2018 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: 5/27/2018

Budget

- Total Project Value
  - $1.15 million
  - $1.14 million

Barriers Addressed

- PEM fuel cell and electrolyzer performance and durability

Partners

- LANL: Dr. Yu-Seung Kim
- UConn: Dr. Jasna Jankovic
- ORNL: Dr. Karren More

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)

Relevance

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

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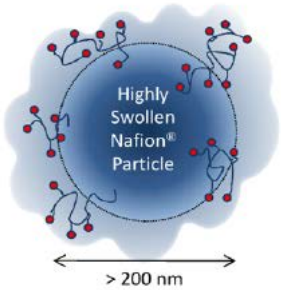
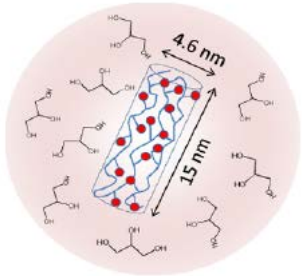
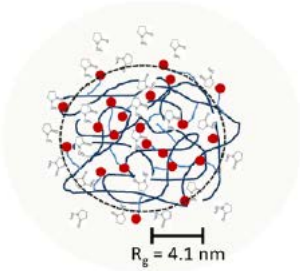


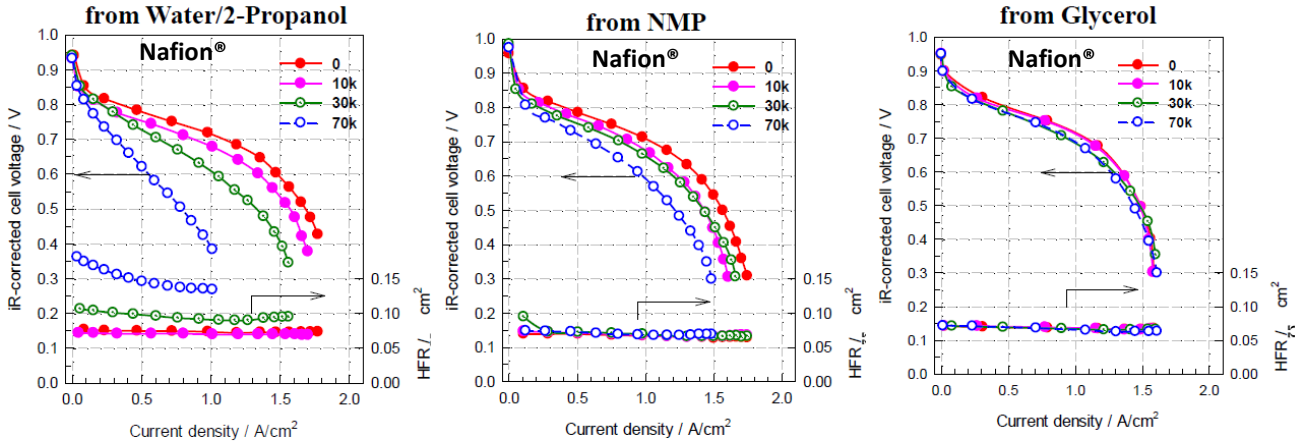
In water/2-propanol



In glycerol



In NMP



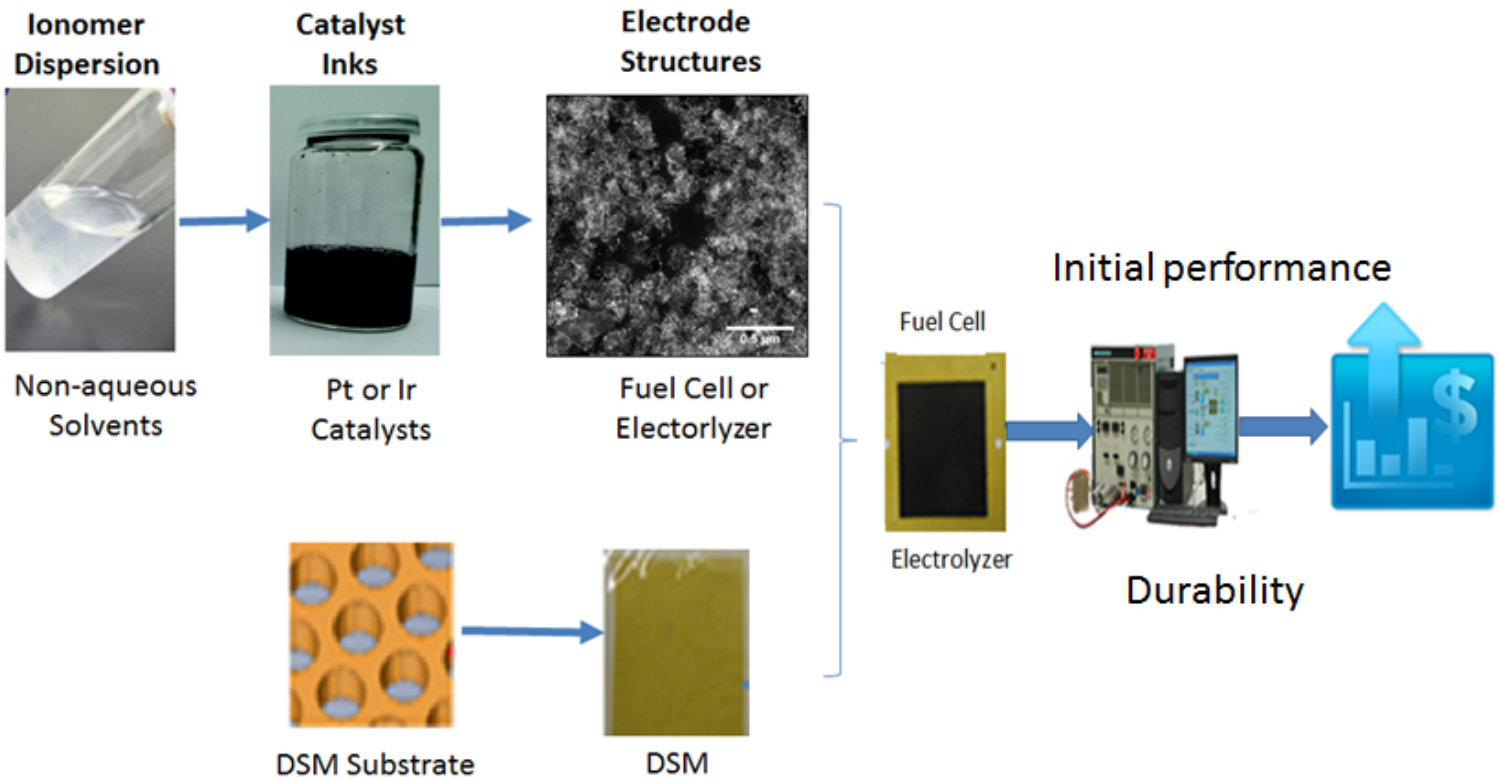
Premature electrode & electrode-membrane interface failure

Performance decrease due to Pt nano-catalyst agglomeration

Performance decrease was compensated with time dependent structural change

Welch et al, ACS Macro Lett., **1**, 1403−1407 (2012).

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

Proposed Phase IIB work

Pt/C Electrodes Fabrication

Catalyst: Tanaka Pt (47 w.t. %)/C Membrane: Nafion 212

Magnetic Stirring- 2 days

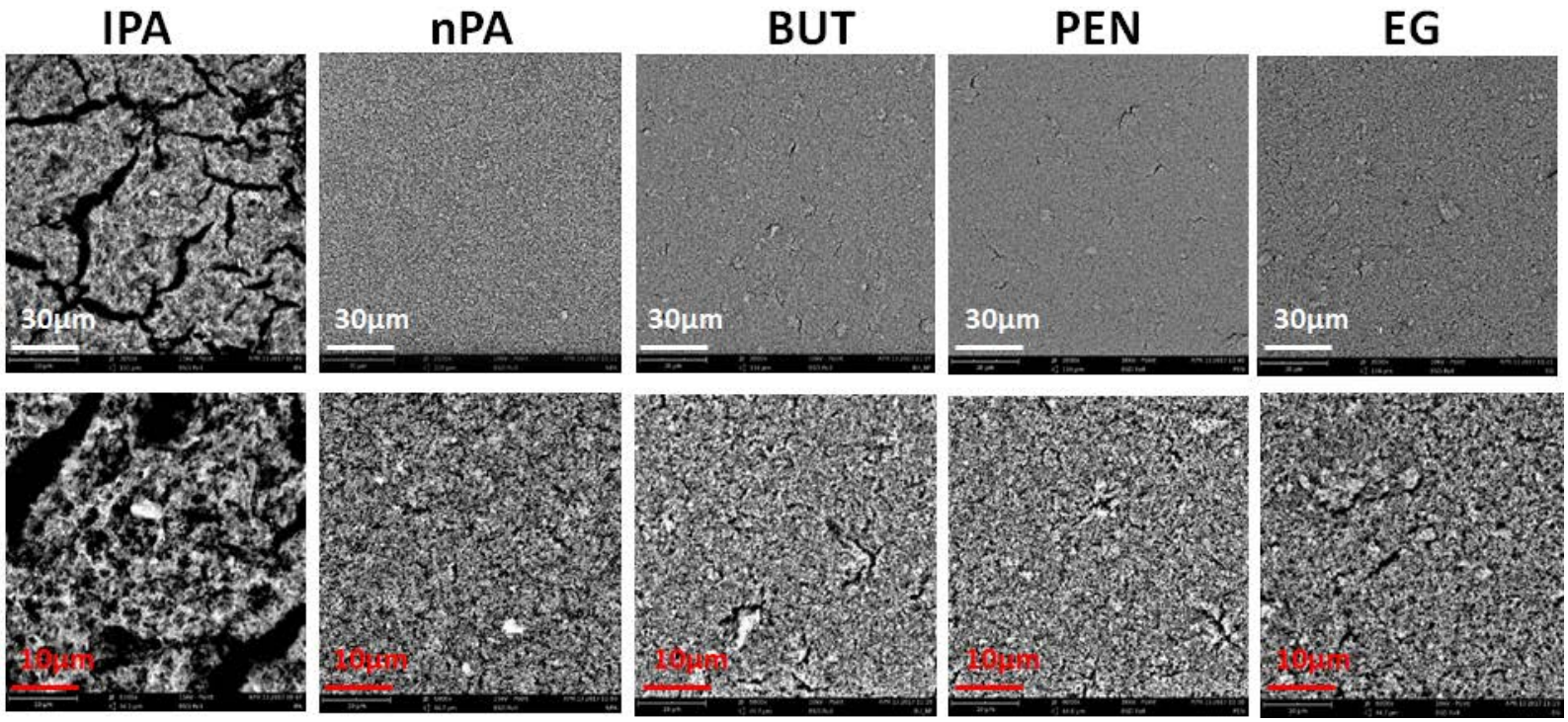
Mayer Bar Coating

- 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

Solvents	Boiling Point (°C)	Viscosity @ 25°C (cP)
IPA	82.6	1.96
NPA	97	1.96
EG	197.3	16.9
BUT	235	89.24 @ 20°C
PEN	242	114.6

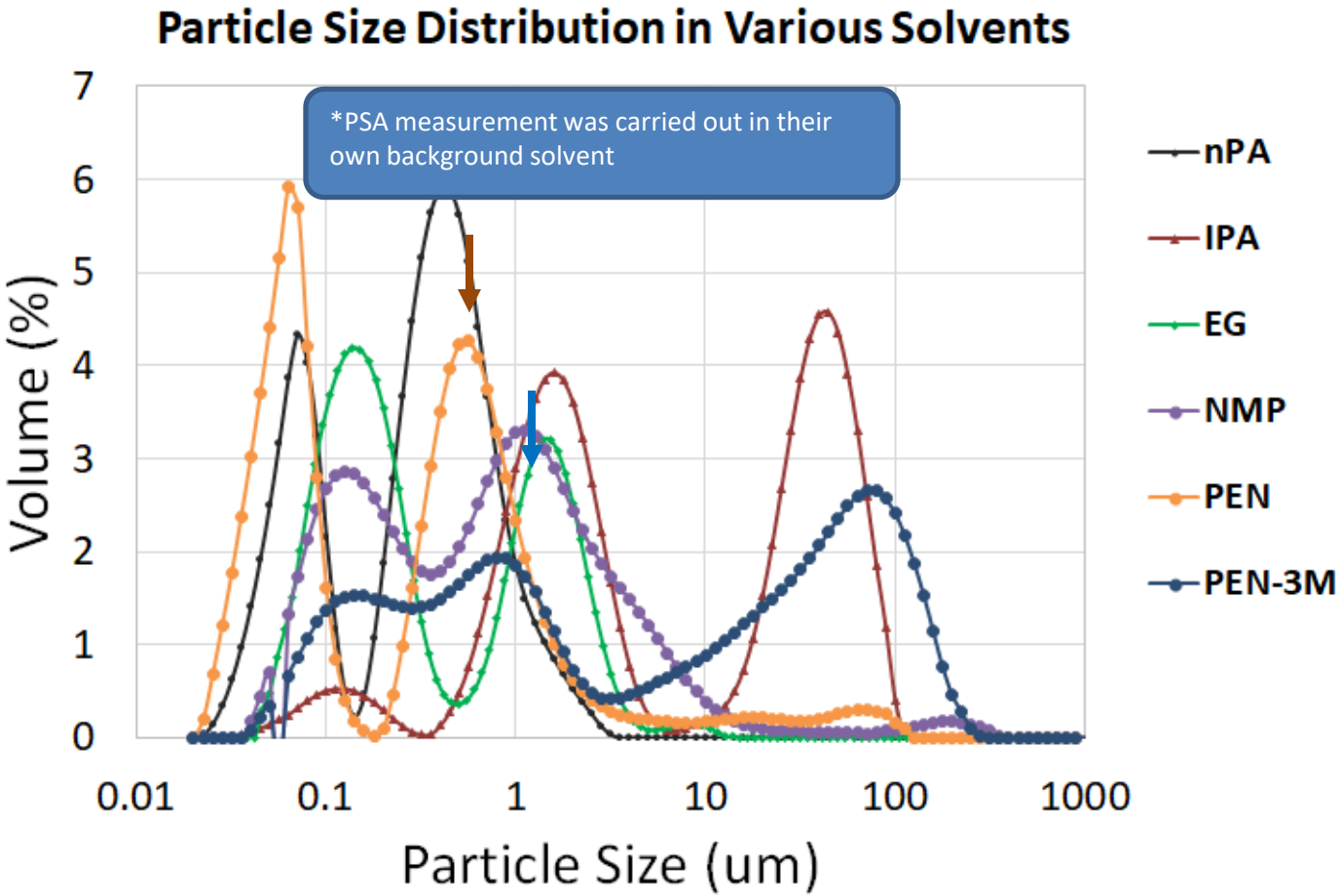
Accomplishment: More Non-Aqueous Ionomer Dispersions (Giner)



Sample Abbreviation	Description	I/C	Pt Loading (mg/cm2)
IPA	Nafion in 2-propanol/water	0.6	0.19
NPA	Nafion in 1-propanol/water	0.6	0.175
EG	Nafion in ethylene glycol	0.6	0.21
BUT	Nafion in butanediol	0.6	0.19
PEN	Nafion in pentanediol	0.6	0.18
PEN-3M	3M 825 EW in pentanediol	0.6	0.17

Ink Particle Size Distribution

---by laser diffraction particle size analyzer



- ❑ The solvent has significant impact on ink particle size and distribution.
- ❑ Other than IPA/H_2O based ink, the ink with Pentanediol-3M ionomer also exhibits large agglomerates, and its electrode contains many pinholes.

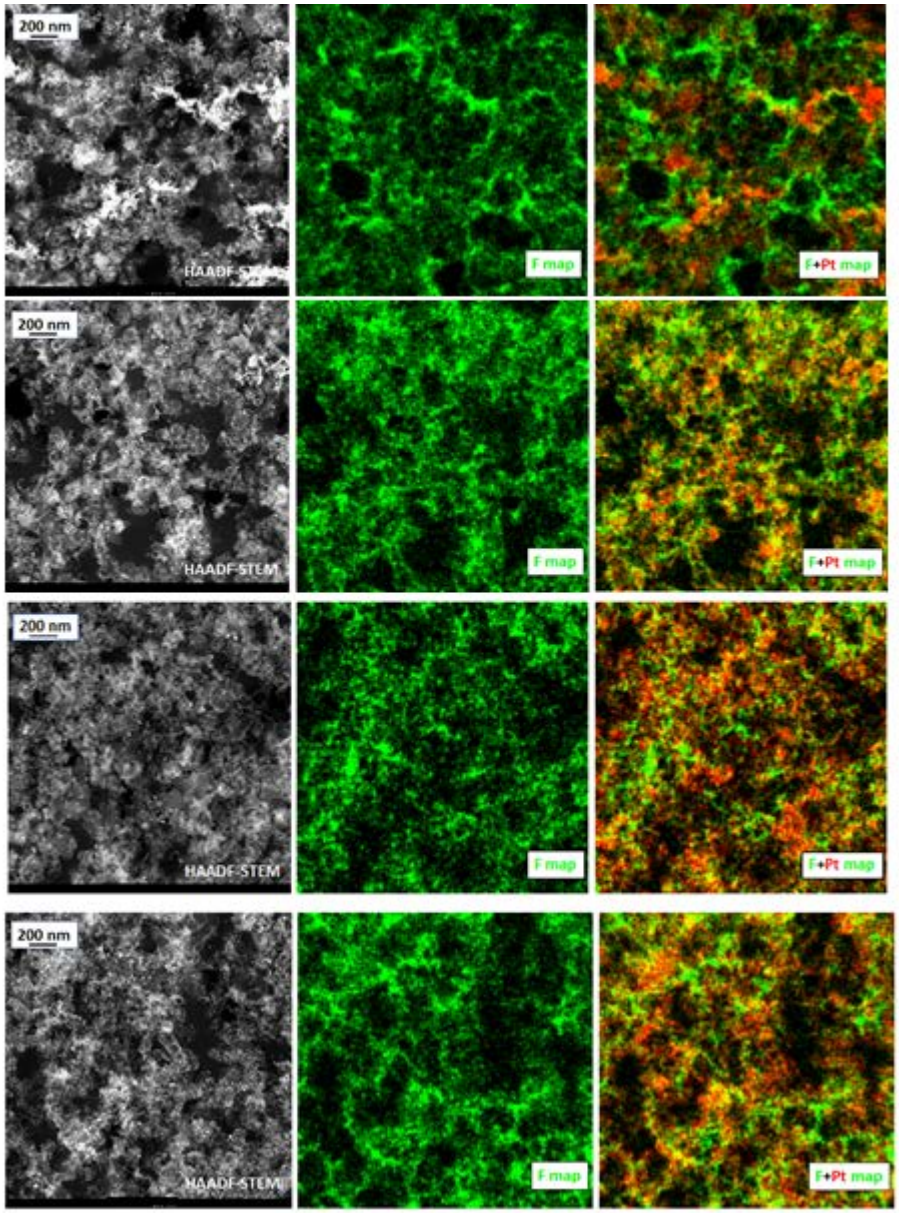
TEM of Fresh Electrodes

IPA

nPA

EG

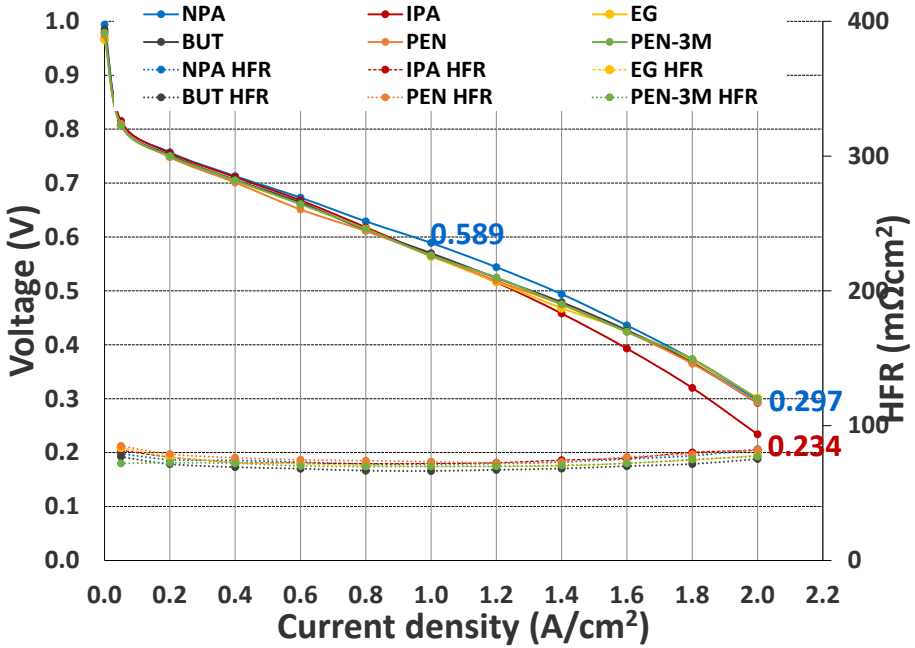
BUT



- Solvent has significant impact on electrode microstructures
  - Better Ionomer and Pt distribution with EG and BUT
  - Smaller secondary pores with EG and BUT

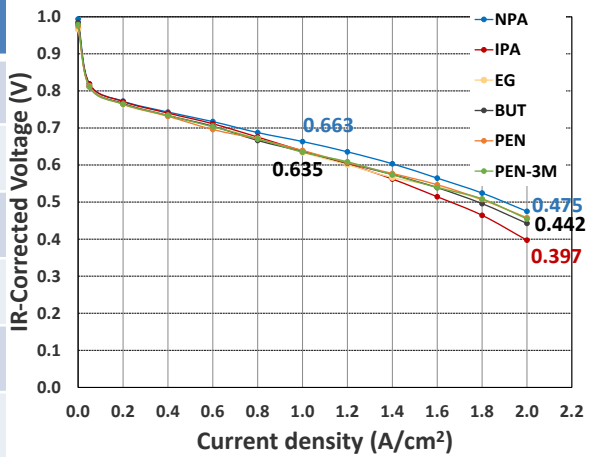
Images taken by Oak Ridge National Laboratory

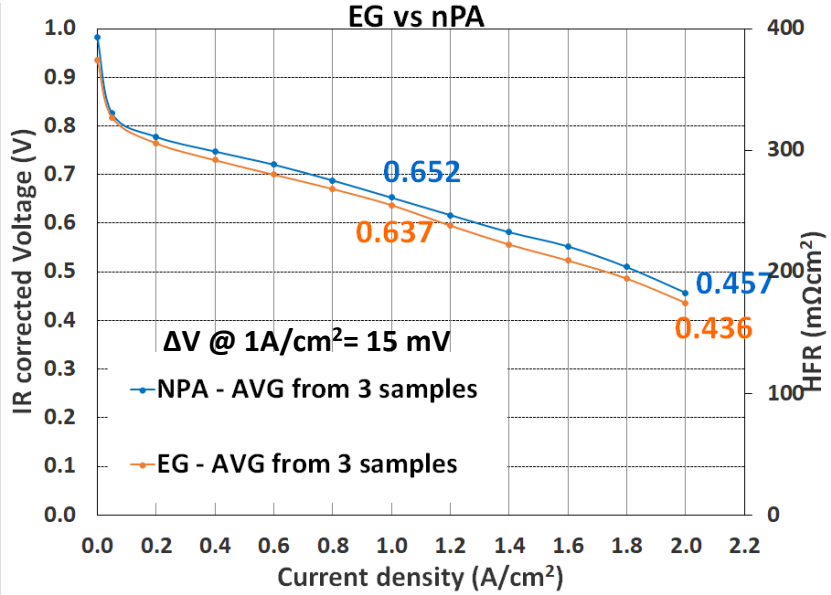
Performance Comparison by Solvents



Sample	Pt Loading (mg/cm2)
IPA	0.19
NPA	0.175
EG	0.21
BUT	0.19
PEN	0.18
PEN-3M	0.17

IR-corrected



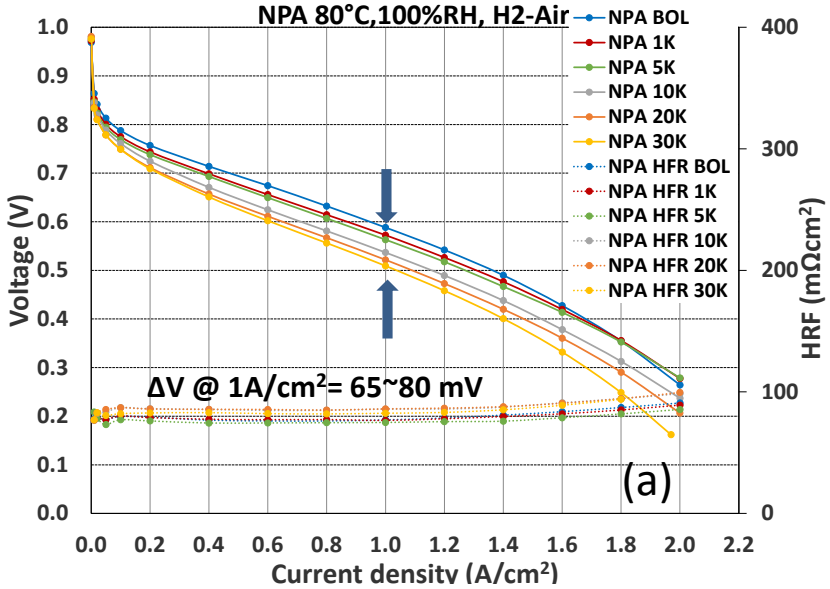


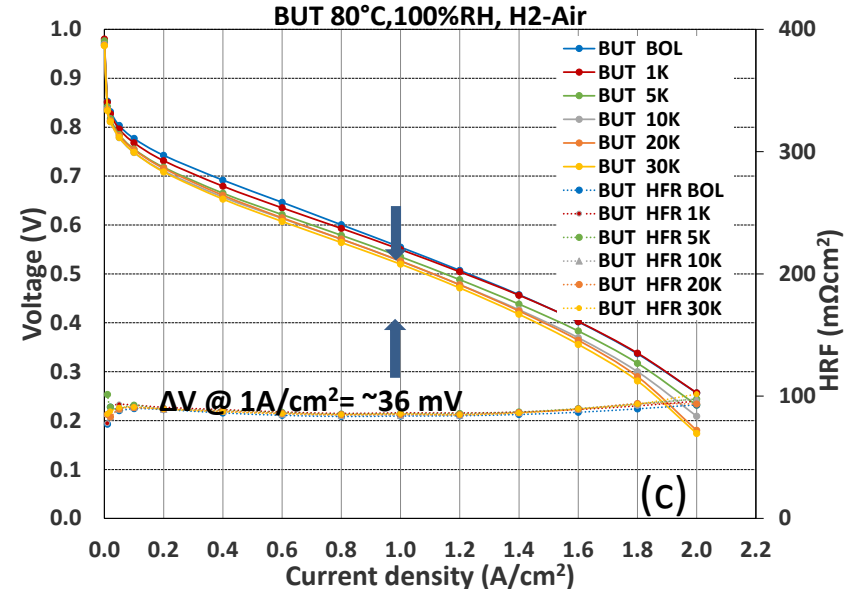
Cell temp: 80 °C, anode: 80 °C, cathode: 75 °C, ambient Pressure

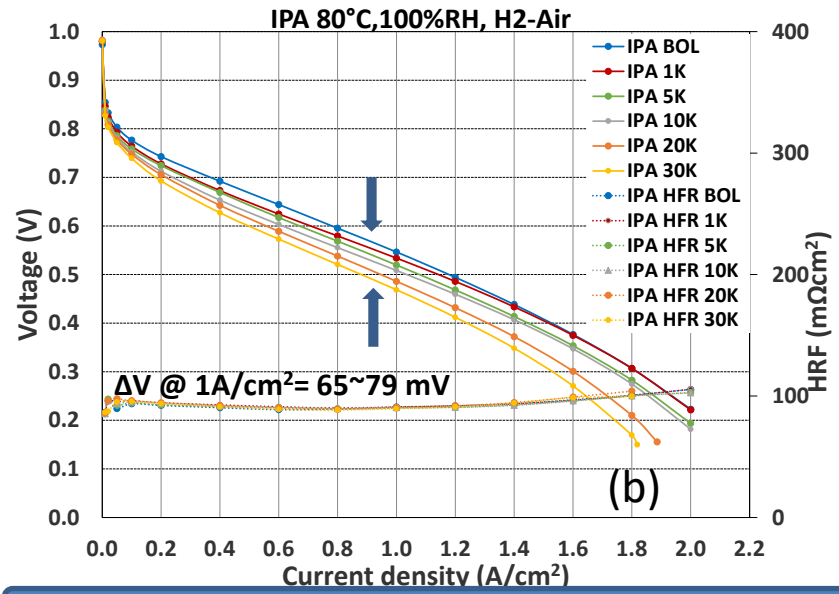
- Performance ranking: nPA > Ethylene glycol ≈ Butanediol ≈ Pentanediol ≈ Pentanediol (3M) > IPA

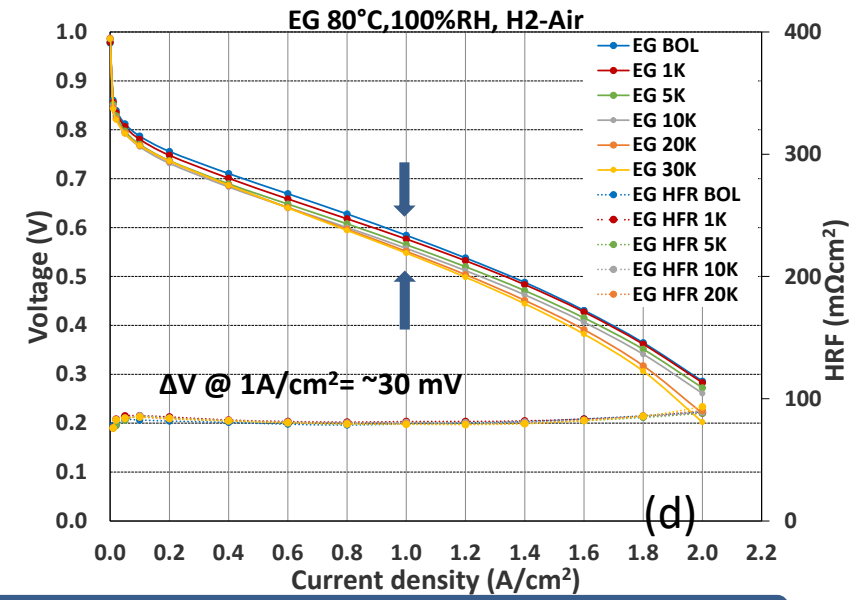
Electrode Durability

Durability test: voltage cycling between 0.6 and 1.0V. @80C, 100%RH, 0.2 SLPM H_2 / 0.075 SLPM N_2



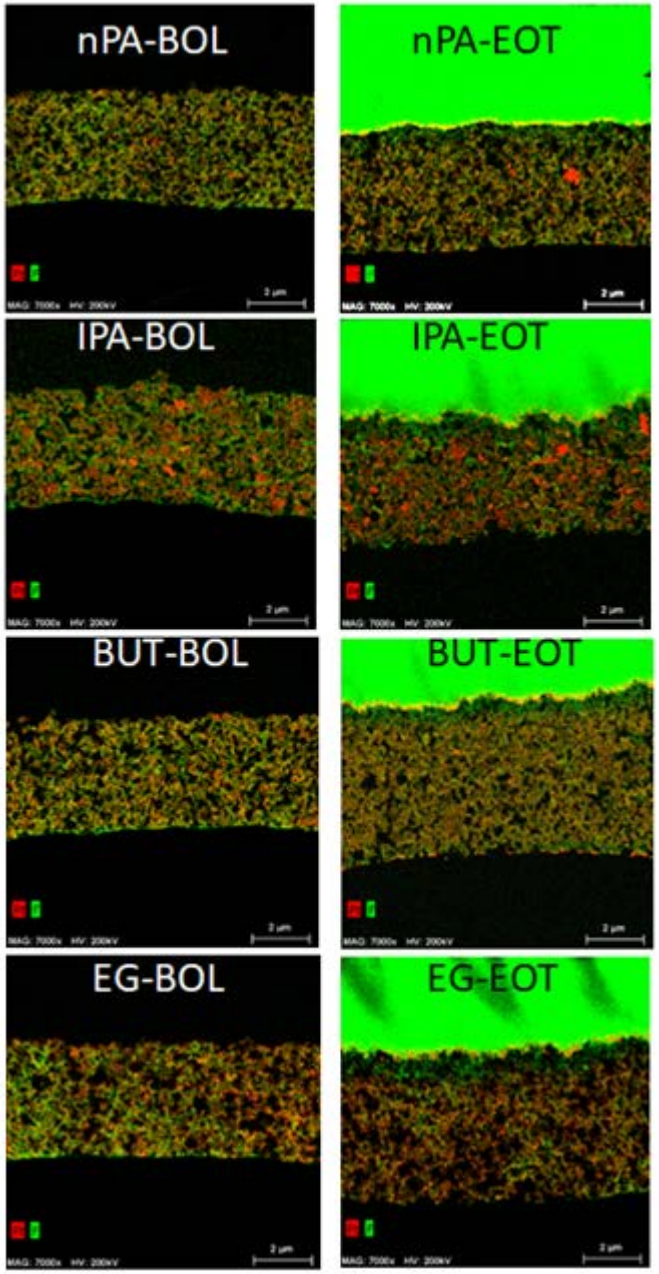






- EG and BUT MEAs demonstrated significantly lower degradation than nPA and IPA baselines.

TEM-EDS maps - quantification:



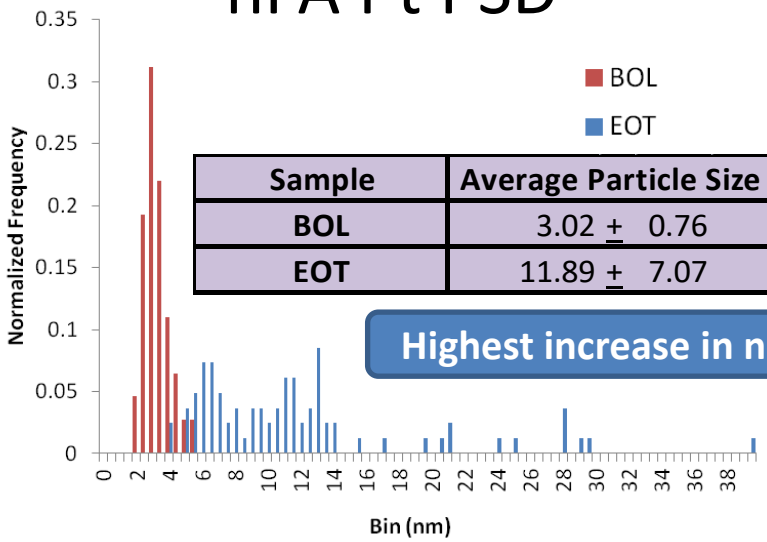
Images taken by UCONN

Sample	Pt loading-XRF, mg/cm²	Pt loading-EDS, mg/cm²	Thickness (TEM), um	Porosity (total), %
nPA BOL decal	0.175	0.18	4.09	68
nPA EOT CCM	0.175	0.12	4.21	71
IPA BOL decal	0.19	0.19	4.38	68
IPA EOT CCM	0.19	0.17	5.13	73
BUT BOL decal	0.19	0.20	4.03	65
BUT EOT CCM	0.19	0.14	5.42	73
EG BOL decal	0.21	0.20	4.08	62
EG EOT CCM	0.21	0.16	5.11	71

- Consistent Pt loading by XRF and EDS
- Uniform ionomer and Pt distribution for nPA and BUT samples
- IPA sample had very non-uniform ionomer and Pt distribution, with a lot of agglomeration of both components
- EG sample had slightly non-uniform ionomer distribution
- All BOL decals had a thin ionomer layer on the cathode-decal interface
- All EOL cathodes show increase in total porosity between 4-14%, with BUT and EG showing the largest change

Pt PSD - quantification

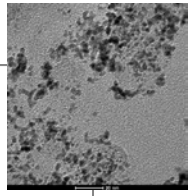
nPA Pt PSD

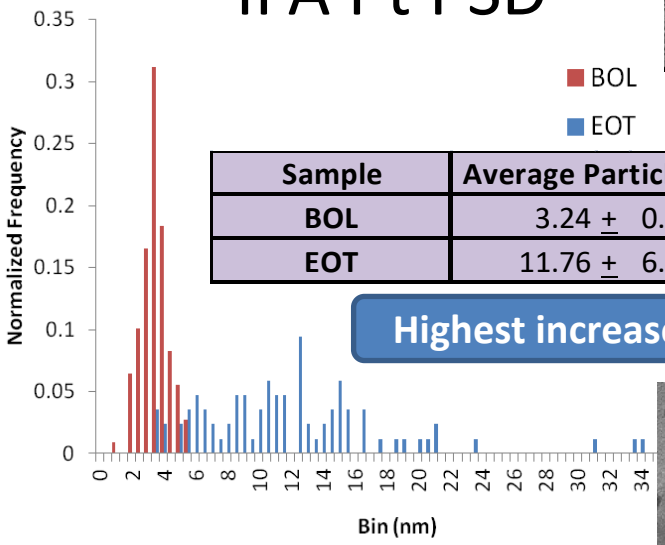


Sample	Average Particle Size (nm)
BOL	3.02 ± 0.76
EOT	11.89 ± 7.07

Highest increase in nPA

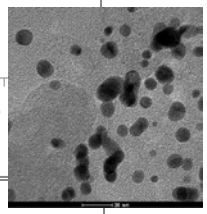
IPA Pt PSD



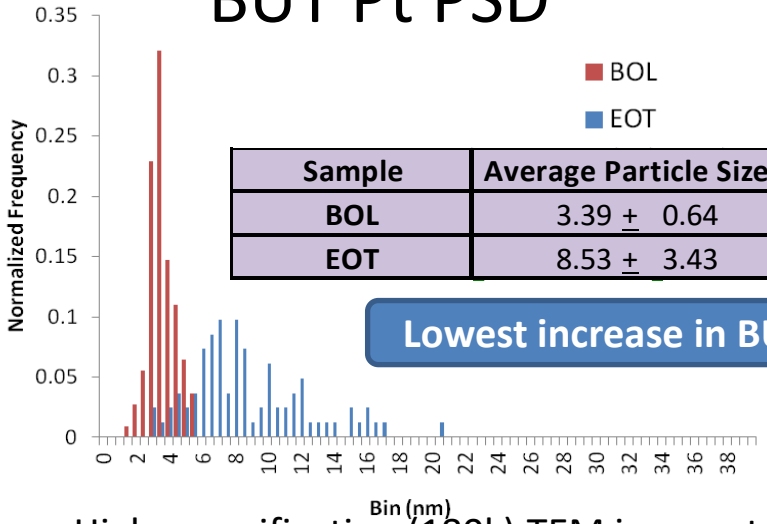


Sample	Average Particle Size (nm)
BOL	3.24 ± 0.85
EOT	11.76 ± 6.43

Highest increase in IPA



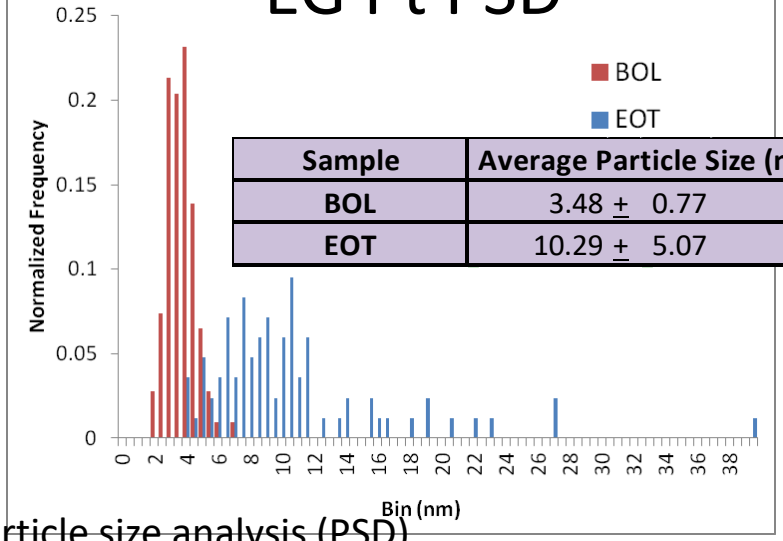
BUT Pt PSD



Sample	Average Particle Size (nm)
BOL	3.39 ± 0.64
EOT	8.53 ± 3.43

Lowest increase in BUT

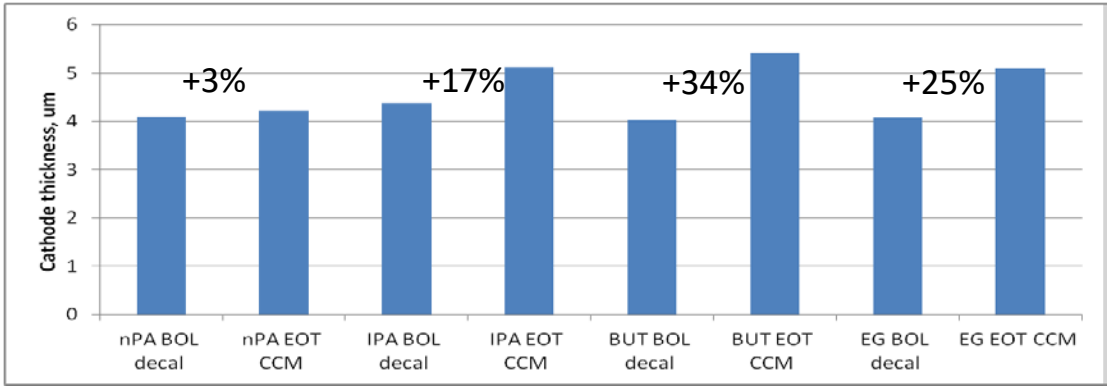
EG Pt PSD

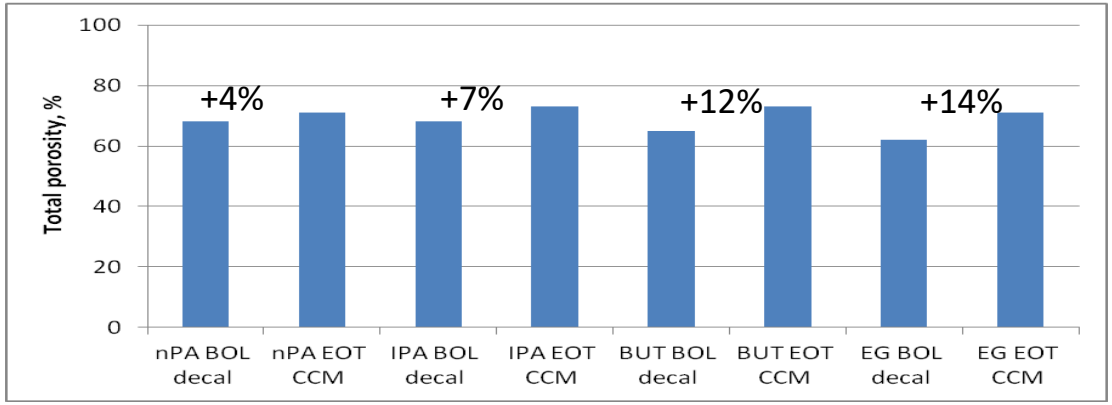


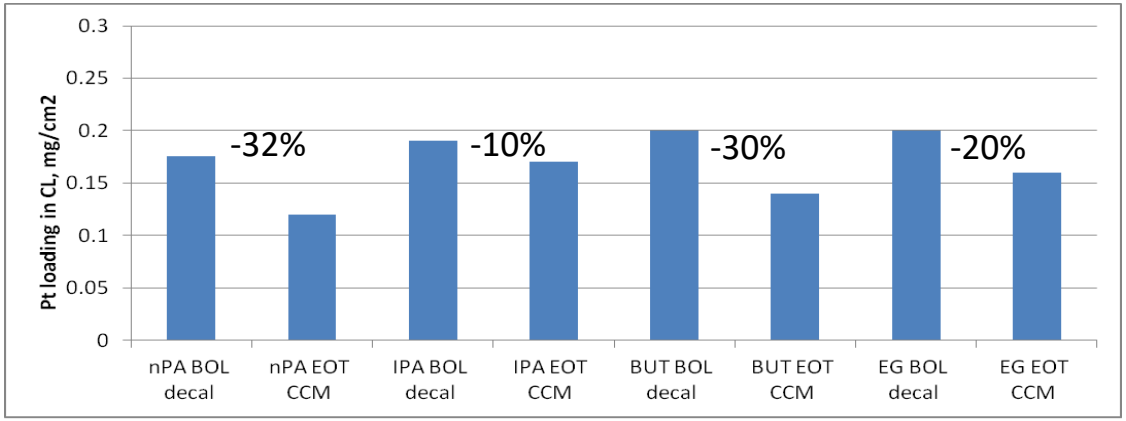
Sample	Average Particle Size (nm)
BOL	3.48 ± 0.77
EOT	10.29 ± 5.07

- High magnification (180k) TEM images taken for Pt particle size analysis (PSD)
- EG and BUT: smaller particle size increase (200 particles were measured for PSD for each sample)

Sample Comparison







- All cathodes experienced increase in thickness after testing (BUT and EG highest; nPA the lowest increase)
- All EOL cathodes show increase in total porosity between 4-14% (BUT and EG highest)
- All EOL samples experienced Pt loss from the cathode (10-32%) to membrane

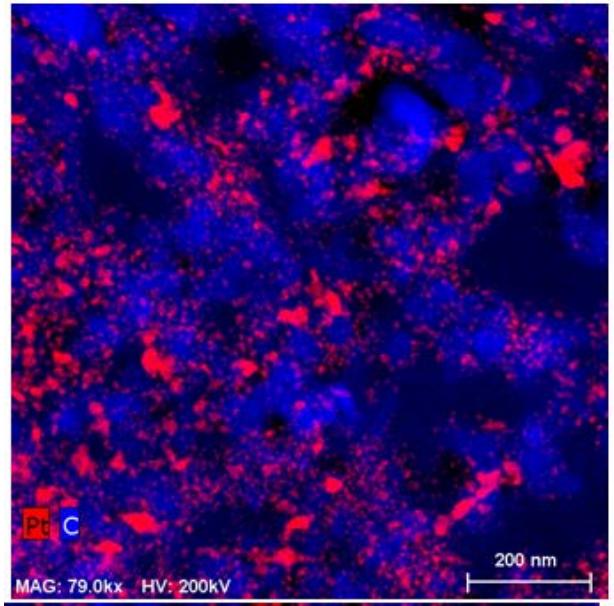
EOT HR TEM-EDS-Pt Distribution

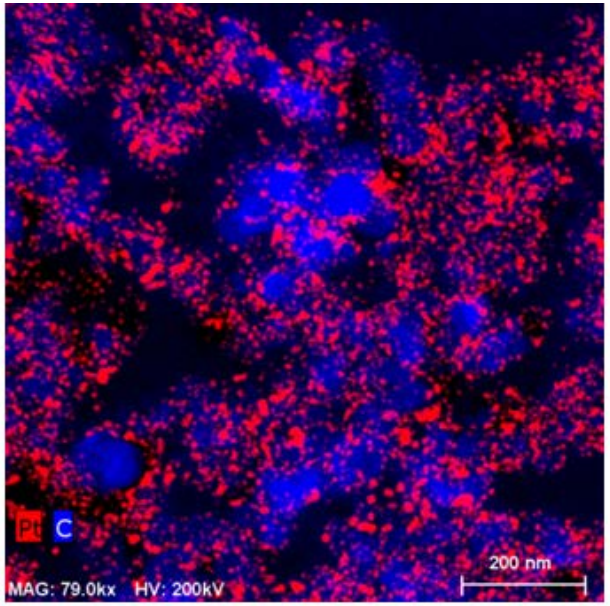
F Fluorine

Pt Platinum

C Carbon

nPA

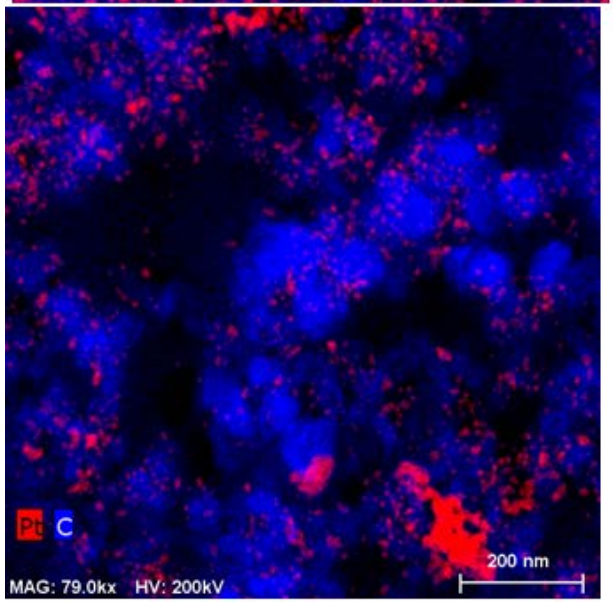


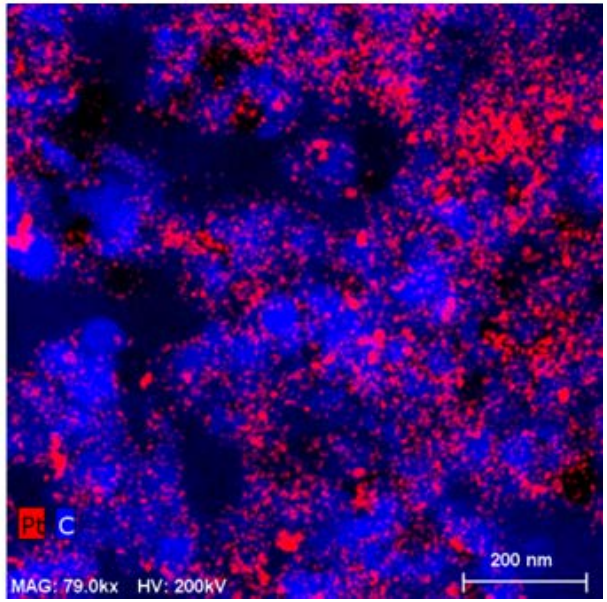


BUT

mild Pt agglomeration

IPA





EG

Images taken by UCONN

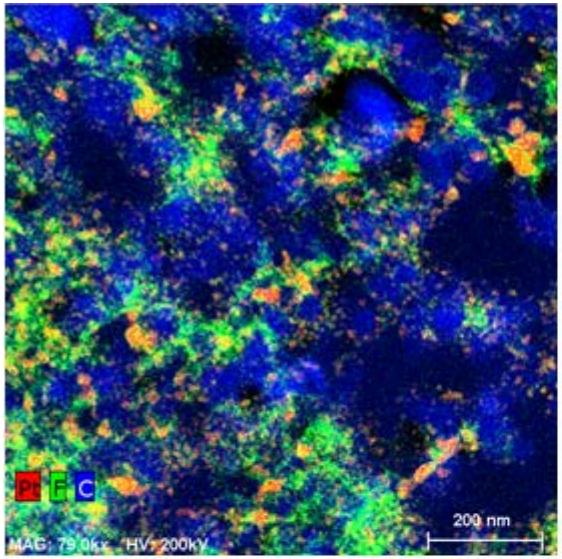
EOT HR TEM-EDS-Ionomer Distribution

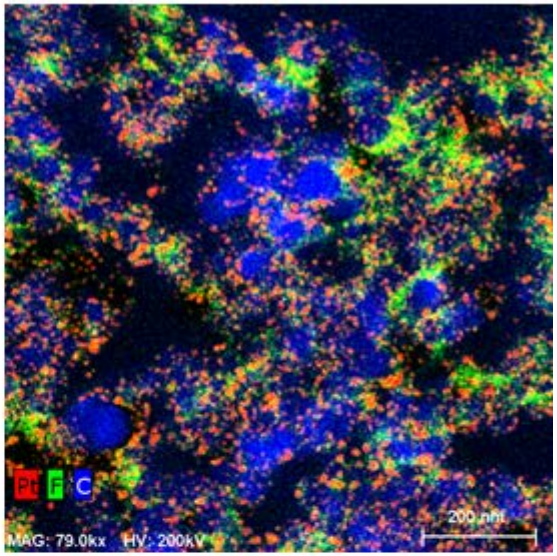
F Fluorine

Pt Platinum

C Carbon

nPA

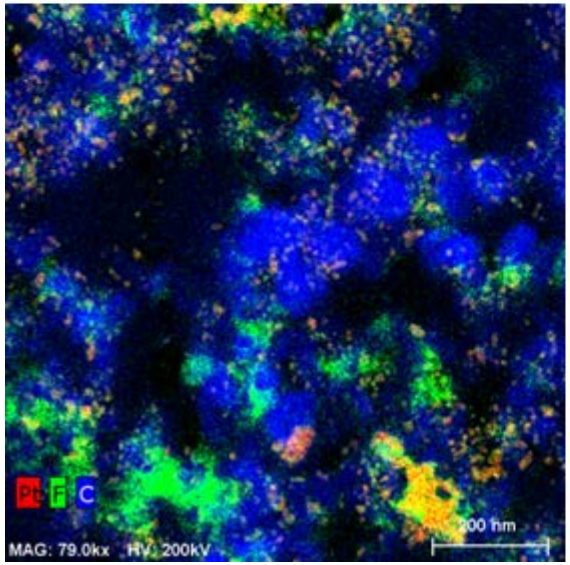


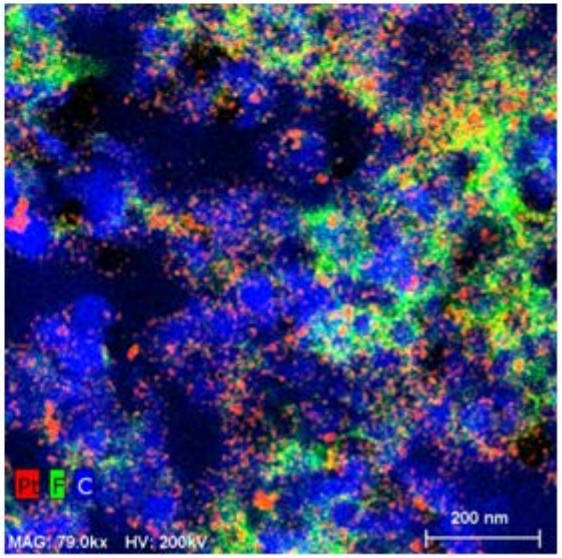


BUT

mild Pt agglomeration

IPA





EG

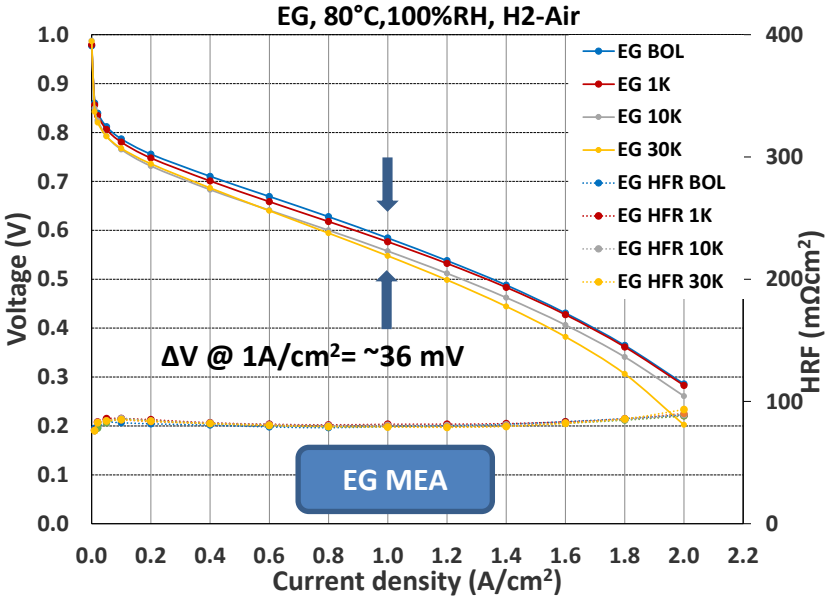
Images taken by UCONN

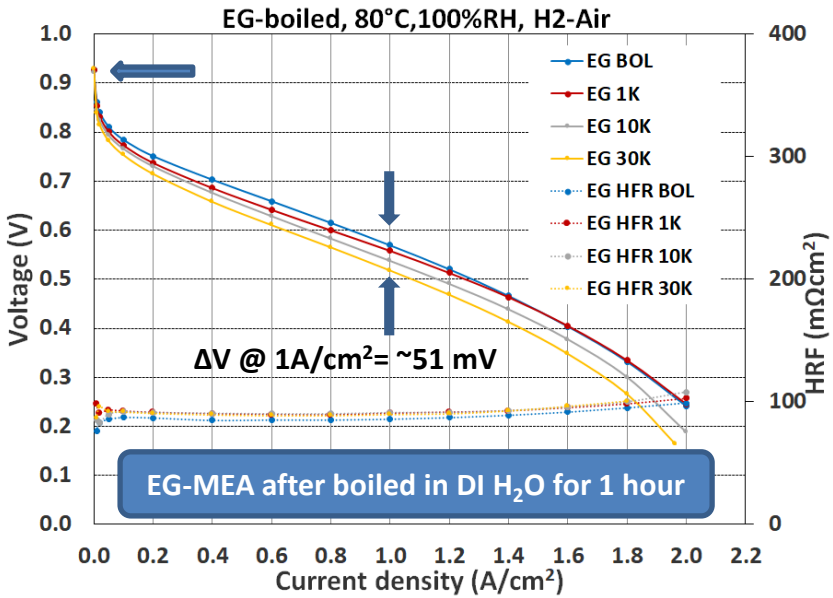
Comparison of MEAs

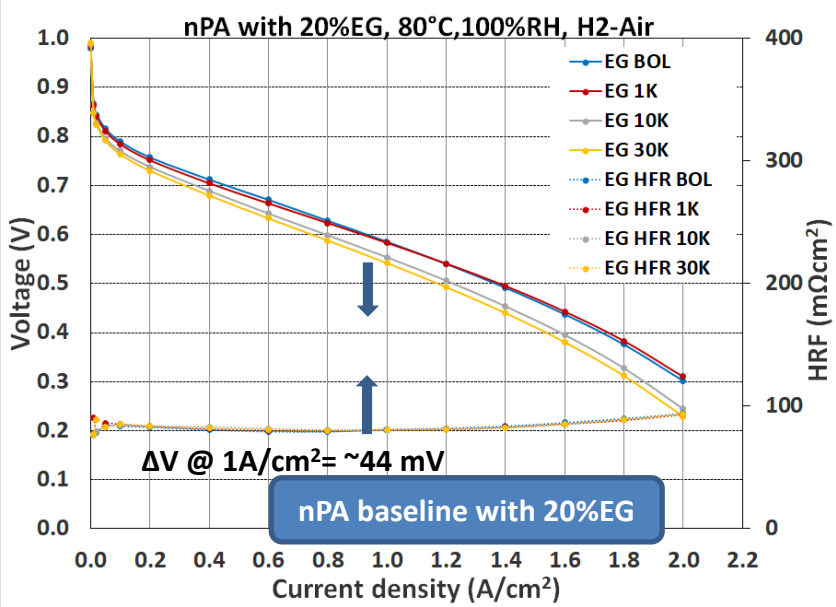
Sample	Pros	Cons
nPA	• Uniform ionomer and Pt distribution • Decent coating quality and ease of drying • Best BOL performance	• Significant Pt agglomeration and particle size growth at EOT • Large degradation upon voltage cycling
IPA	• Common solvent in MEA fabrication • Fast drying	• Large cracks • Non-uniform ionomer and Pt distribution • Significant Pt agglomeration and particle size growth at EOT • Large degradation upon voltage cycling
BUT	• Uniform ionomer and Pt distribution • Decent coating quality when mixing long • Smallest Pt particle size growth • Greatly improved durability upon voltage cycling • Comparable BOL performance	• Dries slowly • May need long time low energy mixing
EG	• Decent coating quality when mixing long • Smaller Pt particle size growth than baseline • Greatly improved durability upon voltage cycling • Comparable BOL performance	• Slightly non-uniform ionomer distribution • May need long time low energy mixing • Dries slowly

EG-based Electrode Durability

Pt loading: ~ 0.21 mg/cm2 for all three cathodes







	ECSA (m^2/g)			Cdl (mF/cm^2)		
cycles	**EG**	**EG-boiled**	**nPA-20%EG**	**EG**	**EG-boiled**	**nPA-20%EG**
0	50	44	58	16	15	22
1000	41	40	53	15	13	18
10000	32	27	26	13	11	17
30000	26	24	24	12	10	15

- After boiling, EG-MEA exhibits slightly lower OCV, and higher voltage degradation.
- With nPA baseline, adding 20%EG helps to lower the degradation to be similar as EG sample

Summary

- Ionomer dispersions in a variety of solvents have been investigated; solvent affects ionomer morphology and re-conformation
- Ionomer dispersions impact the electrode structures in the BOL and EOT, including ionomer distribution, catalyst distribution, porosity and thickness etc.
- Ionomer dispersions influence fuel cell electrode performance and durability. Samples with high boiling point solvent-dispersed Nafion ionomer demonstrate greatly improved durability and comparable performance as baseline
- The good durability in EG and BUT samples may be related to the trace amount of high boiling point solvents in the electrode, which help to protect the Pt from growing fast during voltage cycling;
- Electrode restructing upon voltage cycling (thicker and more porous electrode @EOT) may provide more resiliency to mitigate electrode deformation and transport loss.

Future Work

- Perform TEM of fresh MEAs compared to decals and decayed MEAs
- Further test the non-aqueous ionomer based electrode under more realistic accelerated stress testing (AST) conditions
- Explore state-of-the-art components integrated with non-aqueous ionomer to make low Pt and high power MEAs (Phase IIB)
  - High-performance Pt and its alloys
  - Thin membranes (DSM)
- Electrode scale-up (Phase IIB)

Acknowledgments

- Financial support from DOE SBIR/STTR Program
- Program Manager
  - Ms. Donna Ho
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- Dr. Karren More at ORNL (collaborator)
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- Giner Personnel