2019 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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Project#
FC117

April 29, 2019

Project Overview

Timeline

- Project Start Date: 8/28/2018
  Actually started in 12/2018
- Project End Date: 8/27/2020

Budget

- Total Project Value
  - Phase IIB: $1 Million
  - Spent: $150 K (by 2/28/19)

Barriers Addressed

- PEM fuel cell and electrolyzer performance and durability

Collaborators

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

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

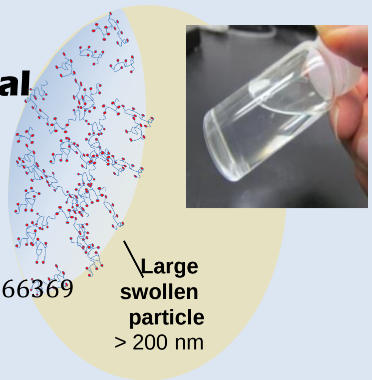
Project Nature

- DOE Technology Transfer Opportunity Project (SBIR-TTO)

Relevance: Ionomer Dispersion Technology

Conventional Ionomer Dispersion

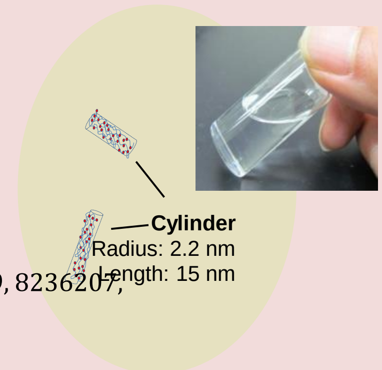
Dupont
European Patent 0066369



- 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

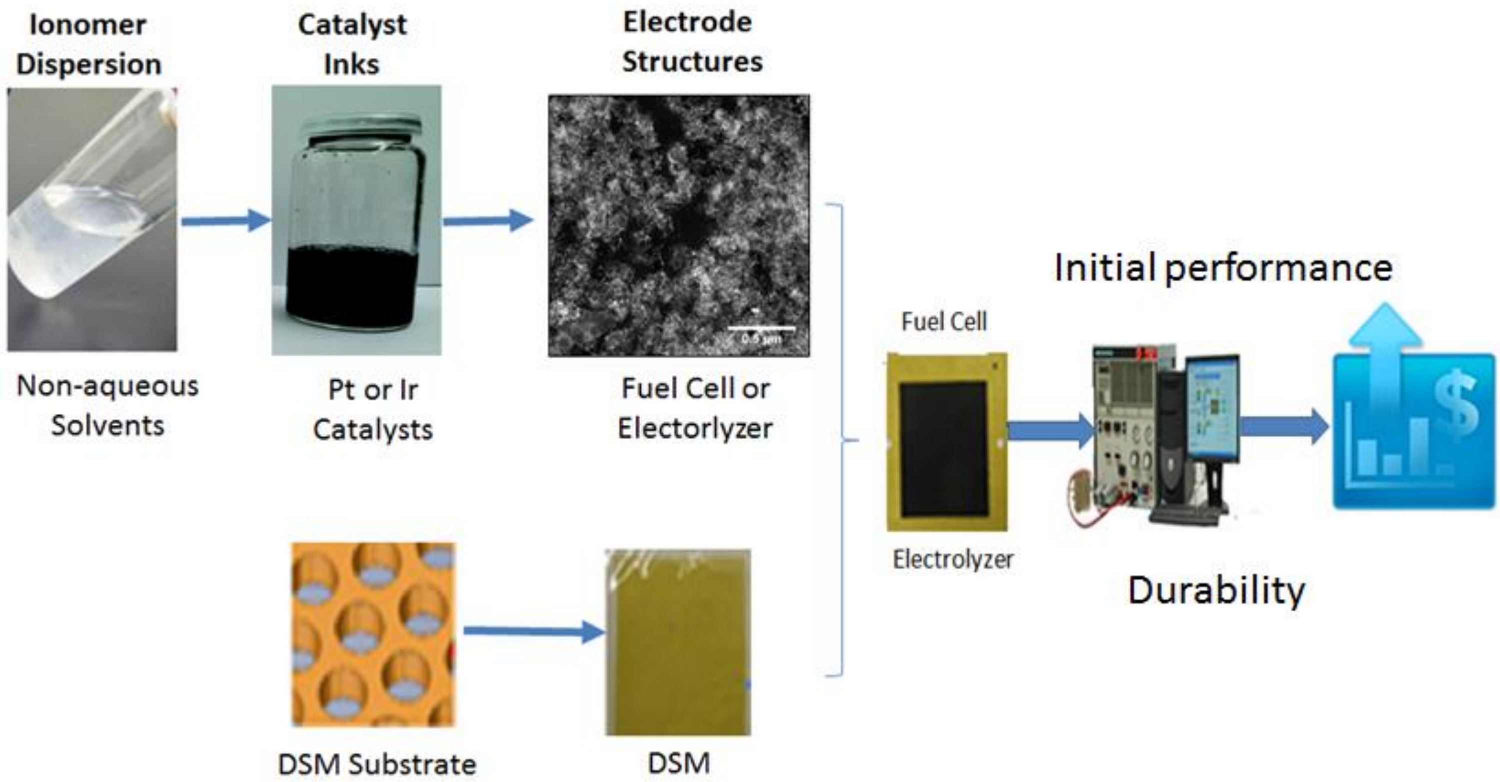
LANL Ionomer Dispersion

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 orders of magnitude difference!!)
- Produces **stable** electrode: cell voltage loss after durability test: 0 mV

Technical Approaches



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 $50\text{-}100cm^2$ full MEAs

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

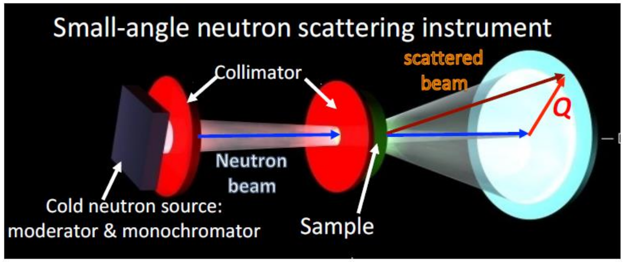
Profitability
- Fuel Cell MEAs for external customers
- Electrolyzer MEAs for Giner MW stacks

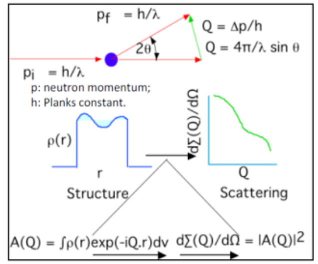
Performance Tasks

Task	% Time	Year 1 (Quarters)				Year 2 (Quarters)			
		1	2	3	4	5	6	7	8
1. Identify scalable methods for ink preparations	25								
2. Develop large-scale MEA production	30								
3. Construct and test 20-kW stack	35								
4. Perform techno-economic analysis	5								
Report	5		X		X		X		X

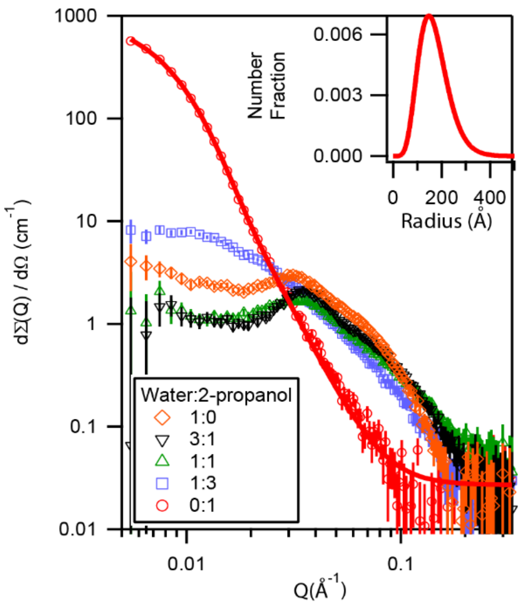
Objective: Develop high value roll-to-roll processes for membrane casting and electrode coating using non-aqueous ionomer and advanced catalysts for PEM fuel cells and electrolyzers.

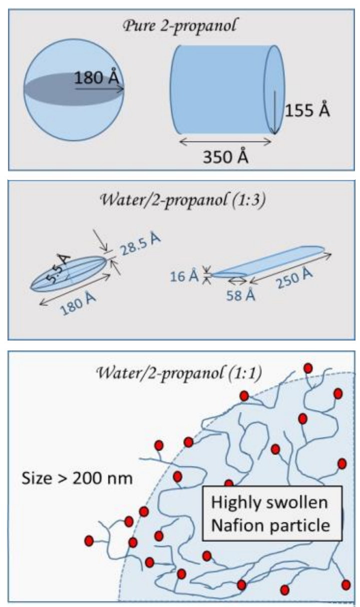
Accomplishment: Ionomer Particle morphology

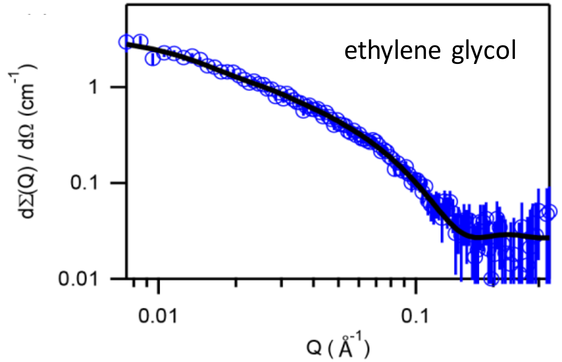




Nafion dispersion morphology was examined by small angle neutron scattering (SANS). Analysis of the SANS data is done by model calculations using the Fourier transfer relation between the structure, ρ (r) and the observed scatter, d ∑(Q)/dΩ.





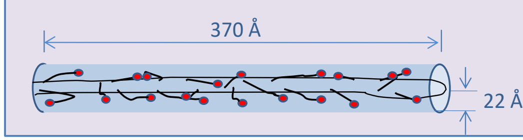


Ethylene glycol: **Cylindrical particles**

cylinder length: 370 Å and radius: 22 Å,

SLD: 2.5 × 10^{-6} $Å^{-2}$,

Solvent volume fraction: ~0.42.



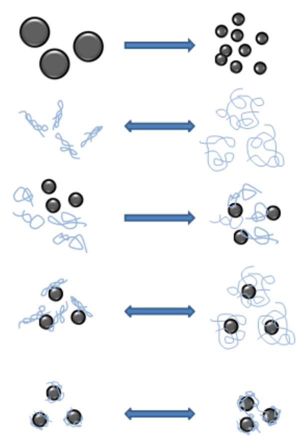
- SANS experiments indicates that the dispersion particle size of Nafion in water/2-propanol increases with higher water composition. At high water content, mimicking to the last stage of evaporation, the particle size is > 200 nm with fuzzy particles.
- Nafion particle in ethylene glycol is elongated cylinder shape at 2.5 wt.%.
- Further investigation using different solvent system and Aquivion ionomer is ongoing.

Accomplishment: Characterization of Catalyst Inks

- Catalysts
  - Pt/Vulcan (Tanaka 46.7%)
  - IrO_2 (Johnson Matthey)

- Ionomer Dispersions

Sample Abbreviation	Description
IPA	Nafion in 2-propanol/water
NPA	Nafion in 1-propanol/water
EG	Nafion in ethylene glycol
BUT	Nafion in butanediol
PEN	Nafion in pentanediol



Breakdown of core catalyst agglomeration

Ionomer re-conformation in various solvent blend

Ionomer adsorption onto catalyst particle surface

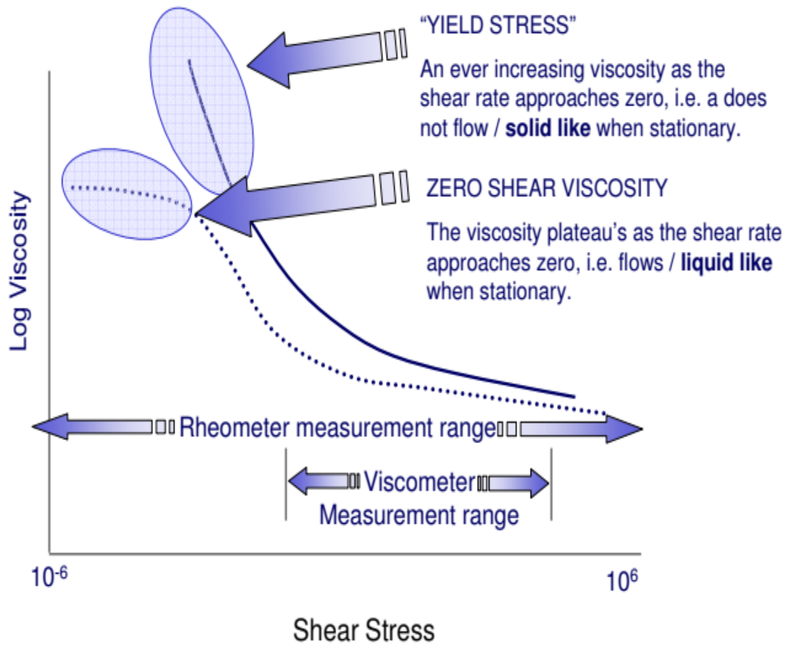
Ionomer re-conformation on particle surface

Formation and breaking-up of flocculation

- Ink Processing Conditions
  - Jar milling
  - 1, 3 and 6 days

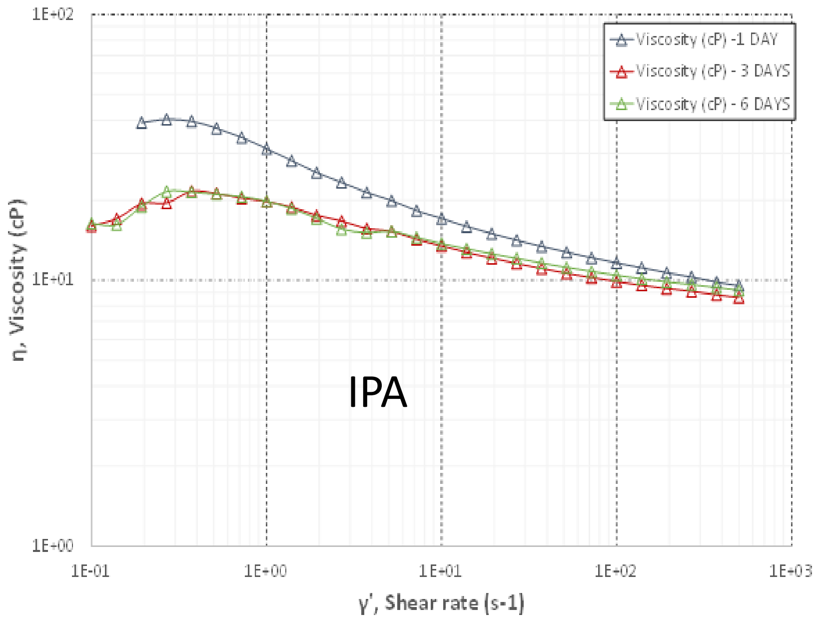
Newly Installed Rheometer for Measuring Ink Rheology

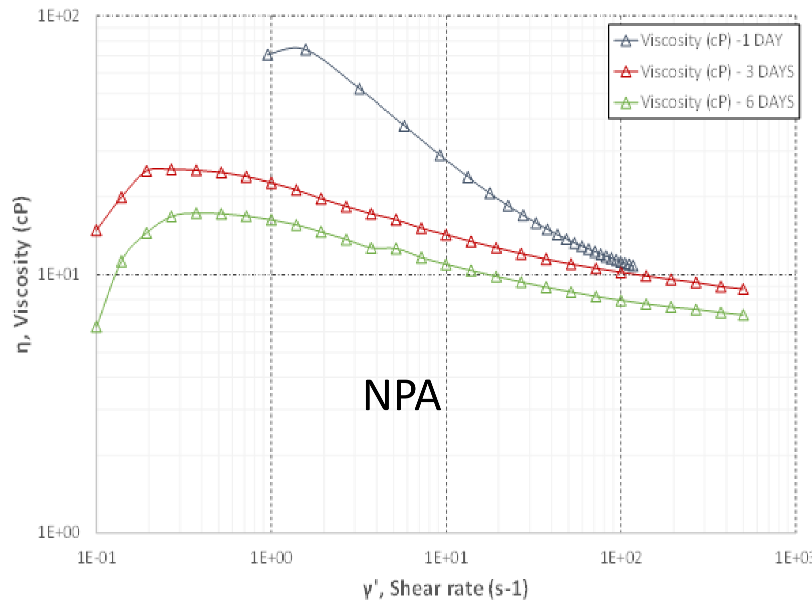
Malvern Panalytical Kinexus Pro$^+$ Rheometer

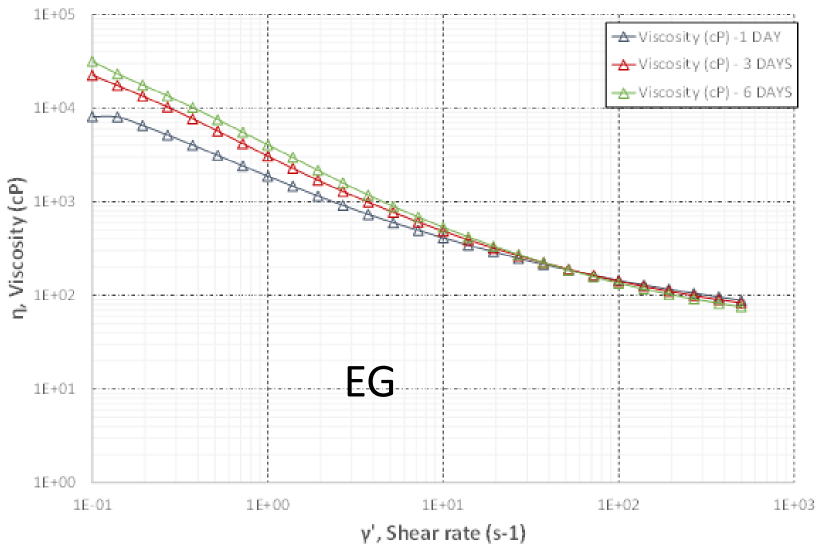


Rheological operations – stress control, shear rate control and direct strain controlled oscillation at demand strain amplitude for accurate control of sample strain history.

Viscosity vs. Shear Rate



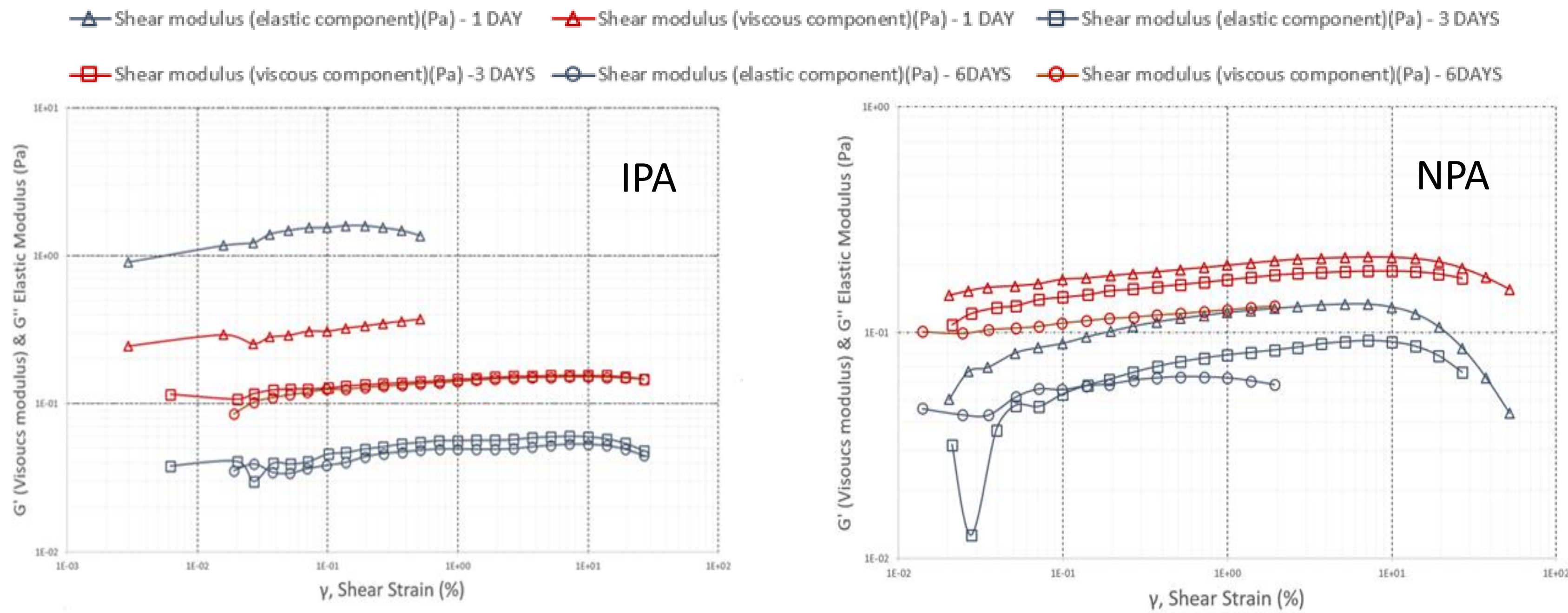


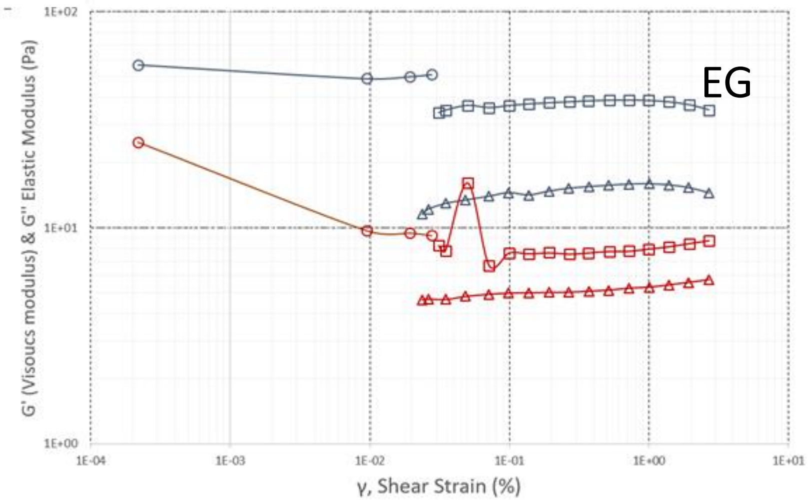


Ink Info: Pt/C catalyst; I/C=0.6

- ❑ EG based Inks had much higher viscosity than IPA and NPA based inks;
- ❑ For IPA and NPA, ink viscosity decreased with time
- ❑ For EG, ink viscosity increased with time

Elastic and Viscous Modulus



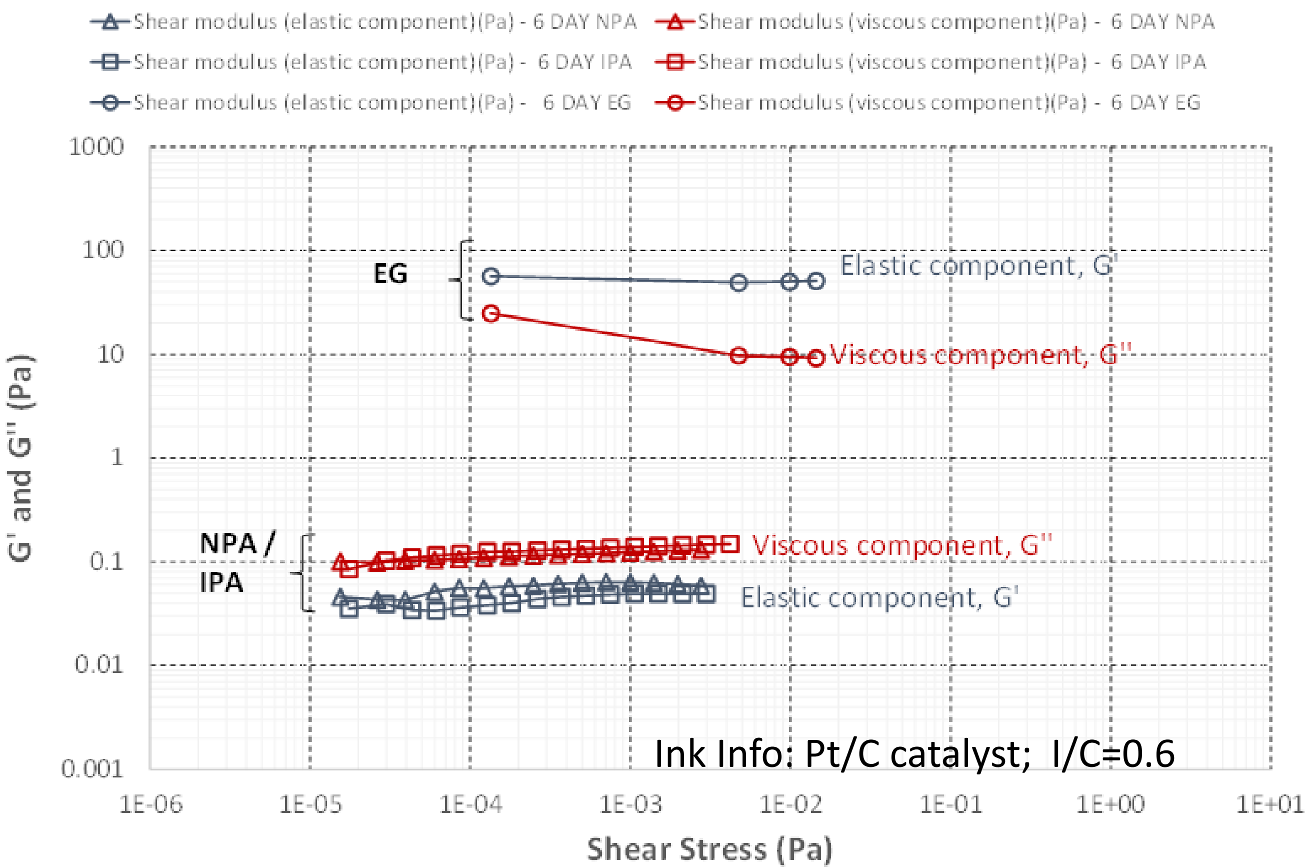


Ink Info: Pt/C catalyst; I/C=0.6

- ❑ EG based Inks had much higher elastic and viscous modulus than IPA and NPA based inks;
- ❑ For IPA and NPA, modulus first decreased and then barely changed after 3 days;
- ❑ For EG, modulus kept increasing with processing time

Elastic component varies likely due to ionomer morphology changes from solvent to solvent

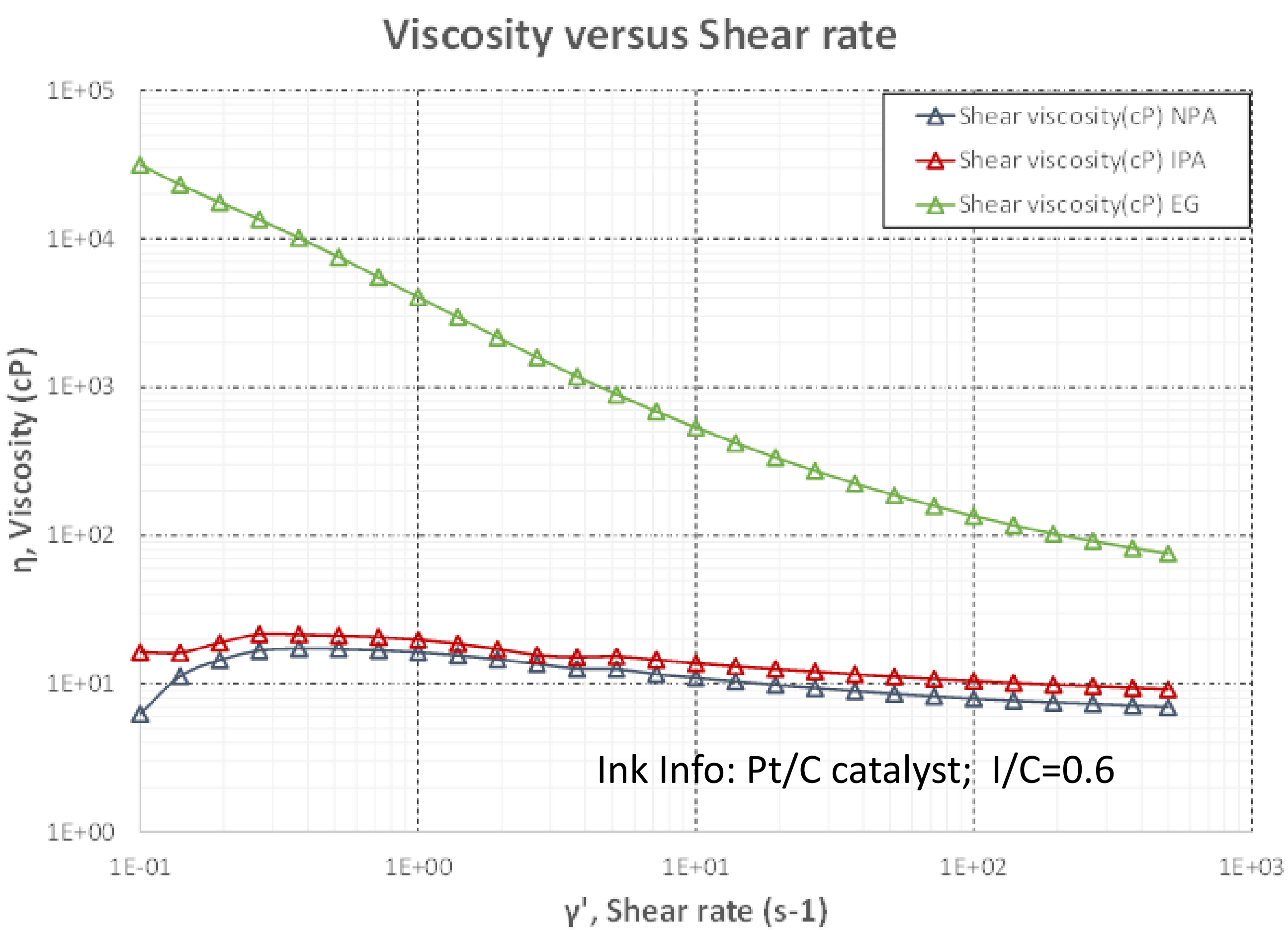
Ink Comparison after 6-day Jar Milling



- ❑ NPA and IPA baseline inks show viscous dominant behavior (G'' > G').
- ❑ EG reveals elastic dominant behavior under Stress.

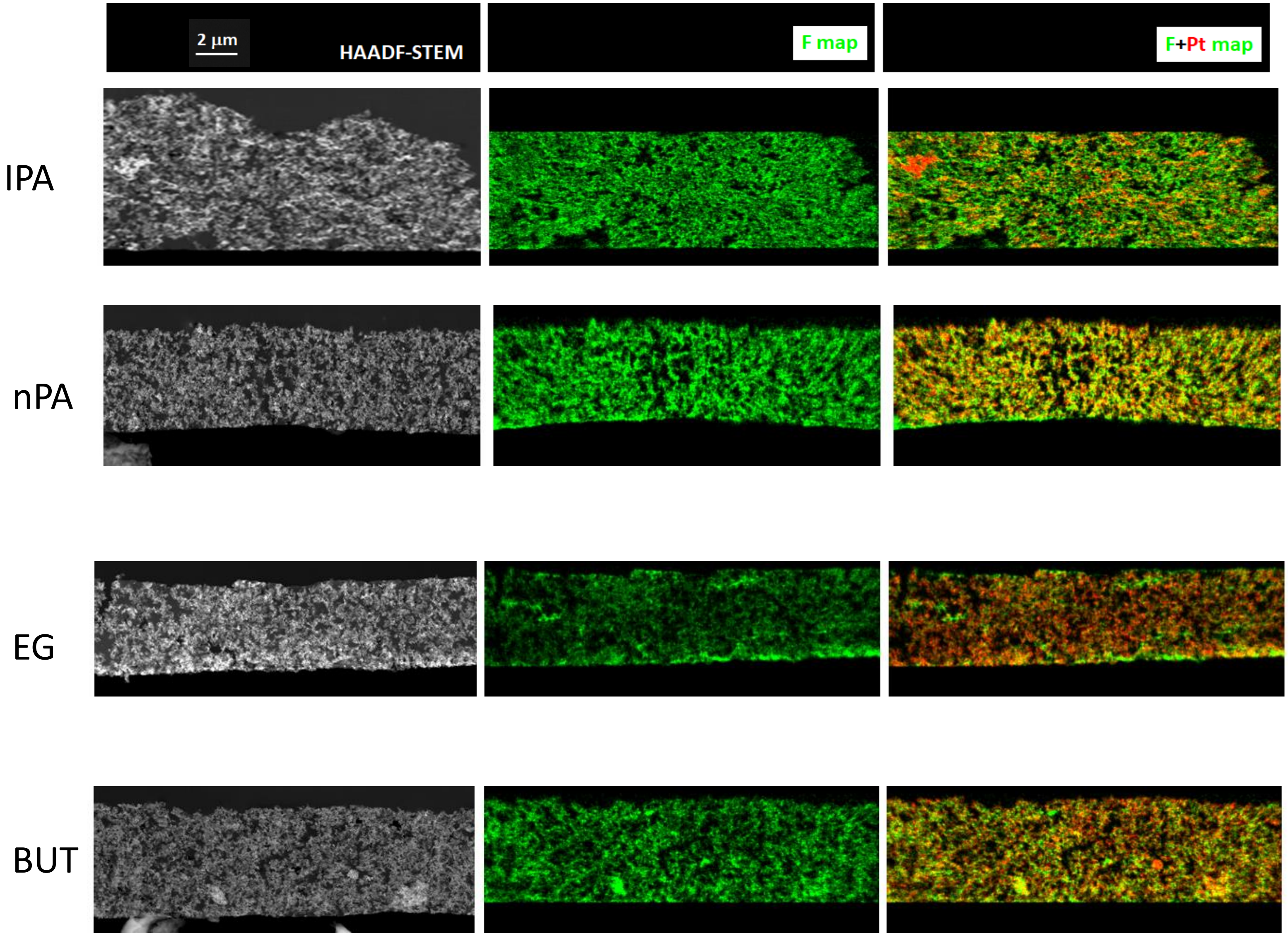
Higher elastic component than viscous component indicates is more stable ink suspension

Ink Viscosity after 6-day Jar Milling



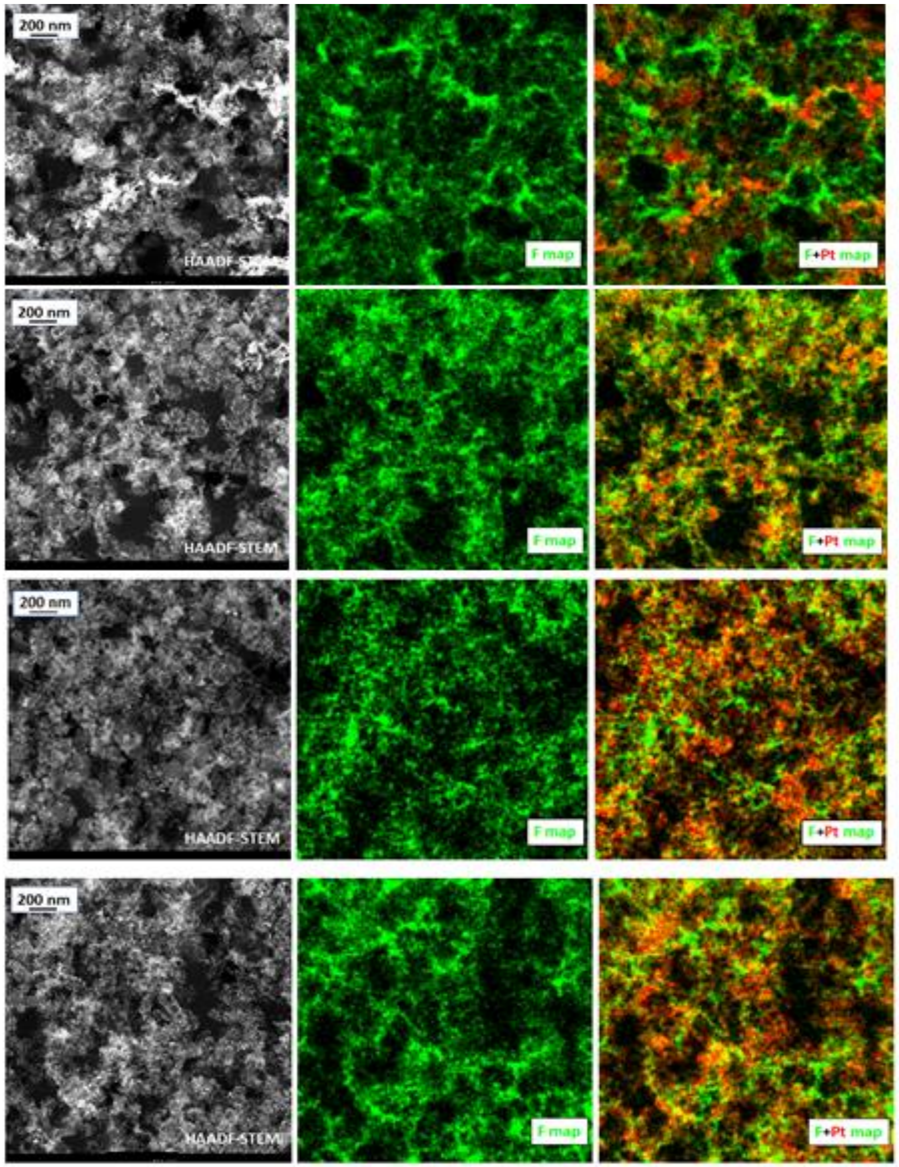
- ❑ NPA and IPA inks showed close and plateauing viscosity
- ❑ EG has a higher viscosity and its viscosity continually increases with decreasing shear rate, without plateauing.

Accomplishment: Fresh CCM Characterization



Images taken by Oak Ridge National Laboratory

Close-up of Fresh CCM Characterization

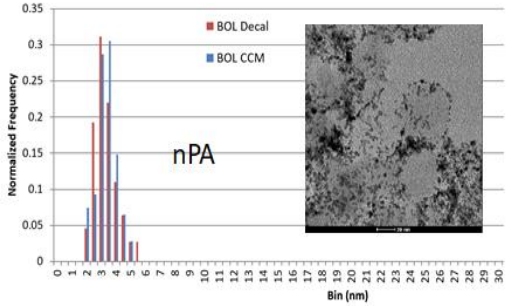


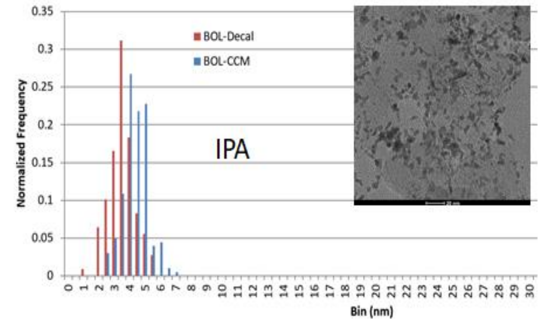
❑ Solvent has significant impact on electrode microstructures

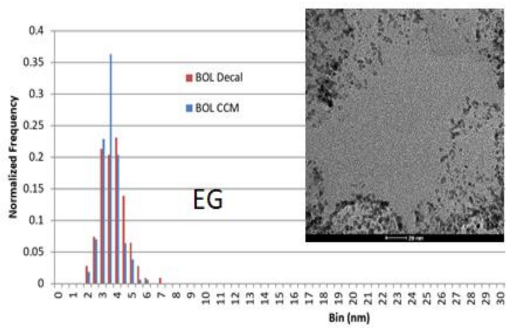
- Better Ionomer and Pt distribution with EG and BUT
- Smaller secondary pores with EG and BUT
- Likely associated with higher elastic and viscous components of catalyst inks

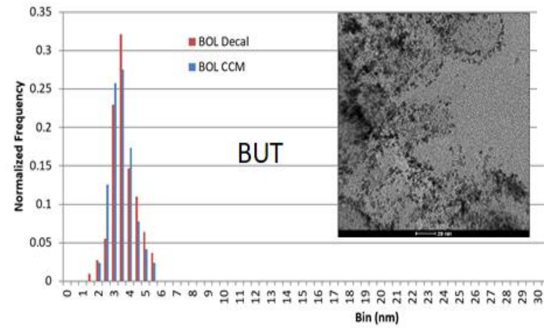
Images taken by Oak Ridge National Laboratory

Particle Size Distribution









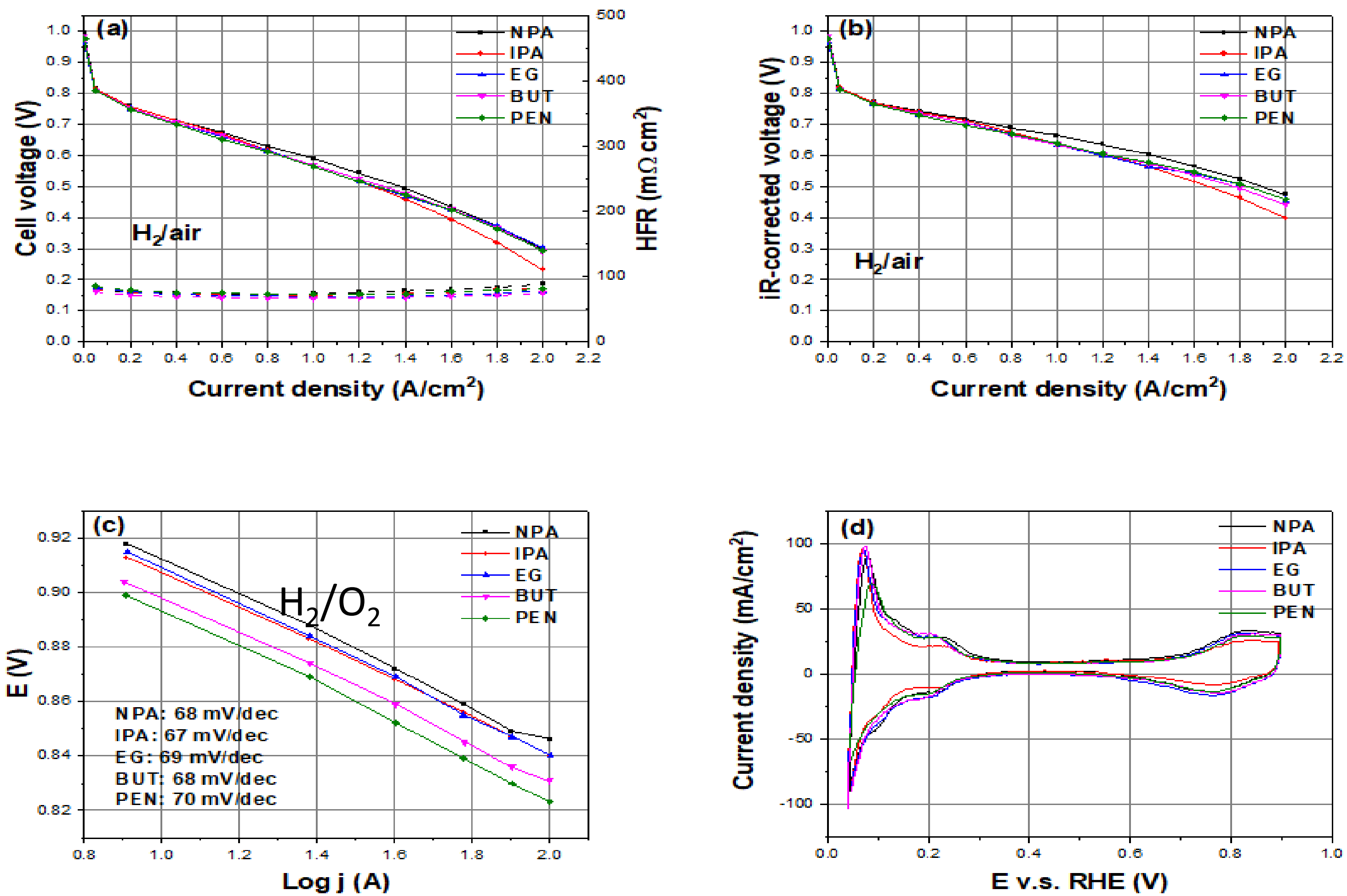
	ECSA (m^2/g)	Average Pt Particle Size (nm)
NPA	52.5	3.02 ± 0.76
IPA	40.0	3.24 ± 0.85
EG	49.8	3.48 ± 0.77
BUT	48.2	3.39 ± 0.64

Ink info:
- Pt/C catalyst;
- 6-day jar-milling

- ❑ Slightly larger particle size for EG and BUT based electrodes
- ❑ NPA and EG demonstrate higher ECSA

Performance Comparison by Solvents

Cathode: Pt/C, 0.2 mg/cm^2, 80 °C, 100% RH, ambient pressure



- ❑ Performance ranking: nPA > Ethylene glycol ≈ Butanediol ≈ Pentanediol > IPA

Accomplishment: CCM Durability after 30,000 Cycles

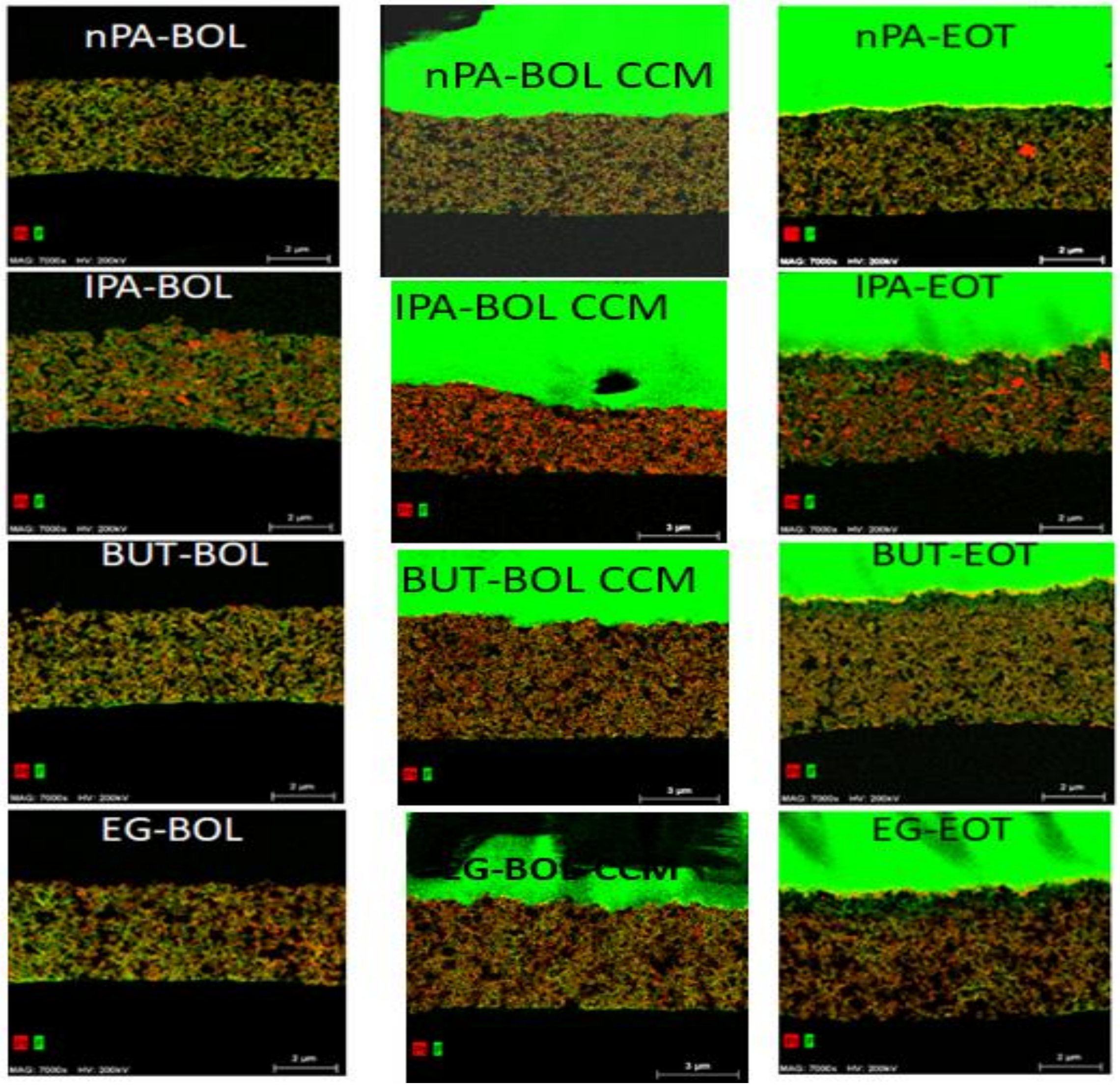
Fresh Decal | Fresh CCM | Tested CCM

IPA

NPA

EG

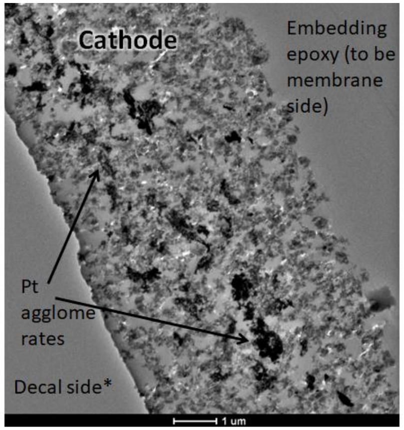
BUT



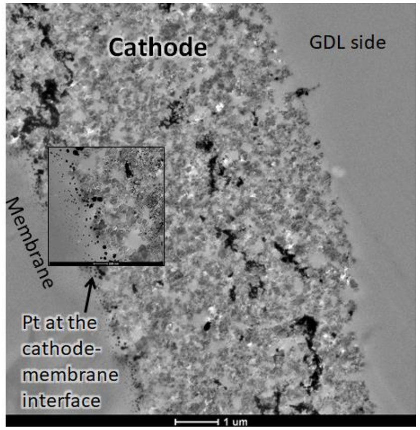
Images taken by University of Connecticut

Observations of Pt Agglomeration and Migration

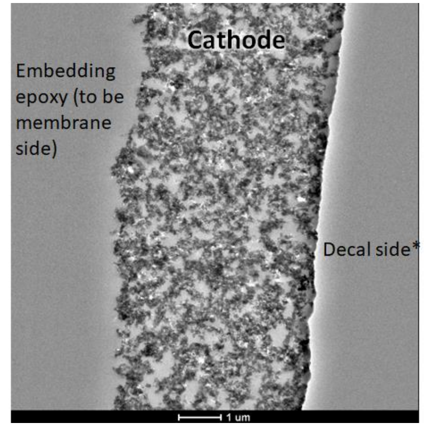
IPA-BOL



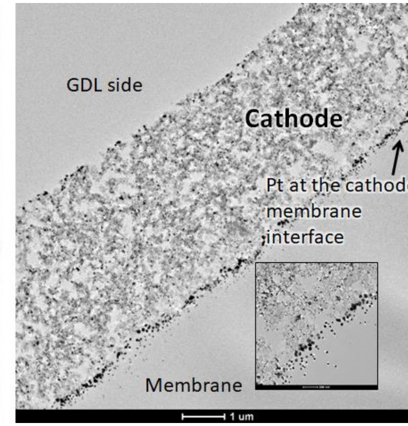
IPA-EOT



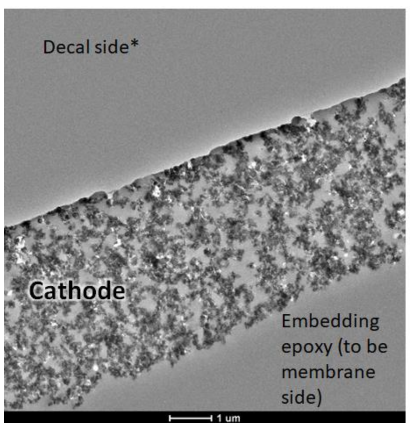
NPA-BOL



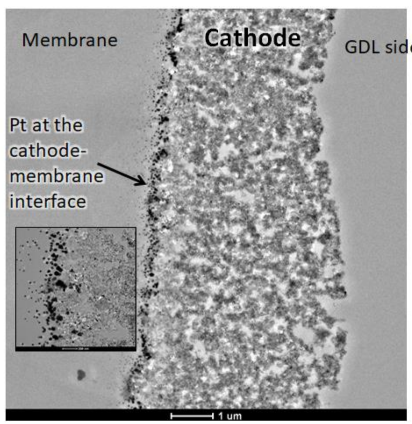
NPA-EOT



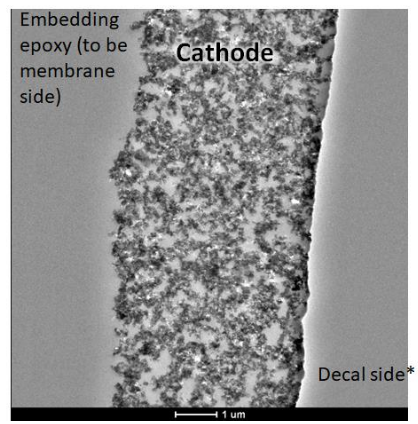
EG-BOL



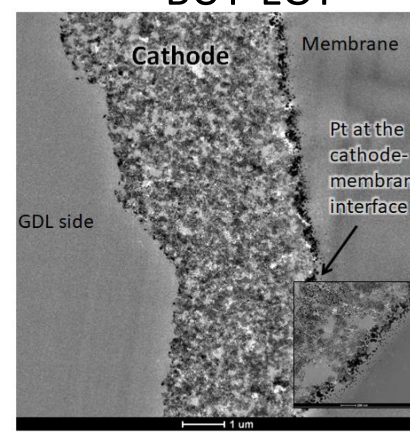
EG-EOT



BUT-BOL



BUT-EOT



Images taken by University of Connecticut

- ❑ IPA based CCM demonstrates severe Pt agglomeration
- ❑ All four CCMs show Pt migration and deposition at membrane/cathode interface

Catalyst Particle Size Charge

IPA

Sample	Average Particle Size (nm)
BOL-Decal	3.26 ± 0.85
BOL-CCM	4.13 ± 0.80
EOT	11.76 ± 6.43

nPA

Sample	Average Particle Size (nm)
BOL Decal	3.02 ± 0.76
BOL CCM	3.06 ± 0.66
EOT	11.89 ± 7.07

EG

Sample	Average Particle Size (nm)
BOL Decal	3.48 ± 0.77
BOL CCM	3.29 ± 0.59
EOT	10.29 ± 5.07

BUT

Sample	Average Particle Size (nm)
BOL Decal	3.39 ± 0.64
BOL CCM	3.22 ± 0.72
EOT	8.53 ± 3.43

- ❑ Catalyst particle size barely changes from decal to CCM
- ❑ Catalyst particle size of EG and BUT based CCMs increases least

Changes of Pt Loading, Thickness and Porosity

Sample	Pt loading-XRF, mg/cm^2	Pt loading-EDS, mg/cm^2	Thickness (TEM), um	Porosity (total), %
IPA BOL decal	0.19	0.19	4.38	68
IPA BOL CCM	0.19	0.19	5.06	70
IPA EOT CCM	0.19	0.17	5.13	73
nPA BOL decal	0.175	0.18	4.09	68
nPA BOL CCM	0.175	0.18	4.23	69
nPA EOT CCM	0.175	0.12	4.21	71
BUT BOL decal	0.19	0.20	4.03	65
BUT BOL CCM	0.19	0.21	5.57	70
BUT EOT CCM	0.19	0.14	5.42	73
EG BOL decal	0.21	0.20	4.08	62
EG BOL CCM	0.21	0.20	5.25	68
EG EOT CCM	0.21	0.16	5.11	71

- ❑ NPA based cathode barely changed thickness, but lost the most Pt (0.19 to 0.12 mg/cm^2)
- ❑ NPA based cathode barely changed its porosity, while BUT and EG based cathodes increased their porosity most upon voltage cycling.

Summary

- Ionomer dispersions in a variety of solvents were studied by rheometer; Ionomer dispersions impact the catalyst ink rheology including elastic and viscous components. The ink rheology was also impacted by ink processing conditions.

- Ionomer dispersion impacted fresh CCM morphology. EG and BUT based CCMs had better ionomer and Pt distribution although their initial performance was not improved compared to NPA based CCM.

- Ionomer dispersions influenced CCM durability. EG and BUT based CCMs demonstrated less Pt agglomeration and migration, which is consistent with their better fuel cell durability than previously reported, and may link to their higher elastic components.

Team Collaborations/Project Management

Institutions	Roles
Giner Inc. Hui Xu (PI), Magali Spinetta, Shirley Zhong, Fan Yang	Catalyst ink design and characterizations, electrode fabrication, and cell testing
Los Alamos National Laboratory Yu-Seung Kim (co-PI)	Ionomer dispersion preparation and characterizations
Oak Ridge National Laboratory Karren More (collaborator)	Electrode characterizations
University of Connecticut Jasna Jankovic (collaborator)	Electrode characterizations

Future Work

- Correlate rheology of catalyst inks to their electrode morphology and microstructures
- Study catalysts inks using more advanced Pt/C and IrO_2 catalysts
- Evaluate MEA performance and durability using different catalyst inks

Reply to Reviewers' Comments

- The focus is too narrow, and the analyses are not detailed enough. This project does not address all the objectives as listed (at least in this presentation). Knowing that a given deposition process yields good performance is critical and valuable; this work is a start but should have included more comprehensive analyses.

  Reply: We would like to investigate how catalyst inks impact electrode structures and performance. This work will establish quality control to develop large-sized fuel cell and electrolyzer MEAs. We will perform more analysis including catalyst ink particle size, Zeta potential, rheology and correlate them with electrode structure and performance.

- There is a lack of any optimization work or systematic electrode design, as well as a lack of universality of the approach. The Pt loadings in this project are not forward-looking. No design rules were developed.

  Reply: In the Phase IIB project, we will focus on less solvents and perform more optimization on each solvent. We will also use more advanced catalysts and study lower Pt loading (0.1 mg/cm^2). More universal design of experiments (DOE) approach will be used.

- There is limited electrolysis work. Better analysis could further the good data taken. More work and progress could have been made.

  Reply: In the Phase IIB project, we will dedicate more time and resources to electrolysis

- The PI does not appear to be interested in analyzing the data in a way that allows one to draw substantiated conclusions.

  Reply: We will perform more tests for each cell to acquire more information. One example is to isolate local oxygen transport resistance using limiting current density approach.

- It is unclear how large of an advance in either performance or durability will be achieved by this approach.

  Reply: Our focus will be electrode fabrication cost reduction and durability improvement. The durability improvement has been demonstrated in our results.

- The lack of interpretation and dissemination of the results to date is the weakness of this project.

  Reply: We are actually writing two manuscripts that will be published in this year

Acknowledgments

- Financial support from DOE SBIR/STTR Program
- Program Manager
  - Ms. Donna Ho
- Dr. Yu- Seung Kim at LANL (Subcontractor)
- Dr. Karren More at ORNL (collaborator)
- Dr. Jasna Jankovic at University of Connecticut (collaborator)
- Giner Personnel
  - Magali Spinetta, Shirley Zhong, Fan Yang