Ionomer Dispersion Impact on Advanced Fuel Cell Performance and Durability

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Newton, MA

Award DE-SC0012049 **FC117**

2021 Annual Merit Review and Peer Evaluation Meeting

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Project Goal

- Elucidate how solvents impact ionomer dispersion morphology thus changing electrode structures and performance
- Design light and heavy-duty fuel cell MEAs that are mechanically and chemically durable
- Establish catalyst ink property-electrode structure-MEA performance correlation
- Develop processable and scalable MEA fabrication platforms
- Commercialize MEAs with enhanced durability via roll-to-roll (R2R) production

Project Overview

Timeline
- Project Start Date: 8/27/2018
- Project End Date: 8/26/2021

Budget
- Total Project Value
  - Phase IIB: $999,912
  - Spent: $ 893,529

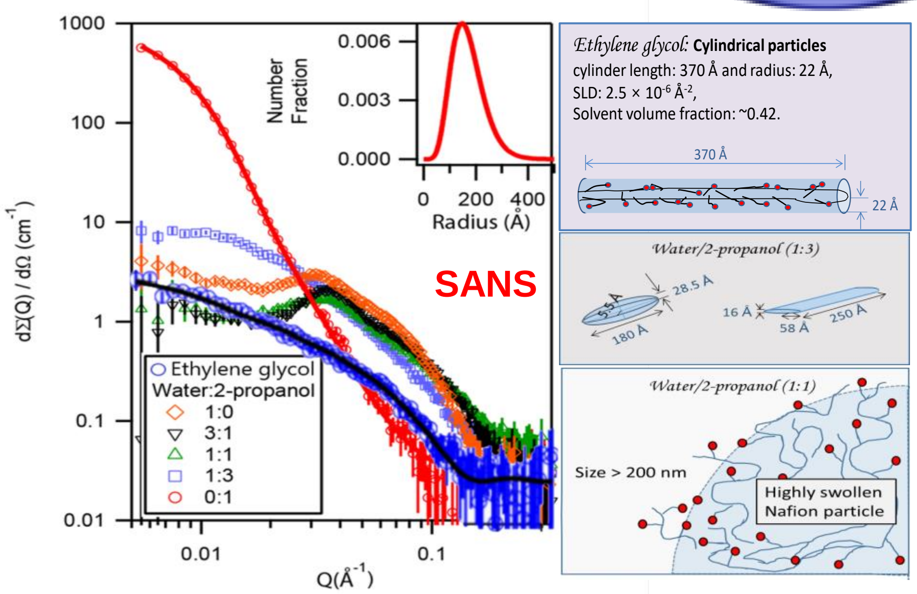
Barriers Addressed
- PEM fuel cell and electrolyzer performance and durability

Contributors
- Giner: Natalie Macauley, Shirley Zhong, and Hui Xu
- LANL: Dr. Yu-Seung Kim (sub.)
- NREL: Dr. Scott Mauger (sub.)
- UConn: Prof. Jasna Jankovic (collaborator)

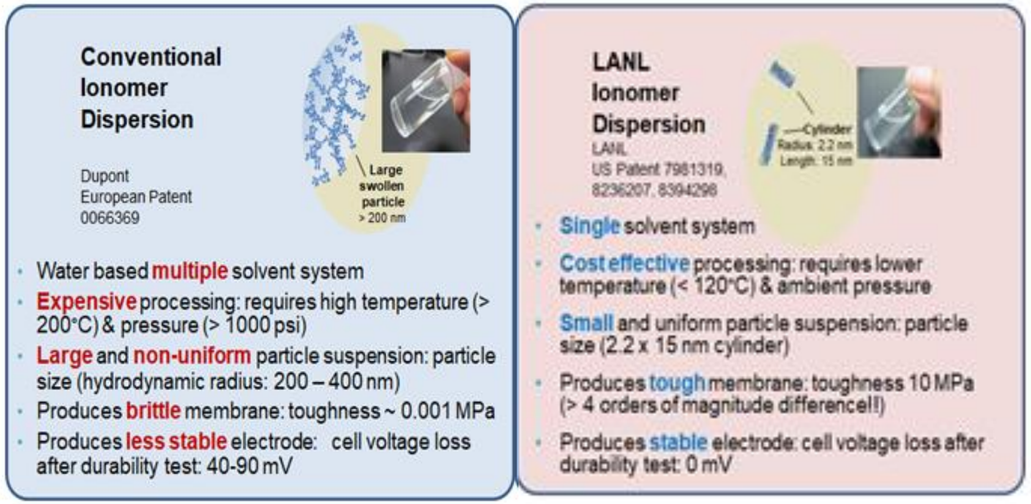
Project Nature
- DOE Technology Transfer Opportunity Project (SBIR-TTO) from LANL

Relevance

- Ionomer is an important component of PEM fuel cells, which may lead to enhanced FC performance and durability to meet DOE FC lifetime targets
- Solvents impact ionomer morphology and interactions with catalysts thus changing electrode performance and durability
- Non-aqueous ionomer dispersion developed at LANL can enhance electrode durability
- Scaling up the ionomer dispersion process (roll-to-roll) will lower the cost of these durable gas diffusion electrodes, leading to a commercial product
- SANS experiments indicate that the dispersion particle size of Nafion in water/2-propanol increases with higher water composition
- At high water content, mimicking 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.%
- Ongoing investigation with different solvent systems and Aquivion ionomer



CHARACTERISTIC	UNITS	2020 TARGETS
Mass activity	A/mg PGM @ 900 $mV_{IR\text{-}free}$	>0.44
Loss in initial activity	% mass activity loss	<40
Performance Loss @0.8 A/cm^2	mV	<30
MEA performance @ 0.8V	mA/cm^2_{geo} @ 800 mV	≥300
MEA performance @ Rated power	mW/cm^2_{geo}	≥1000



Technical Approach

- Correlate catalyst ink properties with electrode structure and fuel cell performance
- Identify MEA improvement pathways toward roll-to-roll (R2R) manufacturing methods and full MEA commercialization
  - Ink characterization: Rheology, Zeta potential, Particle size analysis
  - MEA Performance and Durability
  - Microstructure characterization: SEM & TEM
  - **Commercialization via R2R production**

Rheometer: Catalyst Inks

Microscopy: Electrode Structures

Fuel Cell and Electrolyzer Performance

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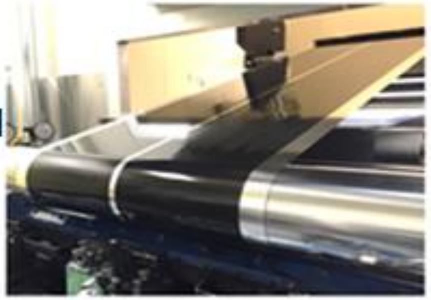
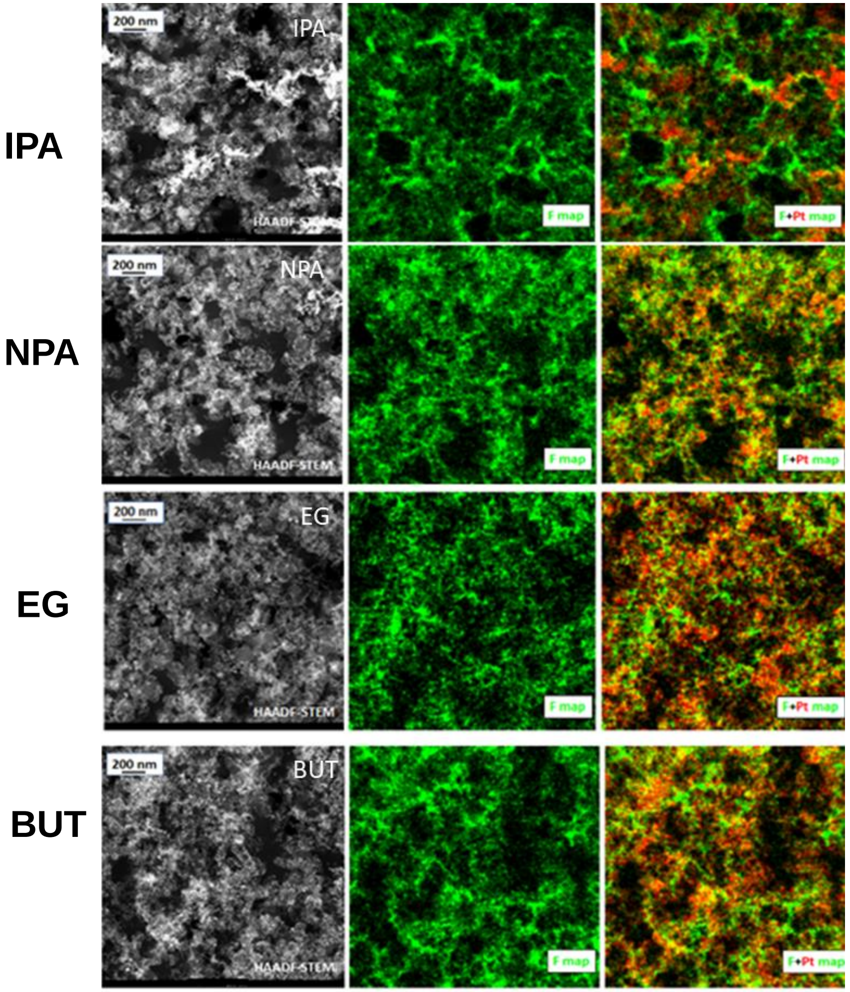
Commercial Coating



Solvent Impact on Electrode Morphology

Close-up of Fresh CCM Characterization

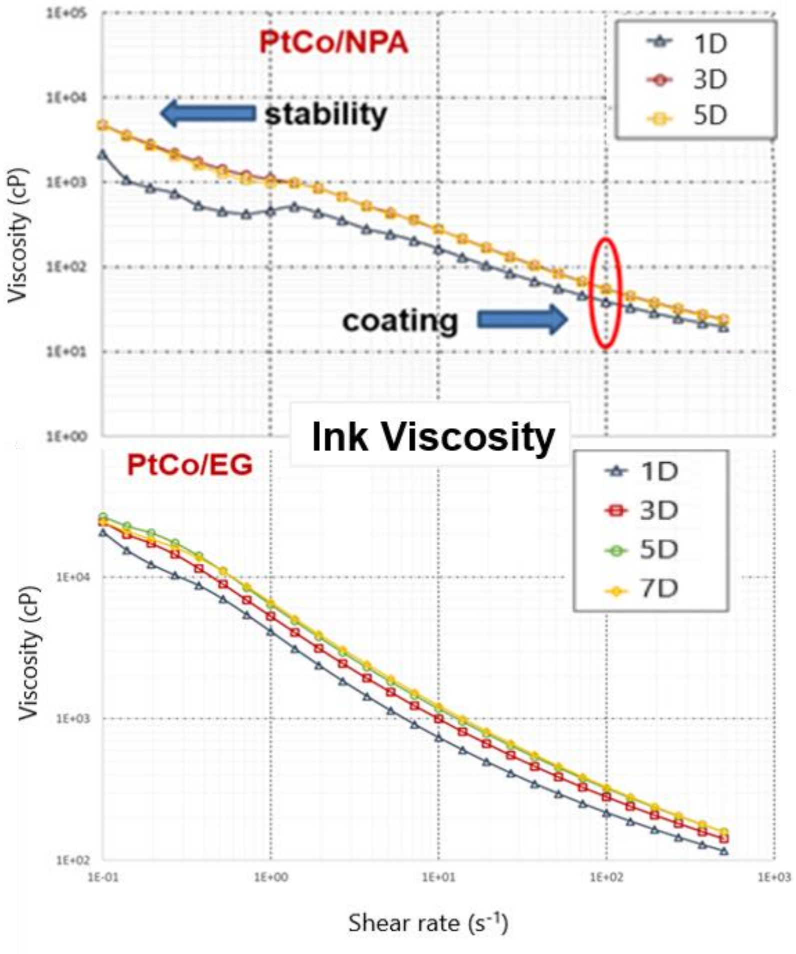


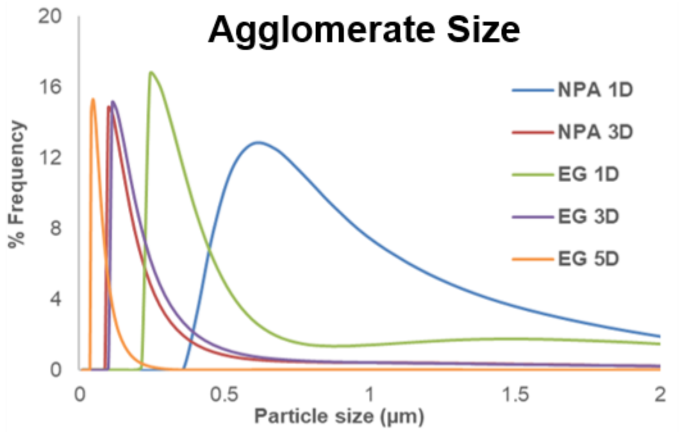
Karren More, ORNL

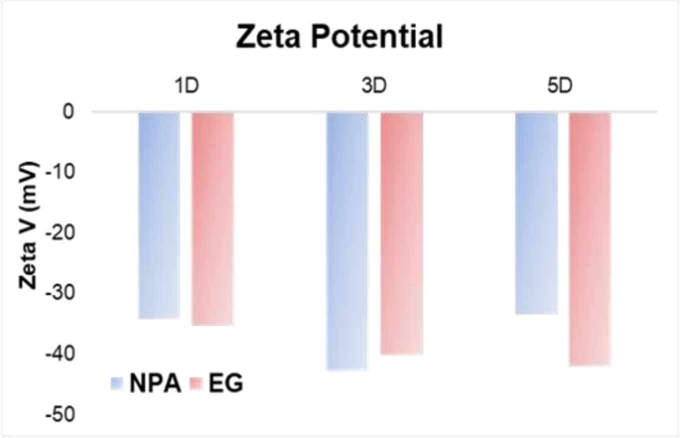
Sample Abbreviation	Description
IPA	Nafion in 2-propanol/water
NPA	Nafion in 1-propanol/water
EG	Nafion in ethylene glycol
BUT	Nafion in butanediol

- ❑ Solvent has significant impact on electrode microstructure
  - 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
- ❑ Multiple solvents were initially investigated for their impact on cathode durability: IPA, NPA, EG, and BUT
- ❑ EG and BUT had better durability than IPA and NPA in 2020 Work
  - Continued investigations with EG in 2021
  - Moved to PtCo catalyst, GDEs and R2R

Accomplishment: Catalyst Ink Optimization





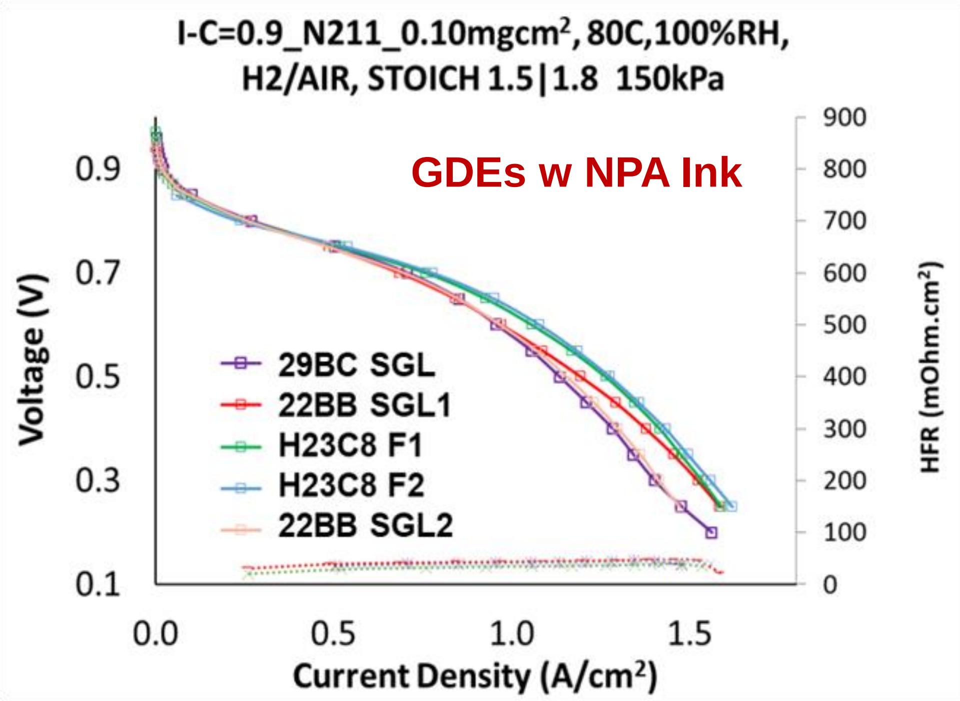


0.1 mg/cm² Pt Cathode Catalyst Ink Composition

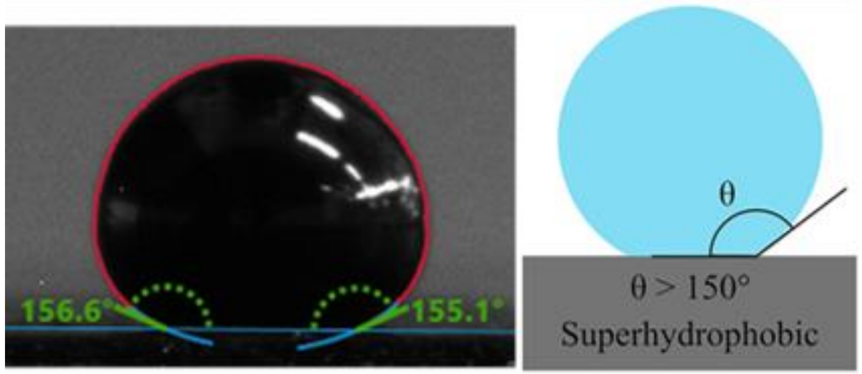
- TKK TEC36F32 PtCo catalyst
- 5 wt.% N212 in EG ionomer
- 20 wt.% D2021 Nafion
- I/C of 0.9
- **Meyer rod coating on GDL**
- Freudenberg H23C8
- Dried on hot plate 90 ℃ 1h
- 5 days in vacuum oven at 150 ℃
- Hot pressed to commercial 0.2 mg/cm² Pt anode and N211

- **Ball milling time was determined by stable viscosity and lowest zeta V:** 3 days for NPA and 5 days for EG
- **Ink Viscosity** gradually increased with mixing time – coating shear rate is ~ 100 s^{-1}
- **Agglomerate size and Zeta potential** gradually decreased with mixing time as ink stabilized

Accomplishment: Coating EG ink on GDL



EG ink high contact angle on GDL



- Shifting from CCM to GDE for viable commercialization
- Tested coating NPA inks on various GDLs: 29 BC, 22BB SGL and **Freudenberg H23C8**
- EG ink did not coat GDLs due to high contact angle of ~155°
- Air plasma treatment enabled GDL coating at Giner
- Applied Nafion overspray to GDE and hot pressed GDEs to half anode CCM

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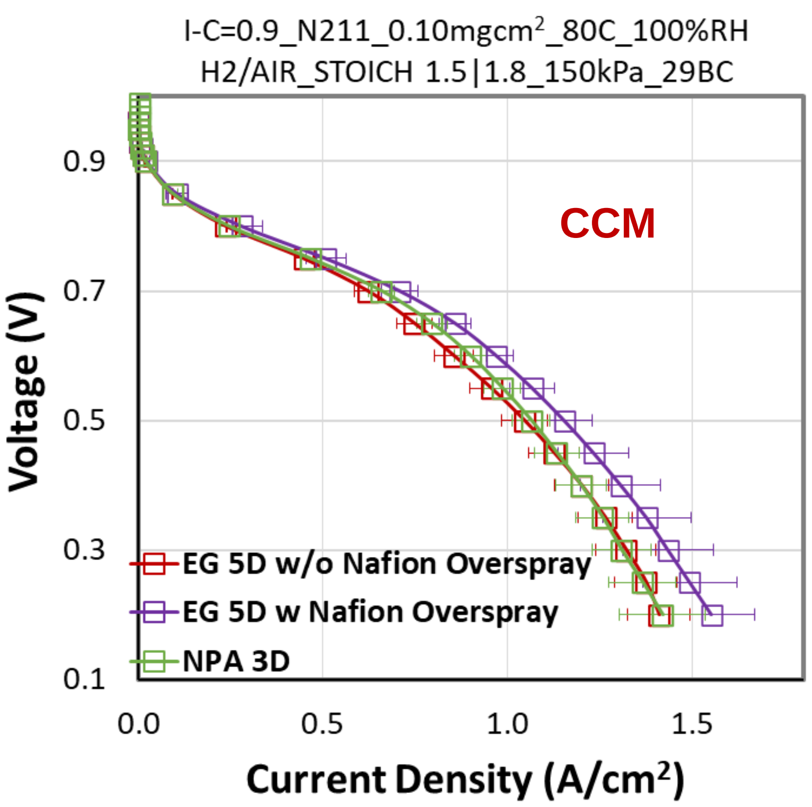
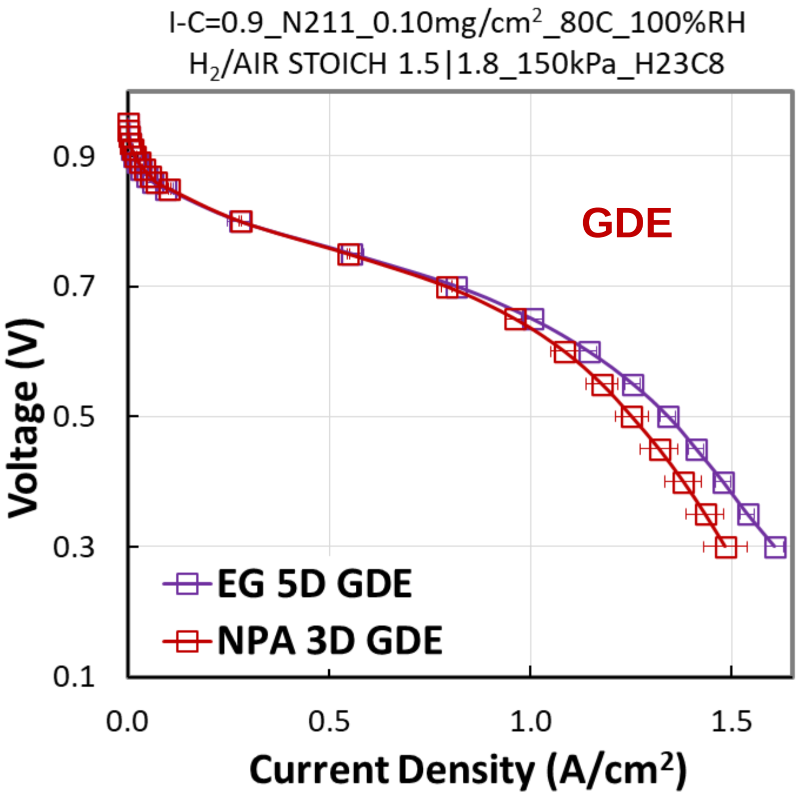
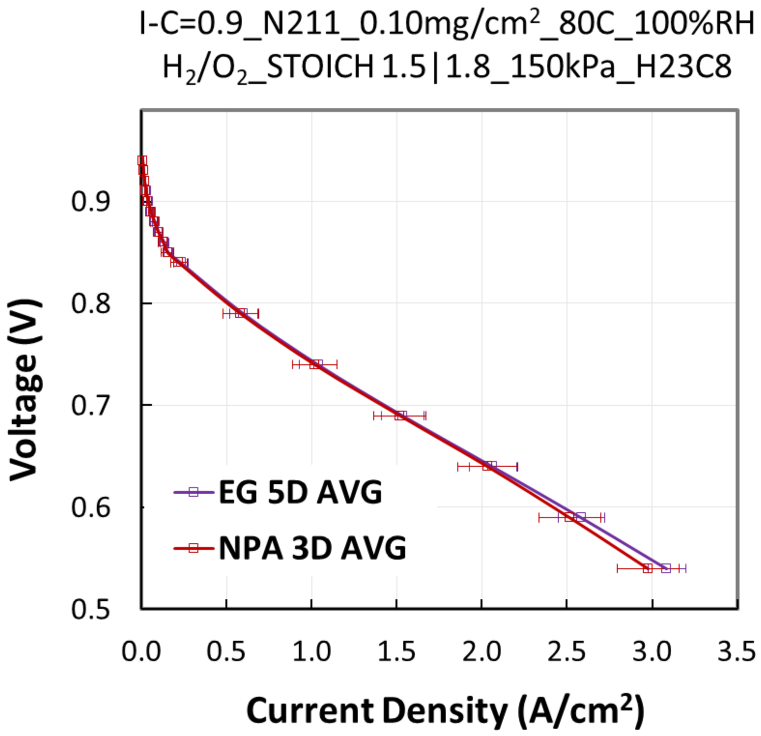
Accomplishment: CCM vs. GDE Performance

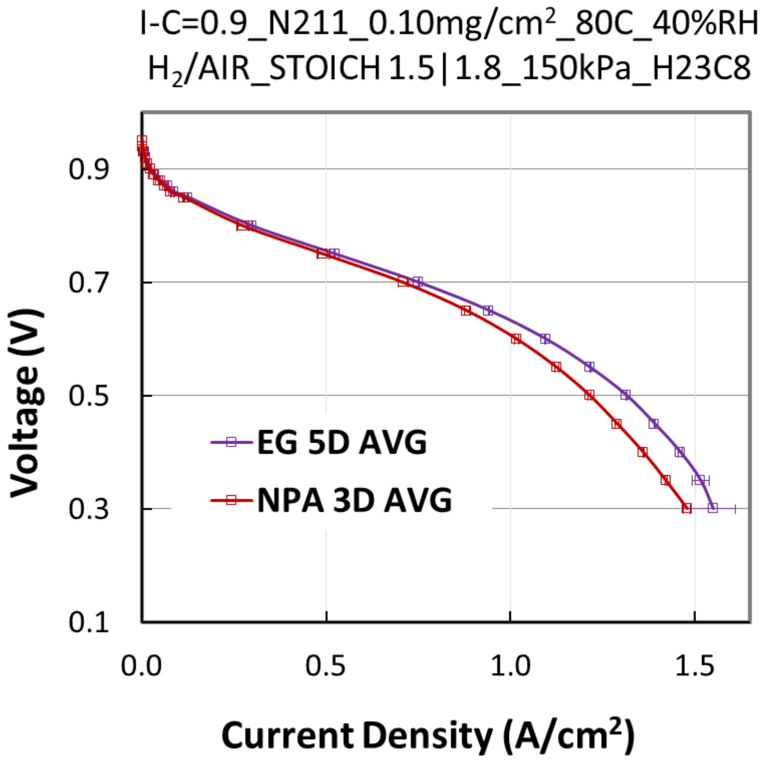


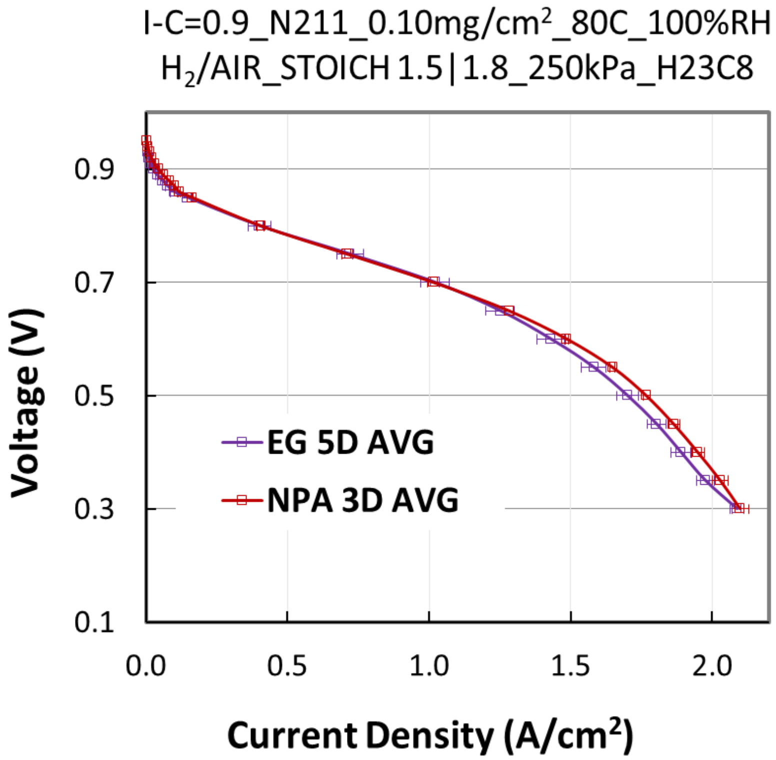


- EG CCM performance matches performance of NPA CCMs
- EG CCMs perform better with a Nafion overspray
- **EG GDEs exceed the performance of EG CCMs and NPA GDEs**
- EG GDEs have better performance in mass transport region than NPA GDEs
  - Both EG and NPA GDEs have a Nafion Overspray

Oxygen and Low RH Performance

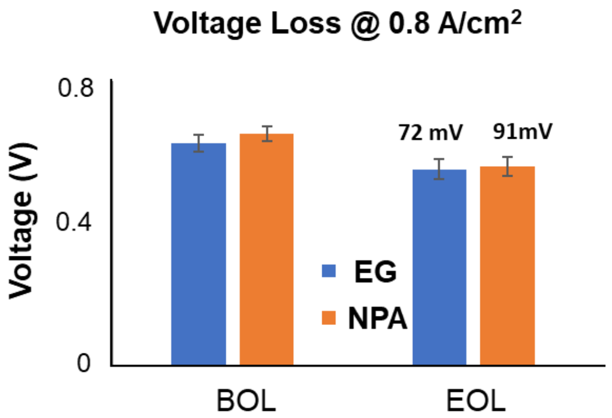


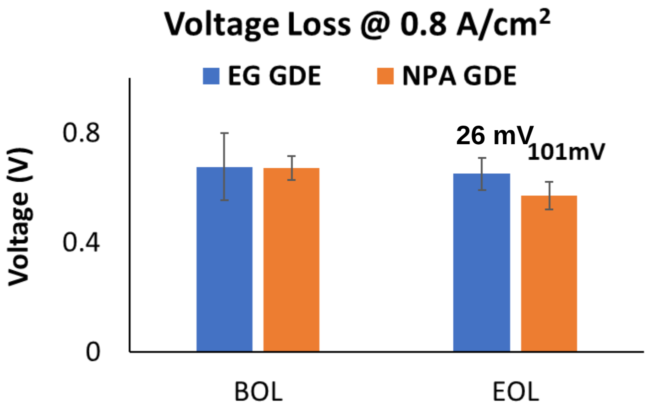




- EG GDEs either match or outperform NPA GDEs
  - 80 ℃, 100% RH, 150kPa in H_2/O_2
  - 80 ℃, 40% RH, 150kPa in H_2/Air
  - 80 ℃, 100% RH 250kPa in H_2/Air

Accomplishment: CCM & GDE Durability

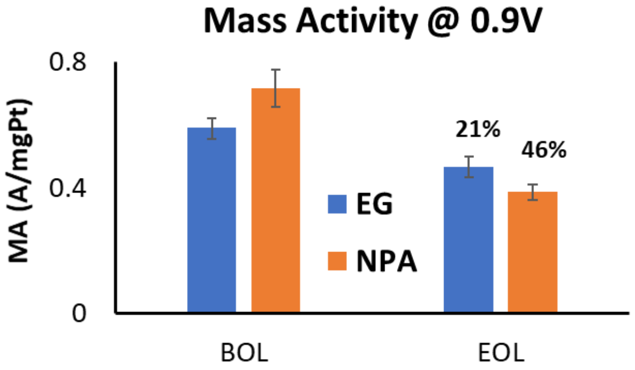


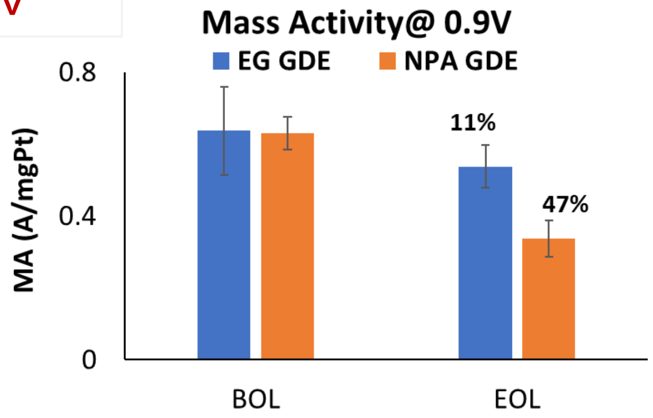


CCM

30K SWAST
0.6-0.95 V

GDE





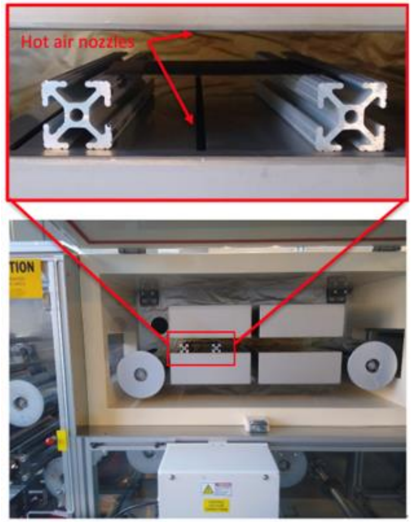
Ion Chromatography was used to evaluate Fluoride Emission Rate from MEA with GDE and hydrocarbon membrane.

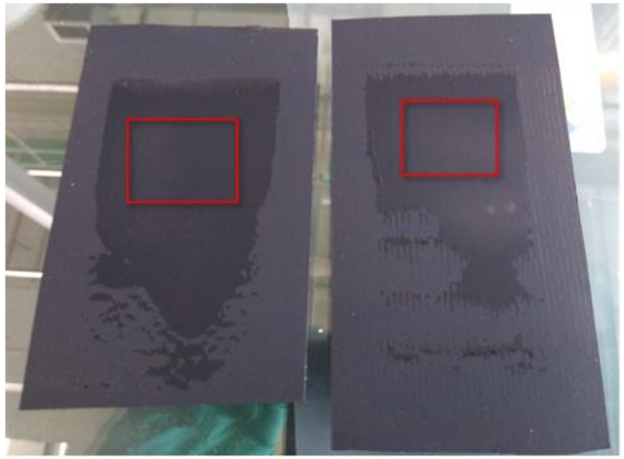
$$FER = \frac{Volume\ (L)\ x\ Concentration(ppm)}{Time\ (h)\ x\ Area\ (cm^2)}$$

Solvent	Cathode FER (µg/h-cm²)
NPA	0.0034
EG	0.0025

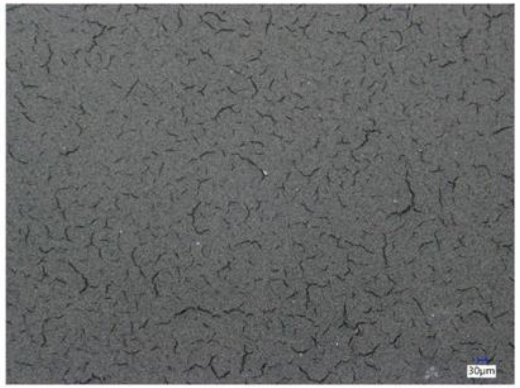
- Giner's EG based GDEs are more durable than NPA GDEs
- At 0.8 A/cm² the EG GDE lost 26 mV vs. 101 mV for NPA GDE after 30K AST
- The EG and NPA GDE lost 11% and 47% of initial mass activity, respectively

Accomplishment: Ink Coating Scale-up





#30 rod left, #60 right.
Red boxes indicate XRF loading measurement region (115 ℃)



#60 rod initial test sample

#30 rod initial test sample

- As-received pre-mixed EG ink was ball milled at ~ 80 rpm for 5 days at ambient temperature
- Two test coatings were made using #30 and #60 Meyer rods
- Samples suspended in NREL's convective R2R oven at **115 ℃** to simulate "**in operando**" conditions
- Cracking observed with # 60 rod vs. # 30 rod is in line with the critical crack thickness concept
  - Rapid evaporation of solvent through catalyst layer

- Loadings via XRF with spatial COV% for 3X3 grid (red boxes)
  - #30 sample: 0.056 (+/-) 4.14% [mg Pt / cm^2]
  - **#60 sample: 0.109 (+/-) 14.3% [mg Pt / cm^2]**

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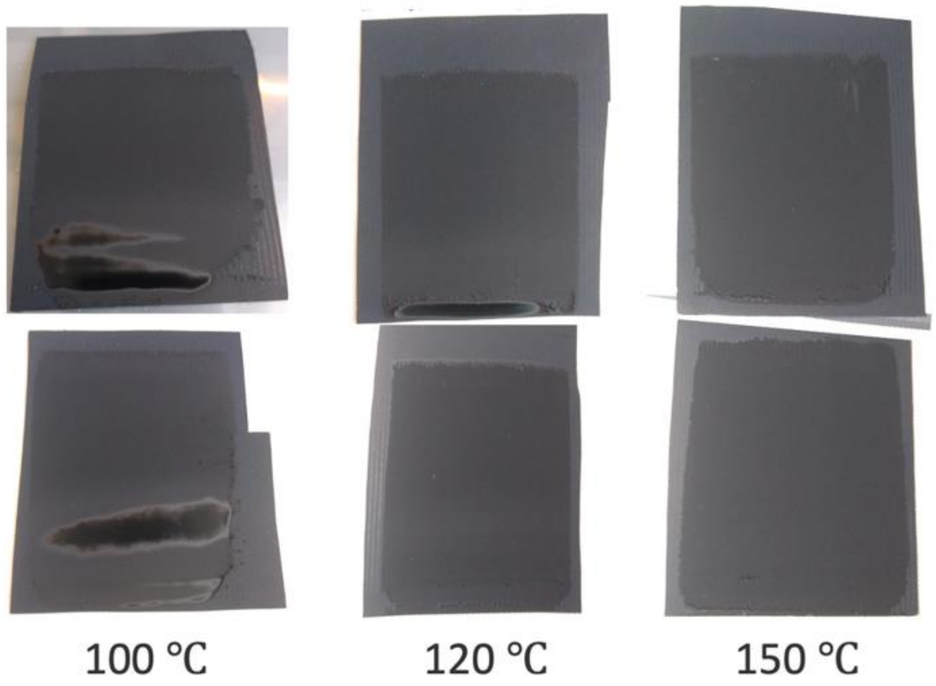
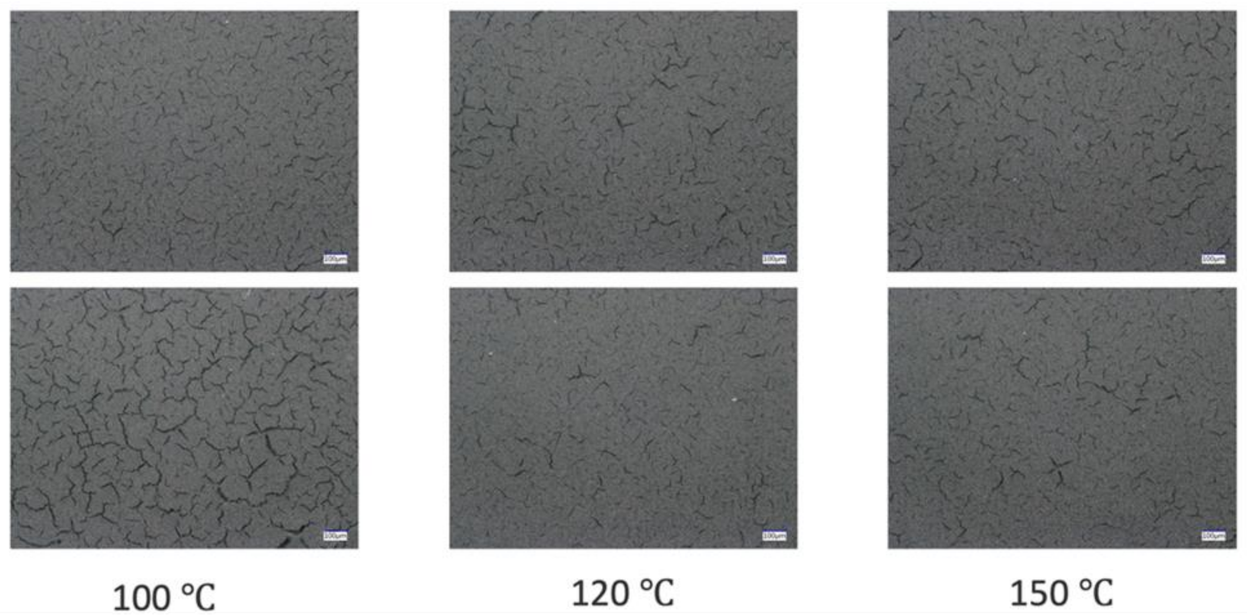
Impact of Ink Heating Temperature



Scale bar is 100 microns



- Rod coated (#60 rod) six samples dried at three temperatures based on evaporation rate calculations (100, 120 and 150 ℃) for **120 seconds** to simulate 1 m/min R2R operation
- 120 ℃ seems sufficient for properly loaded coatings
- 150+ ℃ gives good assurance for complete dryness
- All micrographs taken at 200X with ring and coaxial top-down lighting
- **Lower temperature (slower drying) produced more cracks**

Impact of Mixing Time

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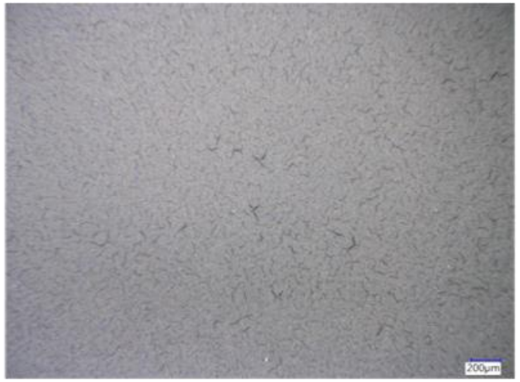
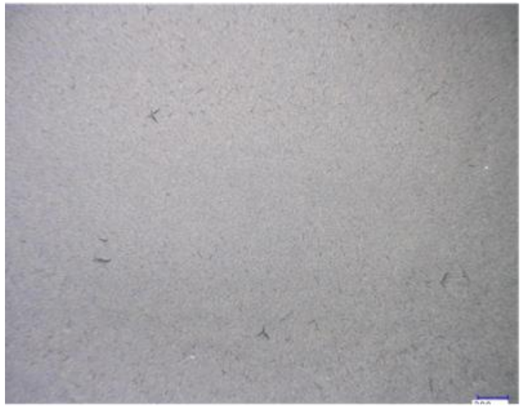
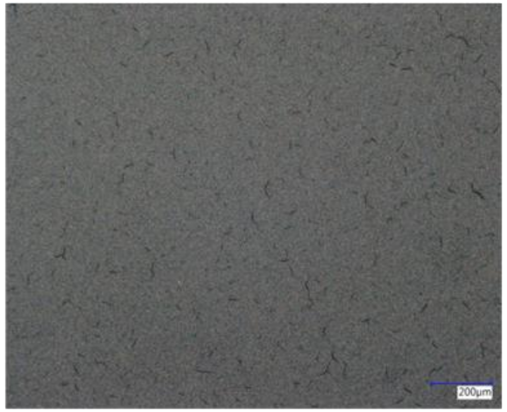
24 Hour Coating 120 ˚C for 2 min 0.1 mg/cm^2 Pt	 100X	 200X
72 Hour Coating 120 ˚C for 2 min 0.1 mg/cm^2 Pt	 100X	 200X

- **72h coating already had less cracking than 24h samples**
- 120h was provided to Giner to eliminate cracking completely
  - 4 GDEs dried at only 120 ˚C for 2 min
  - 2 GDEs dried at 120 ˚C for 2 min then baked at 180 C for 5 min

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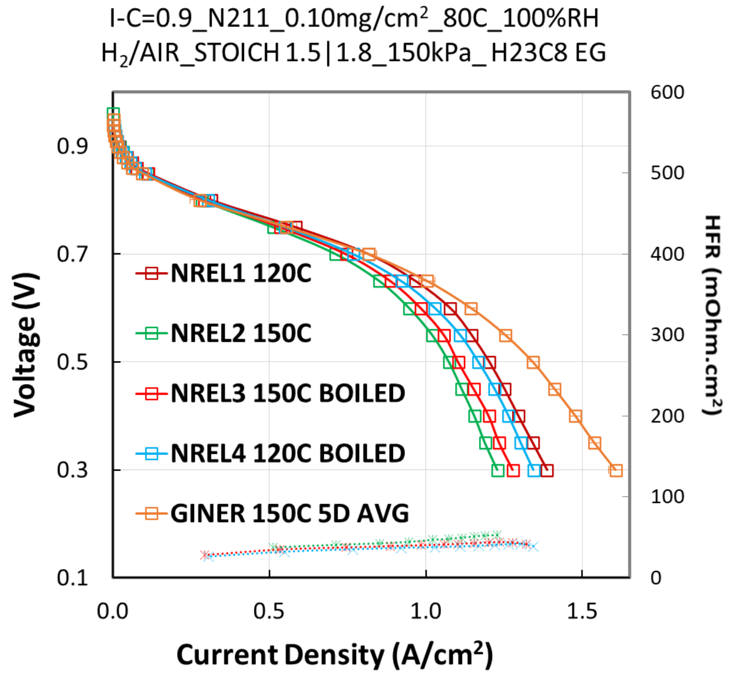
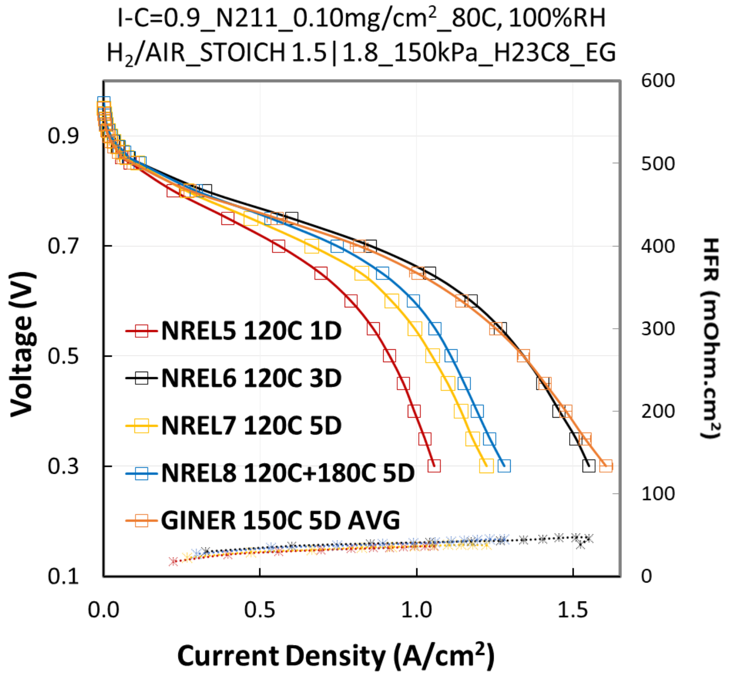
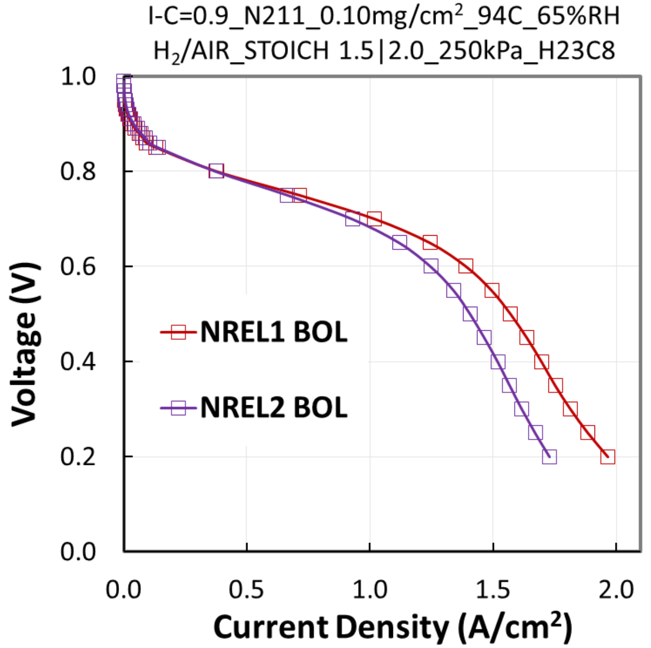
NREL R2R EG GDE Performance







- Drying GDEs at 120 ºC yields better performance than at 150 ºC (NREL1 > NREL2)
- Boiling NREL GDEs in DI water to remove residual EG showed minor changes indicating low to no residual EG (NREL3 & 4)
- 1 and 5 day mixing resulted in poorer performance than 3 day mixing (NREL 5 < NREL6 < NREL 7&8)
- **NREL6: mixed for 3 days, dried 2 min at 120 ºC matched Giner's GDE performance**
- Post bake at 180 ºC for 5 min after baking at 120 ºC for 2 min resulted in better performance(NREL 8 > NREL7)

Responses to Previous Year Reviewers' Comments

This project was not reviewed in 2020

Team Collaborations/Project Management

Institutions	Roles
Giner Inc. Hui Xu (PI), Natalia Macauley, Shirley Zhong	Catalyst ink design and characterization, electrode fabrication, and cell testing
Los Alamos National Laboratory Yu-Seung Kim (co-PI), Gerie Purdy	Ionomer dispersion preparation and characterization
National Renewable Energy Laboratory Scott Mauger (Co-PI), Jason Pfeilsticker	Roll to roll evaluation of EG based ink for gas diffusion electrode fabrication
University of Connecticut Jasna Jankovic (collaborator), Sara Pedram	Electrode characterizations

Remaining Barriers and Challenges

- EG-Based GDE fabrication using R2R at NREL was able to successfully replicate Giner GDEs performance at small scale, but not durability
- Differences in microstructure can lead to variations in durability
- More advanced catalysts and membranes have not been adapted to further enhance fuel cell performance
- More aggressive accelerated stress tests under heavy-duty conditions have not been completed

Any proposed future work is subject to change based on funding levels

Future Work

- Further develop best GDE fabrication practice w/ NREL
  - Optimize solid content to reduce crack formation
    - Reduce thickness of catalyst layer on GDL
  - GDEs dried at <120 ˚C for <2 min
  - Try slot die coating EG ink at NREL
  - Crack free heavy-duty GDEs with 0.2 mg/cm^2 Pt
  - Produce and test 100 cm^2 MEAs
- Scale up assisted by a commercial coating company
- Further work with OEM for GDE sale and commercialization

Any proposed future work is subject to change based on funding levels

Summary

- Impact of non-aqueous solvent on Ionomer dispersion morphology, electrode structure and fuel cell durability was studied
- Efforts were shifted from CCMs to GDEs for viable commercialization
  - Giner GDEs match CCMs for the performance
  - Giner GDEs show improved durability over NPA GDEs
- Collaborated with NREL to scale up GDEs using R2R Process
  - Scale-up with ethylene glycol (EG) solvent is feasible
  - Performance and durability improvement needed via ink optimization
- Reached out to fuel cell OEMs for sales
  - Durability is highly favorable
  - Need to be cost competitive
- Acknowledgements

  - Financial support from DOE SBIR/STTR Program under award #DE-SC0012049
  - Program Manager: Ms. Donna Ho
  - Dr. John Kopasz for project suggestions

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- Dr. John Kopasz at ANL for project suggestions

Technical Backup and Additional Information

Technology Transfer Activities

- **Look into Potential End Users**
  - Ballard (Canada)
  - Plug Power (New York)
  - Nikola (Arizona)

- **Partial Feedback**
  - Long Durability (target has been met)
  - Low Price: GDEs over CCMs;
    R2R for automation
  - Quality Control (catalyst ink control)

Progress Toward DOE Targets

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- Met the following DOE 2020 performance and durability targets

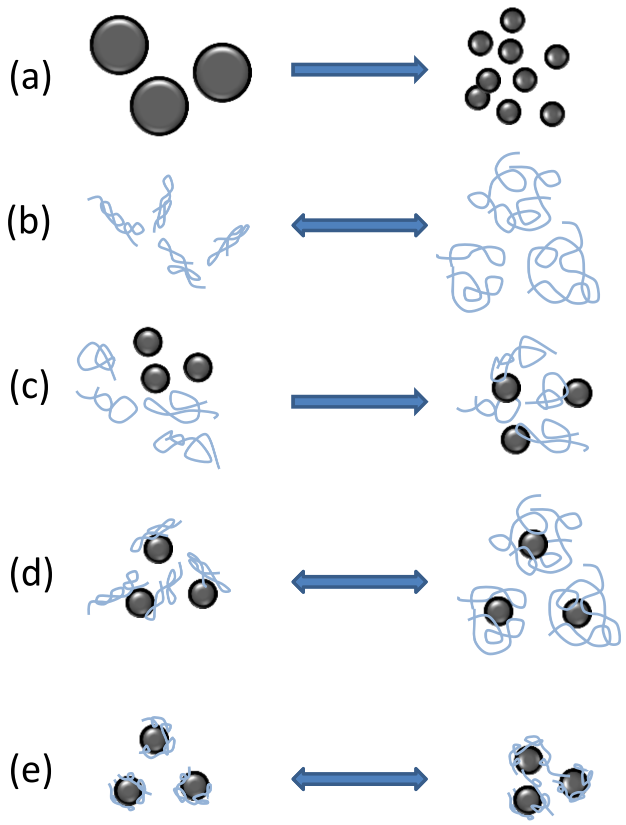
DOE Fuel Cell Electrocatalyst and MEA Technical Targets

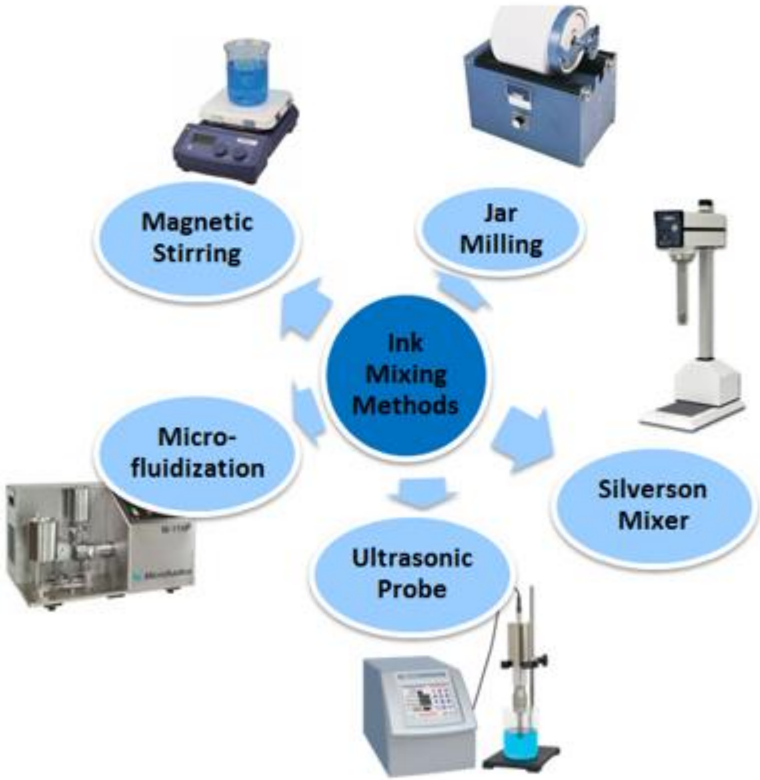
CHARACTERISTIC	UNITS	DOE TARGETS	PROJECT STATUS
Mass activity	A/mg PGM @ 900 $mV_{IR\text{-}free}$	> 0.44	0.82
Loss in initial catalytic activity	% mass activity loss	< 40	17
Loss in performance at 0.8 A/cm^2	mV	< 30	25
MEA performance 80ºC, 150kPa, 100%RH, STOICH	mA/cm^2_{geo} @ 800 mV	≥ 300	316

Publications and Presentations

Chao, Lei ; Yang, Fan ; Macauley, Natalia; Spinetta , Magali; Purdy, Geraldine; Jankovic, Jasna; Cullen, David; More, Karren; Kim, Yu; Xu, Hui, "Impact of Catalyst Ink Dispersing Solvent on PEM Fuel Cell Performance and Durability", *J. Electrochem. Soc.*, 168, 044517 (2021)

Pt/C 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

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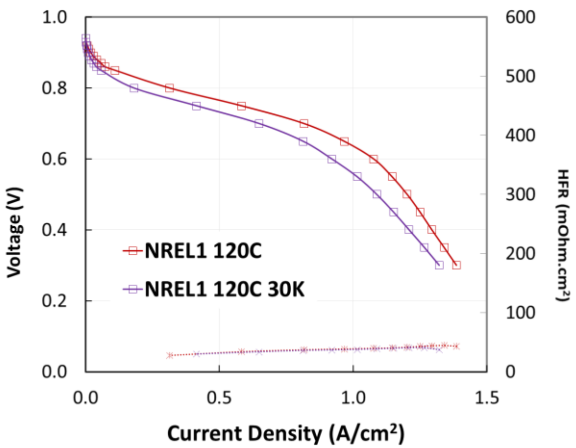
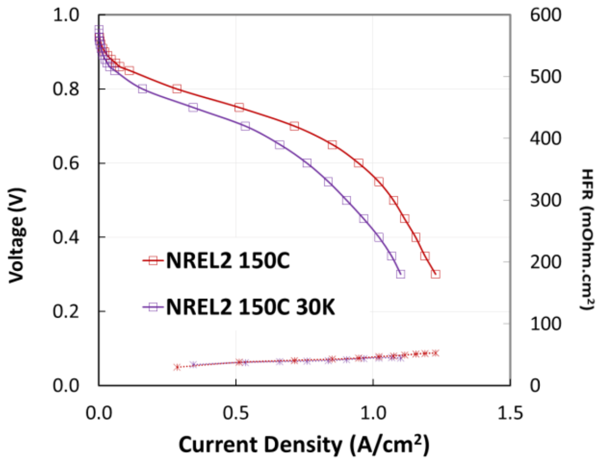
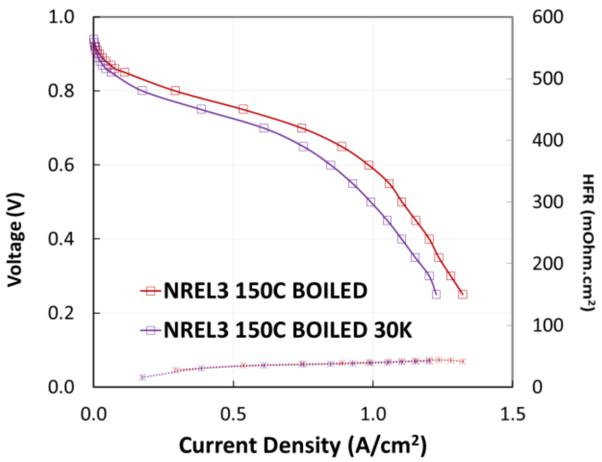
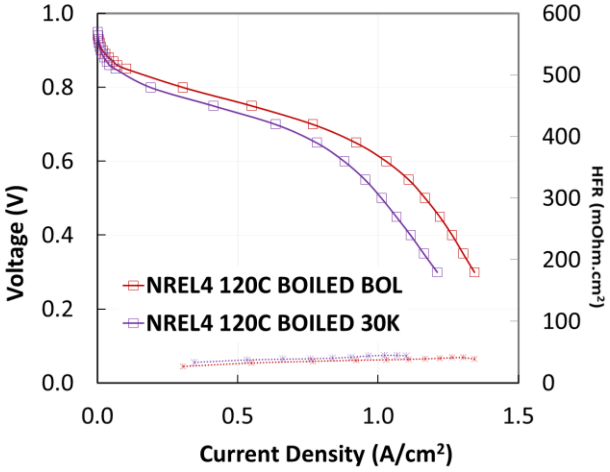
R2R EG GDE Durability

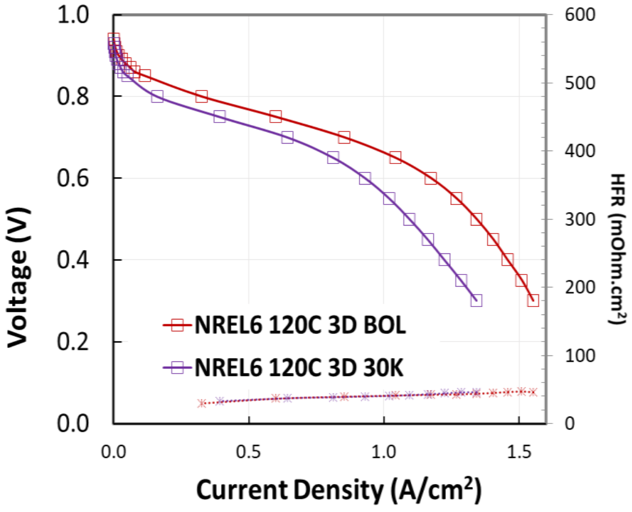
I-C=0.9_N211_0.10mg/cm^2, 80C, 100%RH, H_2/AIR, STOICH 1.5|1.8 150kPa, H23C8 EG











- NREL GDEs were subjected to the 30,000 Square Wave Accelerated Durability Test: 0.6- 0.95V
- NREL GDE (R2R) has not matched Giner GDE (small roller coating) durability

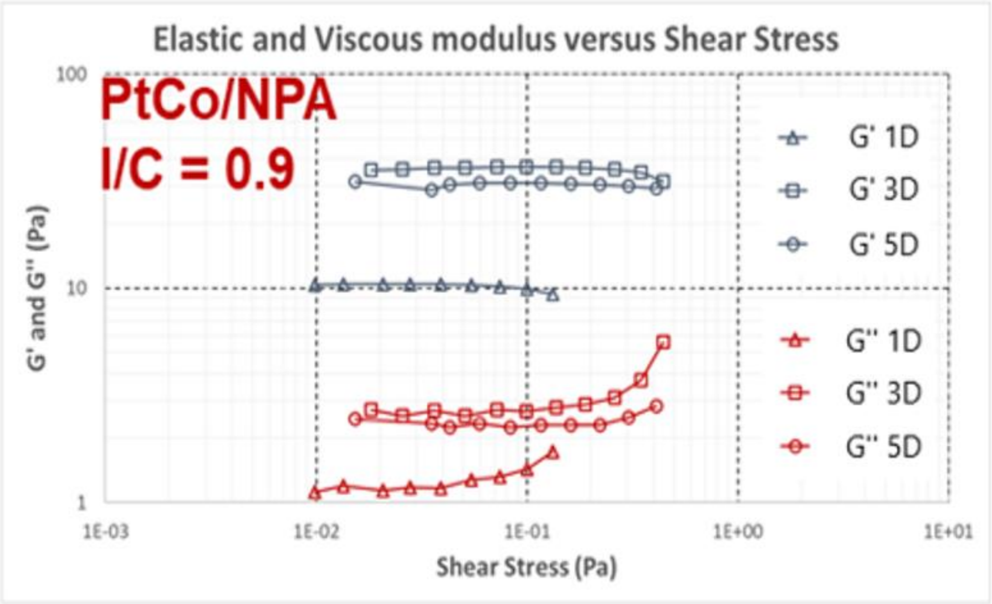
R2R EG GDE Durability

Performance Loss at 0.8 A/cm^2		Mass Activity (A/mg_{Pt})		
EG GDE	**30K**	**BOL**	**30K**	**Loss**
NREL1	50 mV	0.60	0.34	43%
NREL2	95 mV	0.74	0.22	70%
NREL3	56 mV	0.82	0.46	44%
NREL4	49 mV	0.70	0.39	44%
NREL6	56 mV	0.72	0.35	54%
Giner	26 mV	0.56	0.48	17%

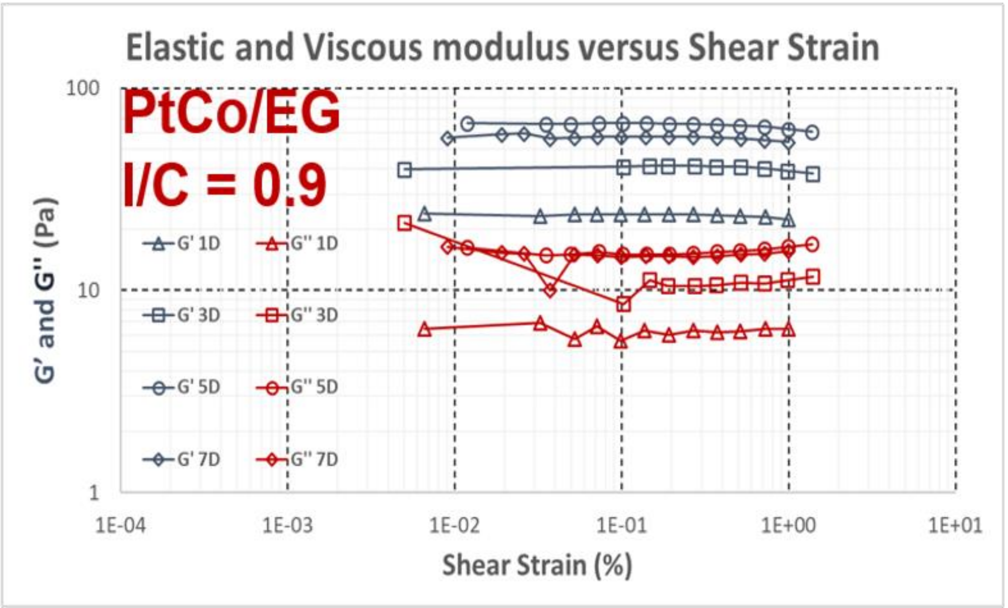
- NREL GDEs were subjected to the 30,000 Square Wave Accelerated Durability Test: 0.6-0.95V
- NREL GDE (R2R) durability did not match Giner GDE (small roller coating) durability

Rheology: Mixing PtCo ink in NPA vs EG

NPA



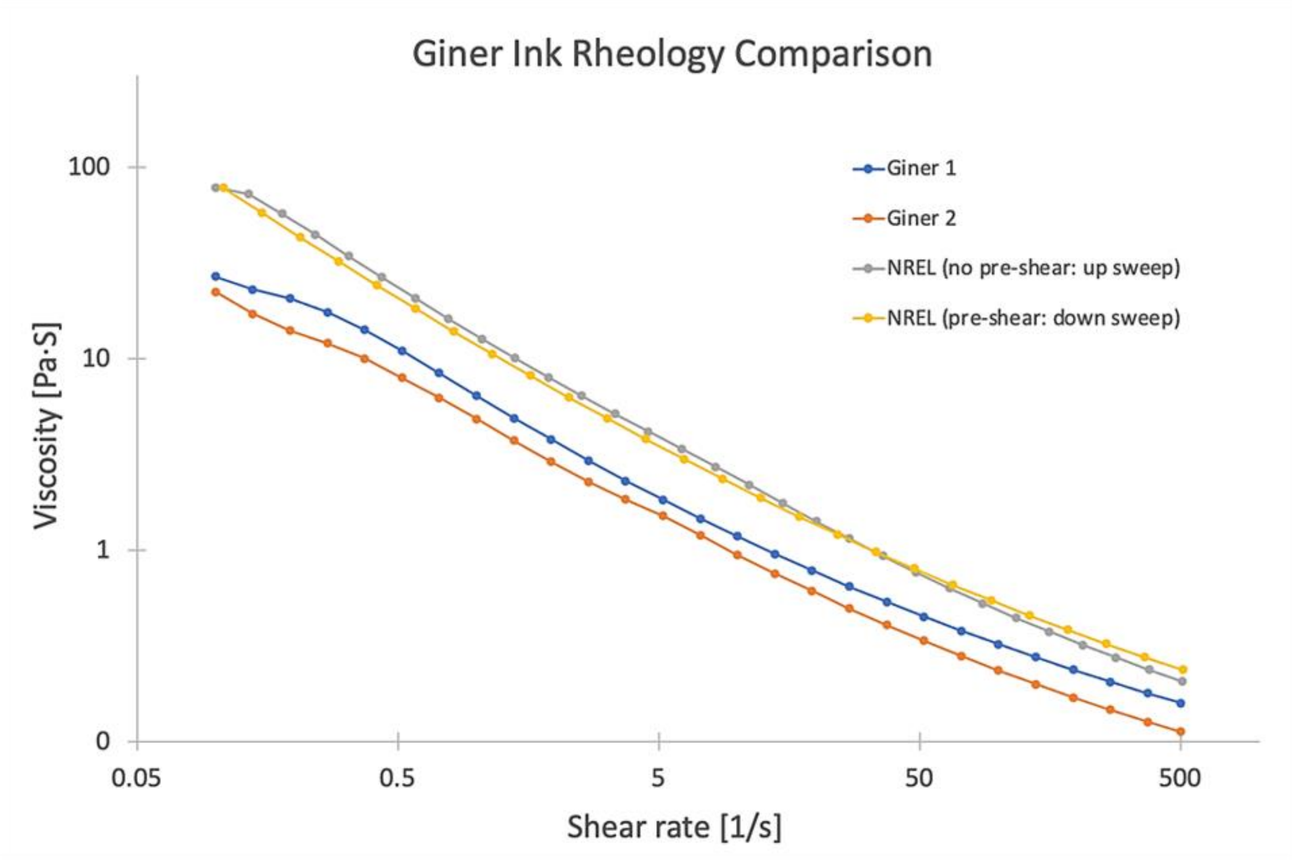
EG



Mixing time determined by stable viscosity: 3 days for NPA and 5 days for EG

- G' Elastic modulus
- G'' Viscous modulus
- Both increase with mixing time

Rheology Comparison



- NREL measurements show ~3X more viscous ink than Giner's
- Increased viscosity and or higher yield stress could have led to better coatability?
- Ink components were sent to NREL to verify