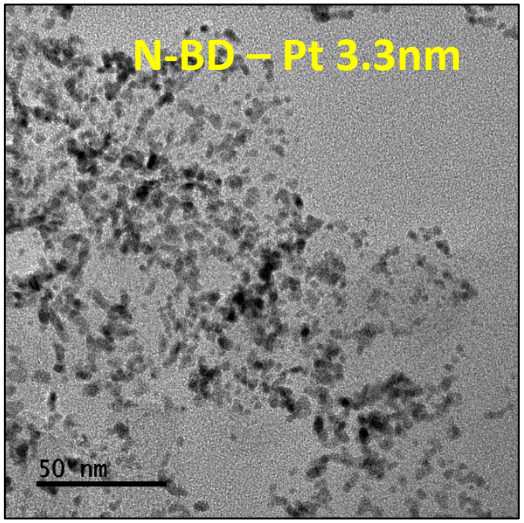
N-EG N-BD N-PD LE-DMAC LE-PD

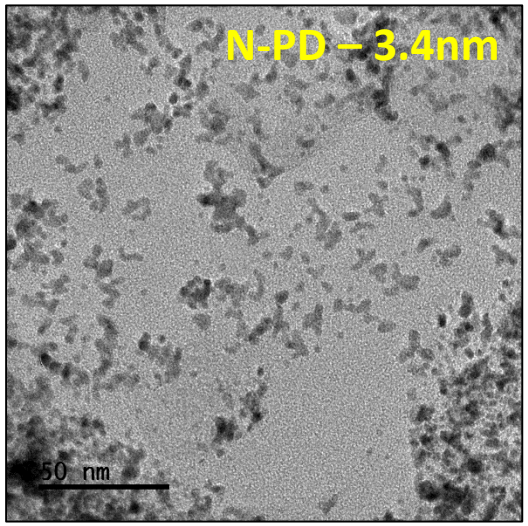
- Ionomer distribution can be clearly evaluated in the low magnification mapping.
- Best ionomer distribution: Ethylene glycol (ionomer aggregates were < 50 nm)
- Worst ionomer distribution: 3M ionomer/pentanediol.
- Ionomer distribution seems to be improved with hydrophilicity of the solvent (need further study)

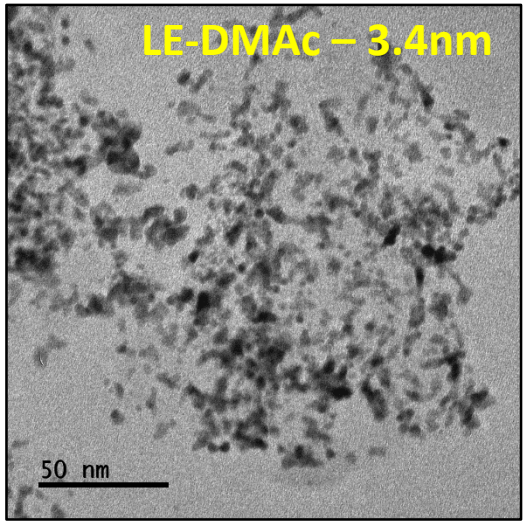
Pt Particle Size Distributions

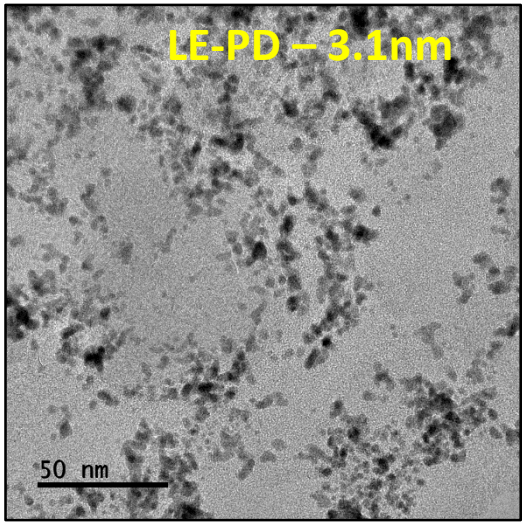




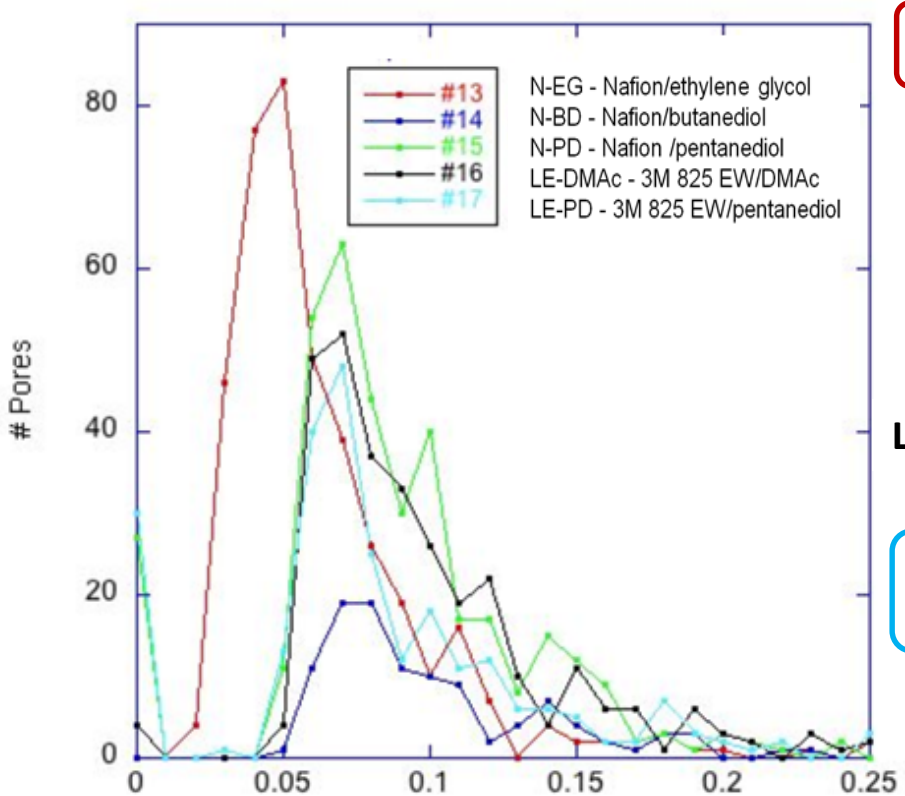








Electrode Size Distribution



N-EG - % porosity = 13%
Avg. secondary pore diameter = 0.057μm)

N-BD - % porosity = 35%
Avg. secondary pore diameter = 0.097μm

N-PD - % porosity = 32%
Avg. secondary pore diameter = 0.086μm

LE-DMAc - % porosity = 37%
Avg. secondary pore diameter = 0.095μm

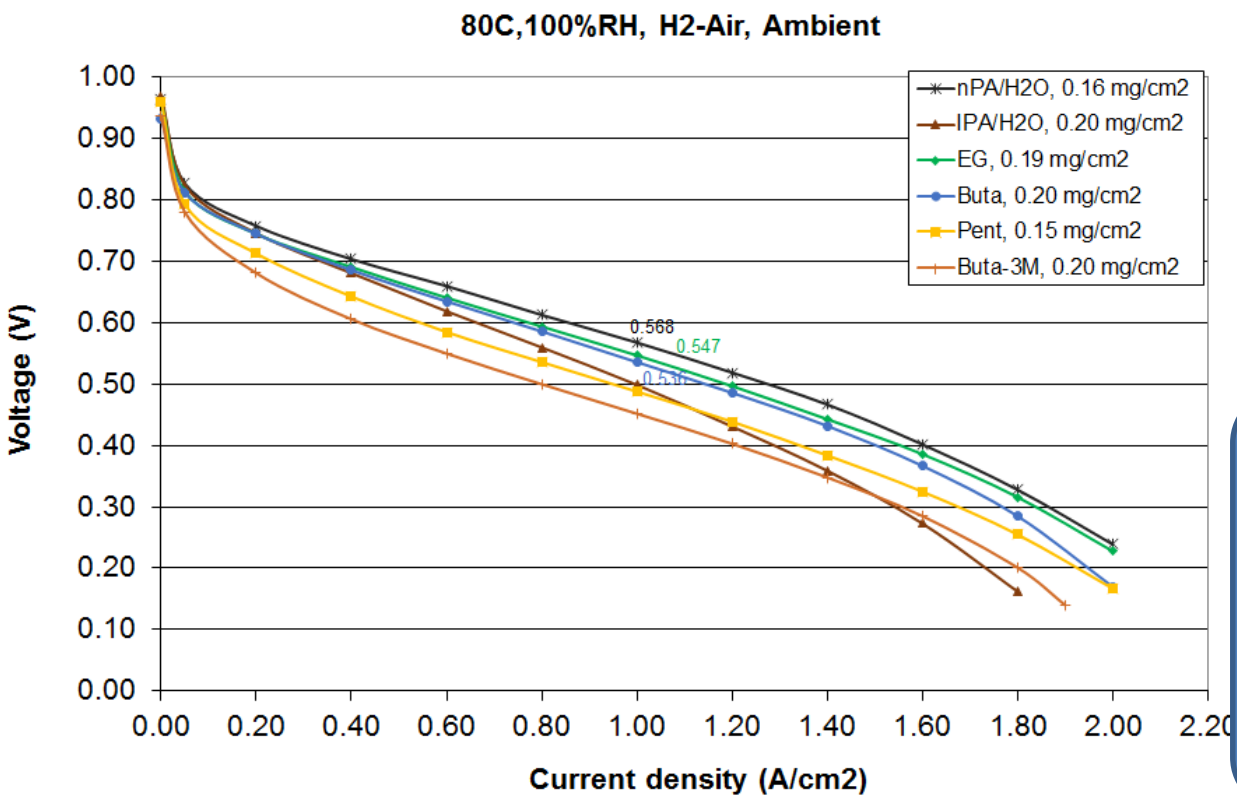
LE-PD - % porosity = 39%
Avg. secondary pore diameter = 0.08μm

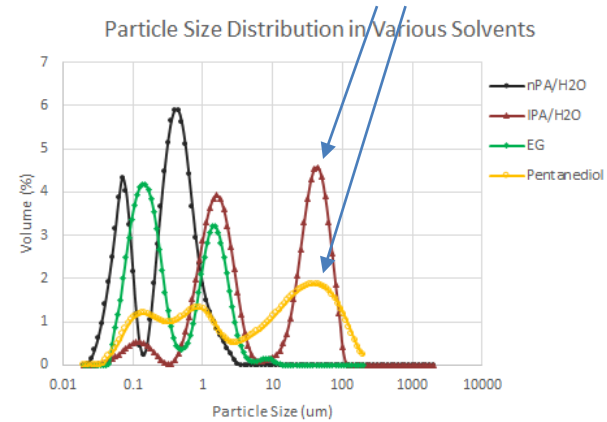
Pore size distribution:

- N-EG is densest electrode with the hightest number of pores and smallest pore sizes.
- N-BD has fewest pores and widest pore size distribution
- N-PD and LE-DMAc had similar pore size distributions
- LE-PD had the lowest overall density (highest porosity)

Accomplishment: Performance Comparison by Solvents

Large agglomerations

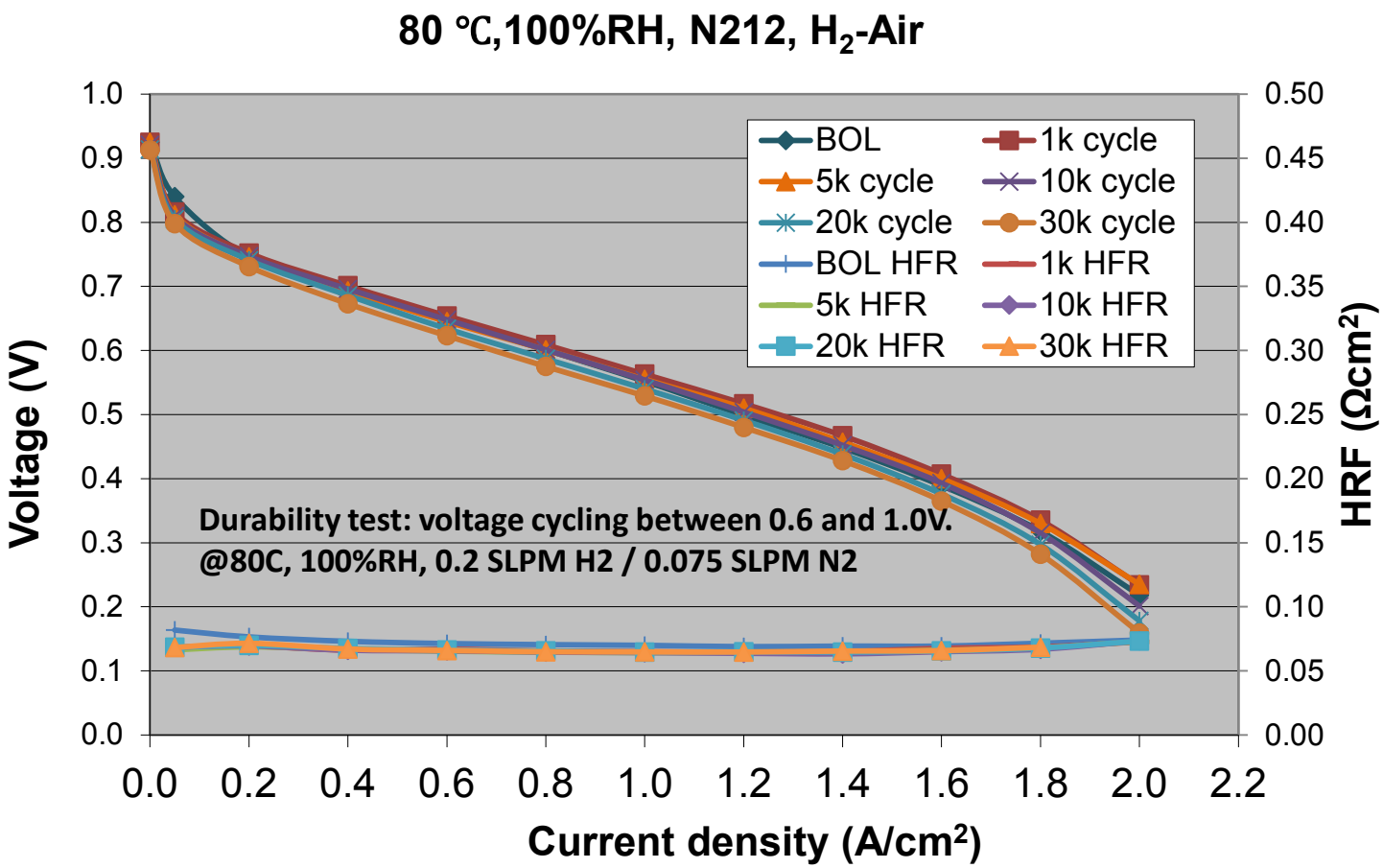




- nPA/H_2O and EG solvent system provide better ink structure, implied by much smaller particle size.
- IPA/H_2O and Pentanediol based solvent system exhibit large agglomerations in the ink, which may account for their bad quality and performance.

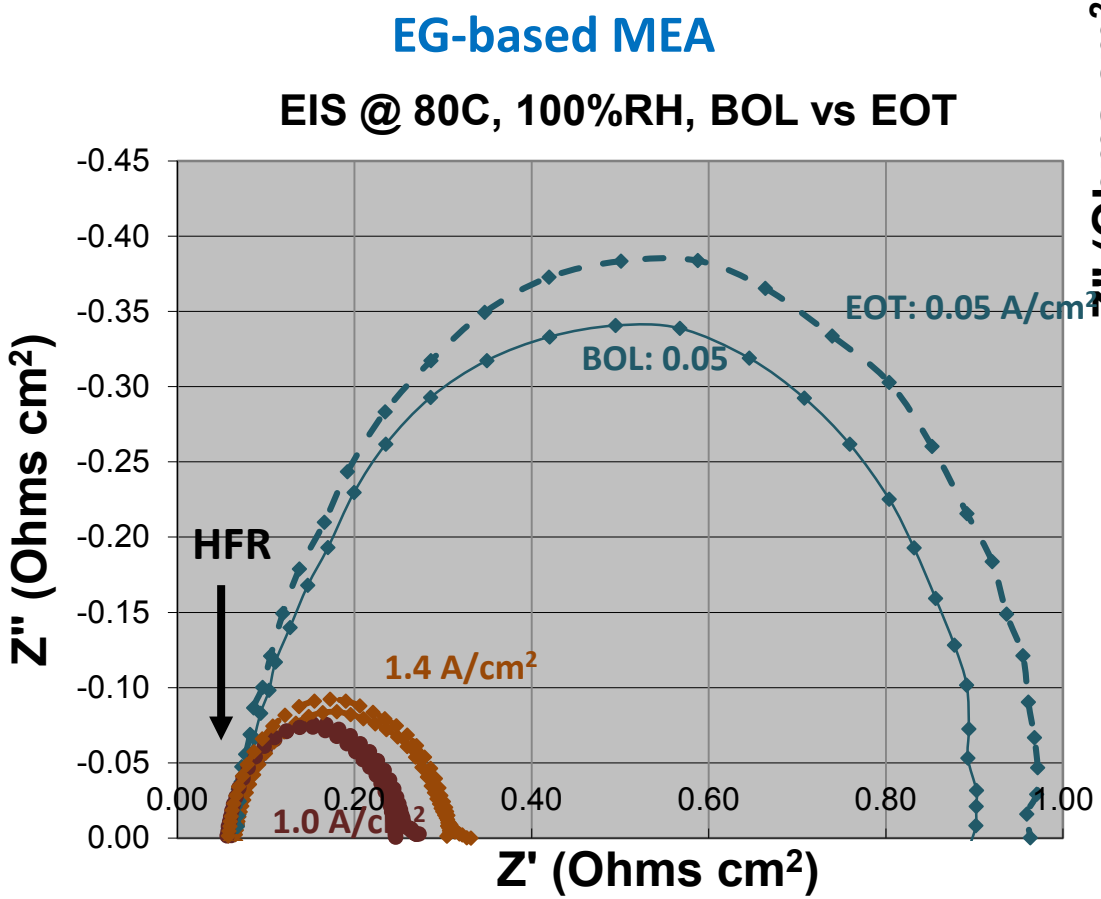
- ❑ Performance ranking: nPA/H_2O > Ethylene glycol > Butanediol > Pentanediol > Butanediol (3M)
- ❑ Due to the fact that poor performance of the IPA/H_2O electrode led to inconsistent results; thus, a more consistent baseline (nPA/H_2O) was chosen for comparison.

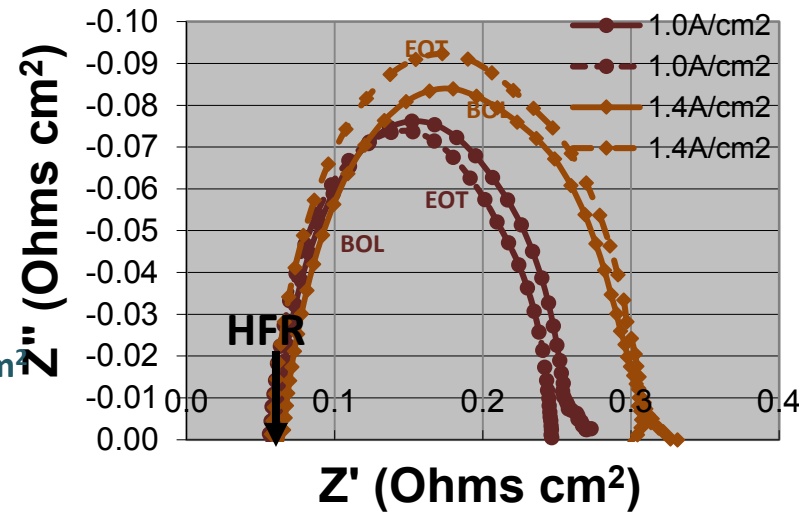
EG Based Electrode Durability



- Voltage loss at 1A/cm^2 from BOL to EOT is 23 mV.
- HFR stays consistent throughout the 30k voltage cycling
- Main loss due to ECSA and enhanced charge transfer resistance

Impedance Analysis Upon Voltage Cycling

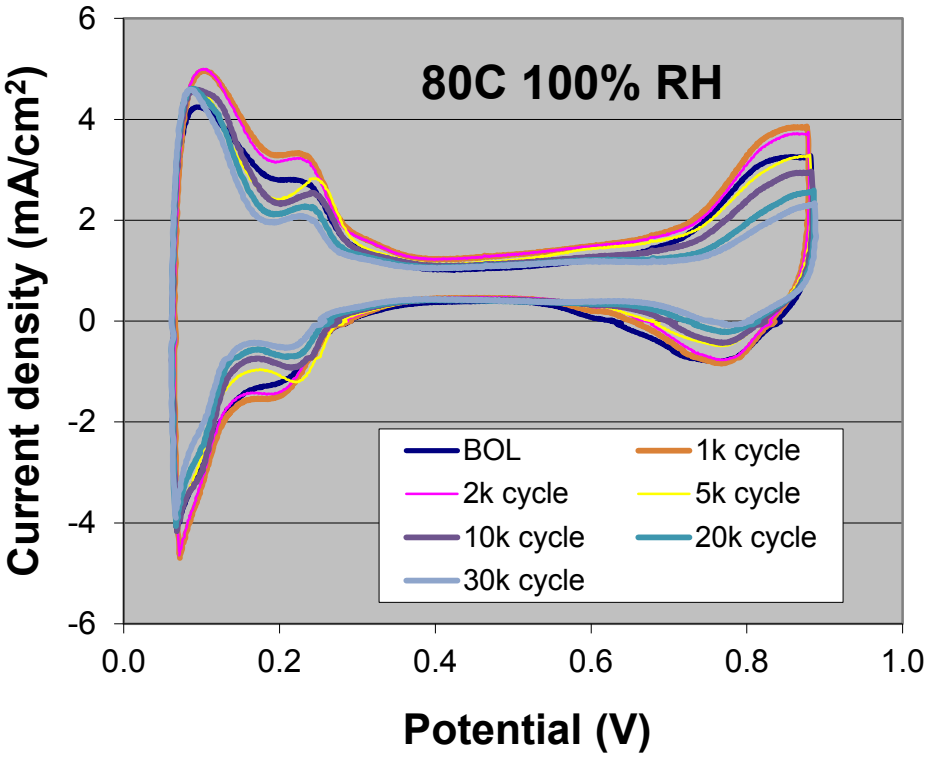


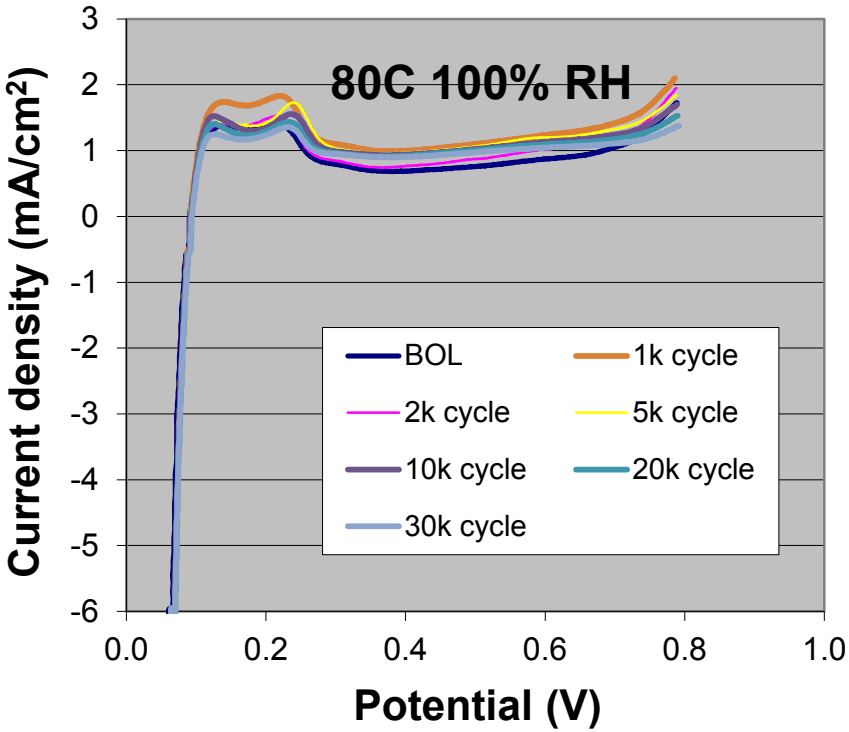


- HFR stays nearly consistent throughout the 30k voltage cycling, as well as at various current densities.
- Major resistance change observed at kinetic region, consistent with CV result
- In mass transport region, no obvious resistance change.

ESCA and H_2 Crossover Upon Cycling

EG-based MEA





- CV plot changes continuously as ECSA decreases during durability test
- Hydrogen crossover current remains nearly consistent

Summary

- Ionomer dispersions in a variety of solvents have been investigated; solvent affects ionomer morphology and re-conformation;
- Ionomer dispersions impact the electrode structures that include ionomer distribution, catalyst distribution and pore size distribution
- Ionomer dispersions influence fuel cell electrode performance. EG-dispersed Nafion ionomer demonstrates the best performance and good durability, likely due to its uniform ionomer distribution and unique pore size distribution.

Future Plans

- Perform SANS of EG and other non-aquaeous solvents based ionomer and catalyst inks;

- Further investigate interactions between non-aqueous ionomer dispersion/ catalysts to develop processable and durable MEA manufacturing practice:
  - Protonic Resistance
  - Local oxygen transport resistance

- Consolidate LANL data and Giner data to achieve more comprehensive information
  - Identical experiment conditions
  - Data reproducibility

- Further apply ionomer dispersion technology to oxygen evolution reaction catalyst in water electrolysis

Acknowledgments

- Financial support from DOE SBIR/STTR Program
- Program Manager
  - Donna Ho
- Dr. Yu- Seung Kim at LANL (Subcontractor)
- Dr. Karren More at ORNL (collaborator)
- Giner Personnel
  - Zach Green, Tom McCallum, Jason Willey
  - Drs. Corky Mittelsteadt and Chao Lei