2020 Hydrogen and Fuel Cell Annual Merit Review Meeting

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

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Newton, MA

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Project ID
FC117

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Project Overview

Timeline
- Project Start Date: 8/27/2018
- Project End Date: 2/26/2021

Budget
- Total Project Value
  - Phase IIB: $1 Million
  - Spent: $734 K

Barriers Addressed
- PEM fuel cell and electrolyzer performance and durability

Contributors
- Giner: Natalie Macauley, Shirley Zhong, Magali Spinetta, and Fan Yang
- LANL: Dr. Yu-Seung Kim (sub.)
- NREL: Scott Mauger (sub.)
- UConn: Jasna Jankovic (collaborator)

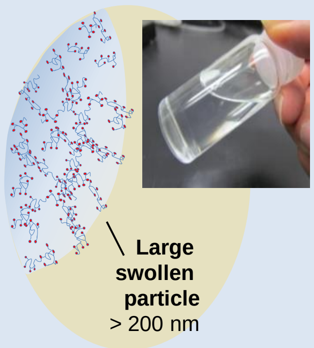
Technical Targets
- Elucidate how ionomer dispersions impact electrode structures and performance
- Create fuel cell MEAs that are mechanically and chemically stable
- Establish catalyst ink property- electrode structure-MEA performance correlation
- Develop processable and scalable MEA fabrication platforms

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

Relevance: Ionomer Dispersion Technology

Conventional Ionomer Dispersion

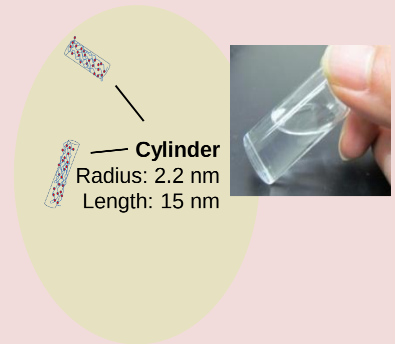
Dupont
European Patent 0066369



- 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

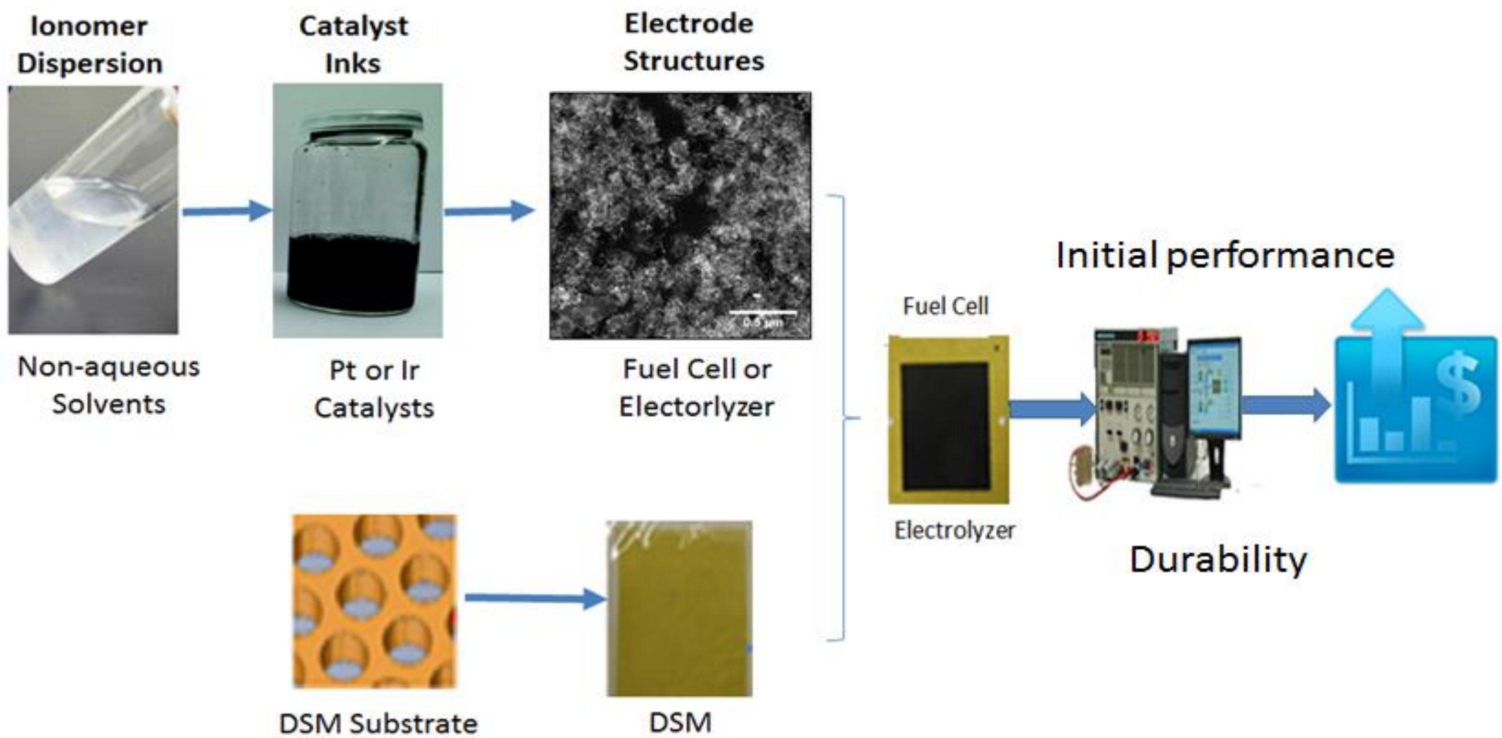
LANL Ionomer Dispersion

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**

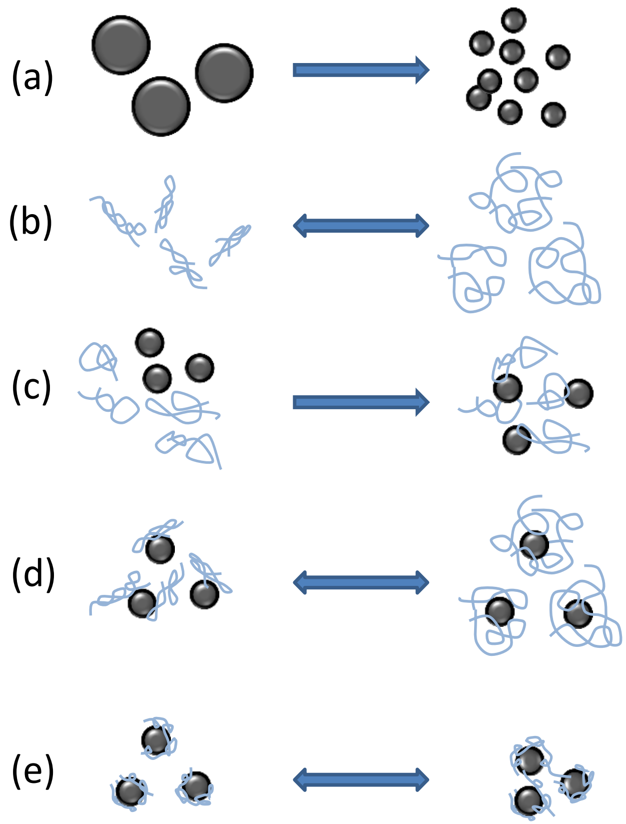
Processibility
- Roll-to-roll production of DSM
- Ultra spraying or roll coater to make MEAs

Scalability
- From LANL 5cm^2 to 50-100cm^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

Background: Pt/C and Ionomer Interaction



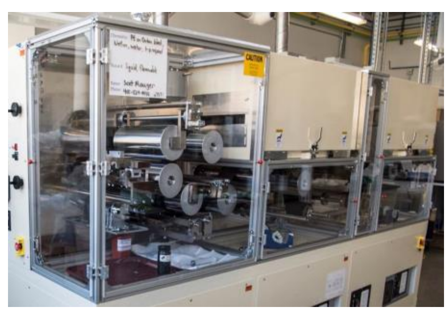
(a) Breakdown of core catalyst agglomeration
(b) Ionomer re-conformation in various solvent blend
(c) Ionomer adsorption onto catalyst particle surface
(d) Ionomer re-conformation on particle surface
(e) Formation and breaking-up of flocculation

Phase IIB Project

- Correlate catalyst ink properties with electrode structure and fuel cell and electrolyzer performance
- Identify MEA improvement pathways toward roll-to-roll manufacturing methods and full MEA commercialization
  - Ink characterization: Rheology, Zeta potential, Particle size analysis
  - MEA Performance and Durability
  - Microstructure characterization: SEM & TEM
  - **Commercialization via Roll to Roll production**
    - TSA with NREL
    - Fuel cell GDE
    - Electrolyzer decal

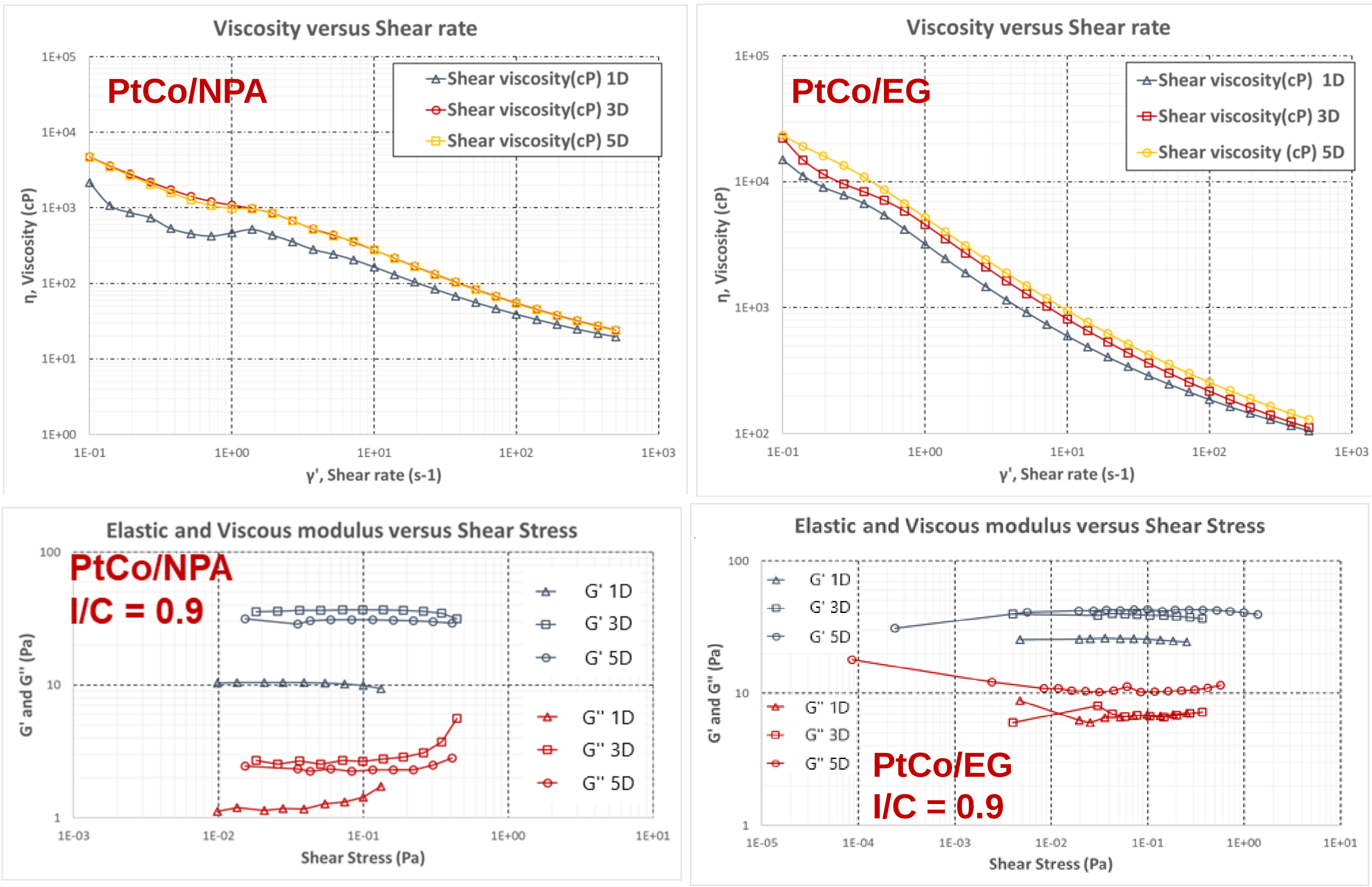
Rheometer: Catalyst Inks

Microscopy: Electrode Structures



Fuel Cell and Electrolyzer Performance

Accomplishment: Rheology on Mixing PtCo Ink

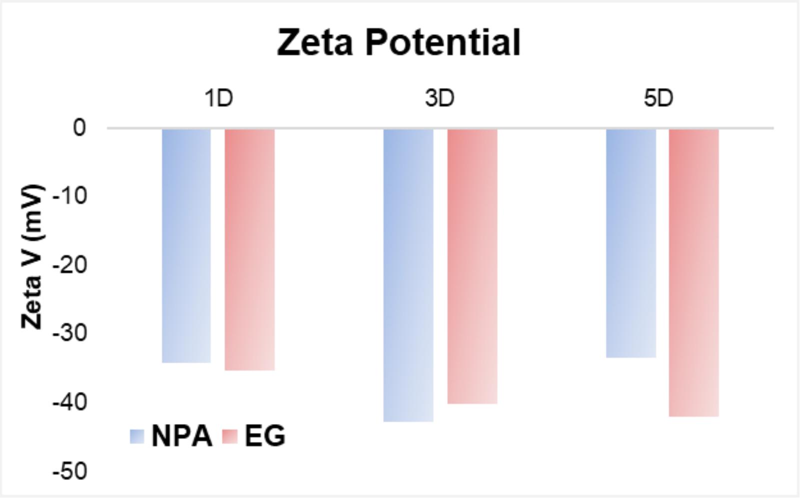


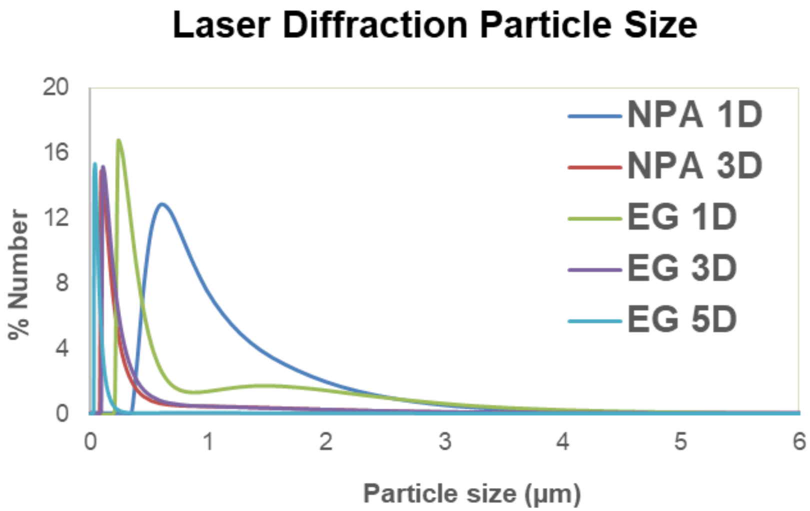
- **Mixing time determined by stable viscosity 3 days for NPA and 5 days for EG**
  - Stable viscosity and highest elastic modulus
  - Elastic dominant inks

G' – Elastic modulus
G'' – Viscous modulus

Zeta Potential & Laser Diffraction

Mixing PtCo in NPA vs EG

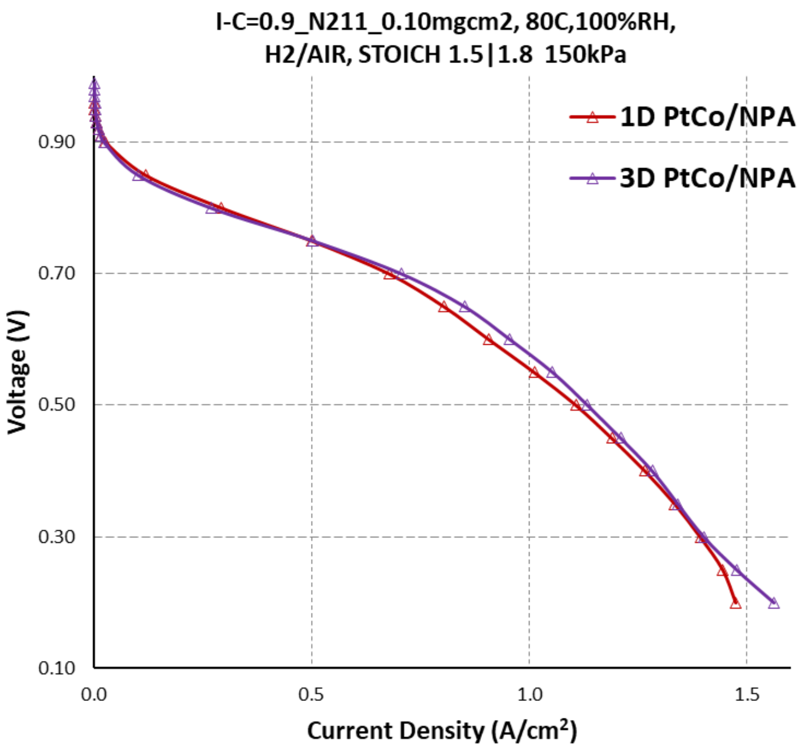


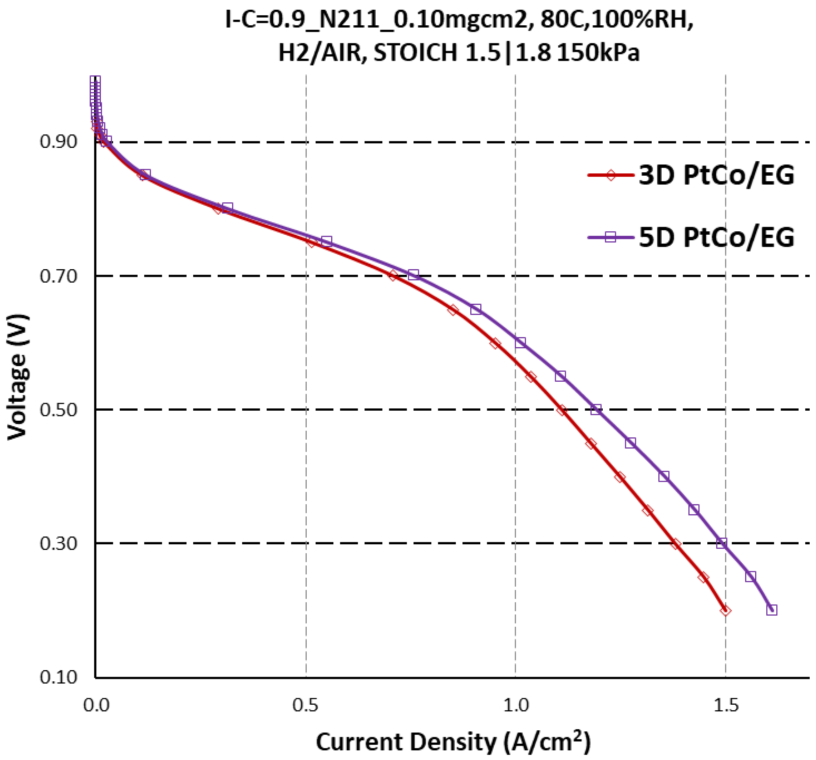


- **Zeta Potential**
  - Gradually decreases with mixing time for EG ink
  - NPA ink has lowest value after 3 days
- **Laser Diffraction Analysis:**
  - Carbon agglomerate size decreases with mixing time for EG ink
  - Dx(50) NPA: 0.789 µm to 0.158 µm after 1 and 3 days
  - Dx(50) EG: 0.369 µm, 0.178µm and 0.063 µm after 1,3 and 5 days

T.M. Riddick, Control of Colloid Stability through Zeta Potential, Book, 1968.

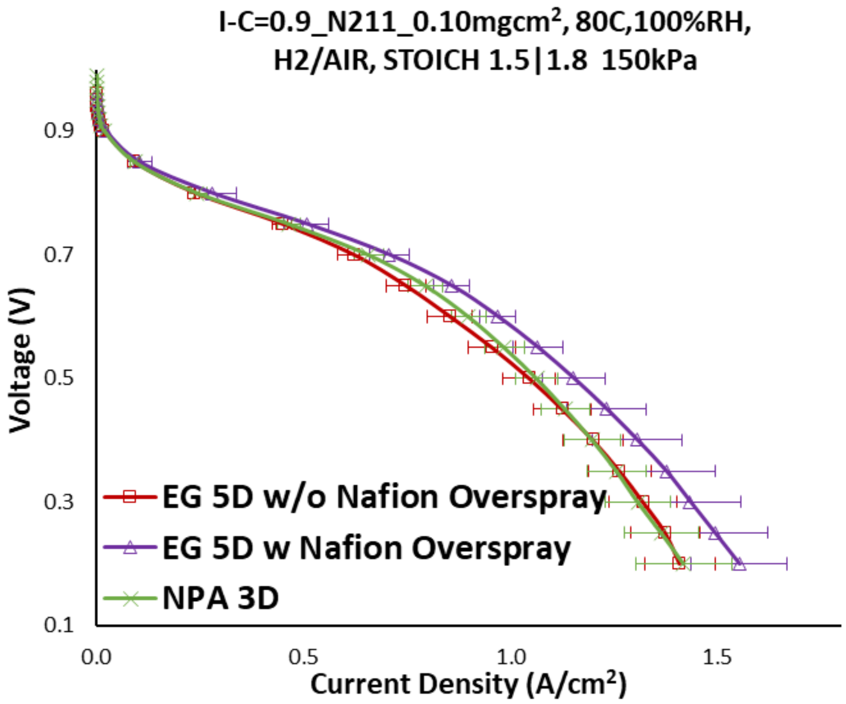
Accomplishment: NPA vs EG Performance





NPA: 3 day mixing shows slightly better performance
EG: 5 day mixing shows better performance

Decal Performance



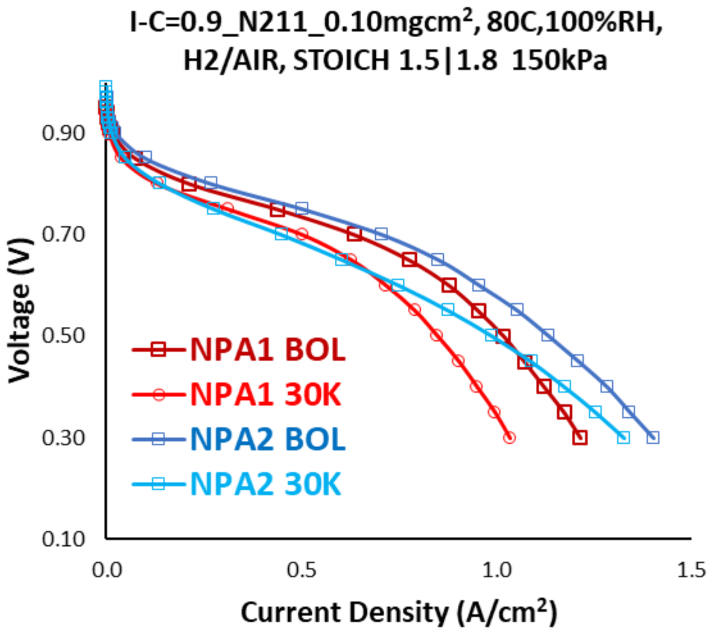
❑ **BOL Performance for Stoichiometric Flows**

- EG MEAs with Nafion overspray performs better than NPA
- EG MEAs without overspray performs similar on average to NPA MEAs
- EG MEA has lower initial sheet resistance than NPA MEA

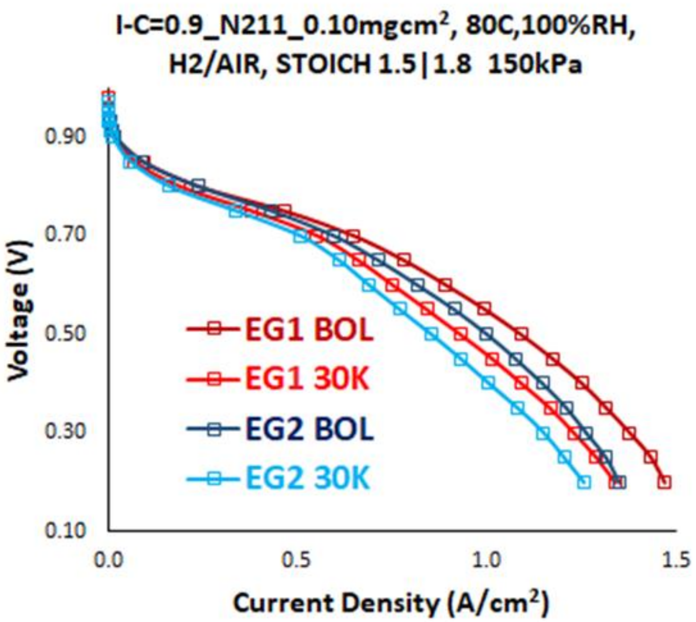
Durability of PtCo in EG vs NPA 30K SW AST

30,000 cycle 0.6-0.95 V Square Wave Accelerated Stress Test (30K SW AST)

NPA



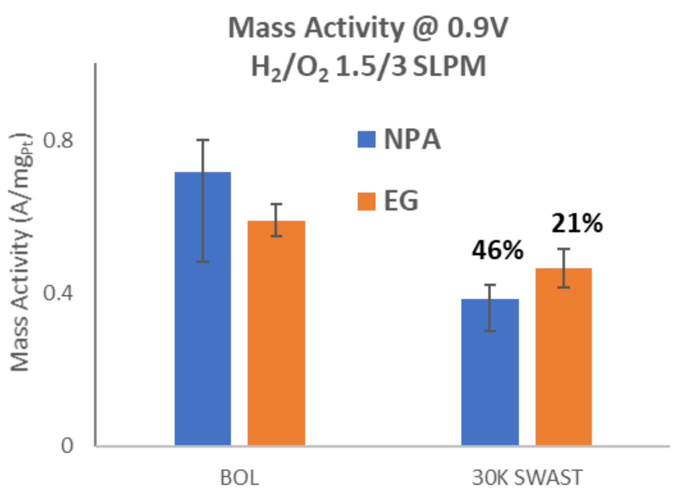
EG

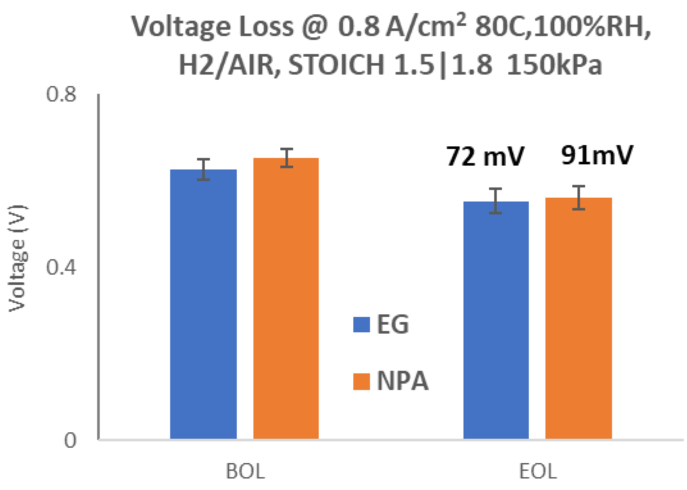


- NPA MEAs degrade faster than EG MEAs without overspray
  - NPA MEAs degrade in both regions
  - EG MEAs degrade more in high current density region

Durability of PtCo in EG vs NPA 30K SW AST

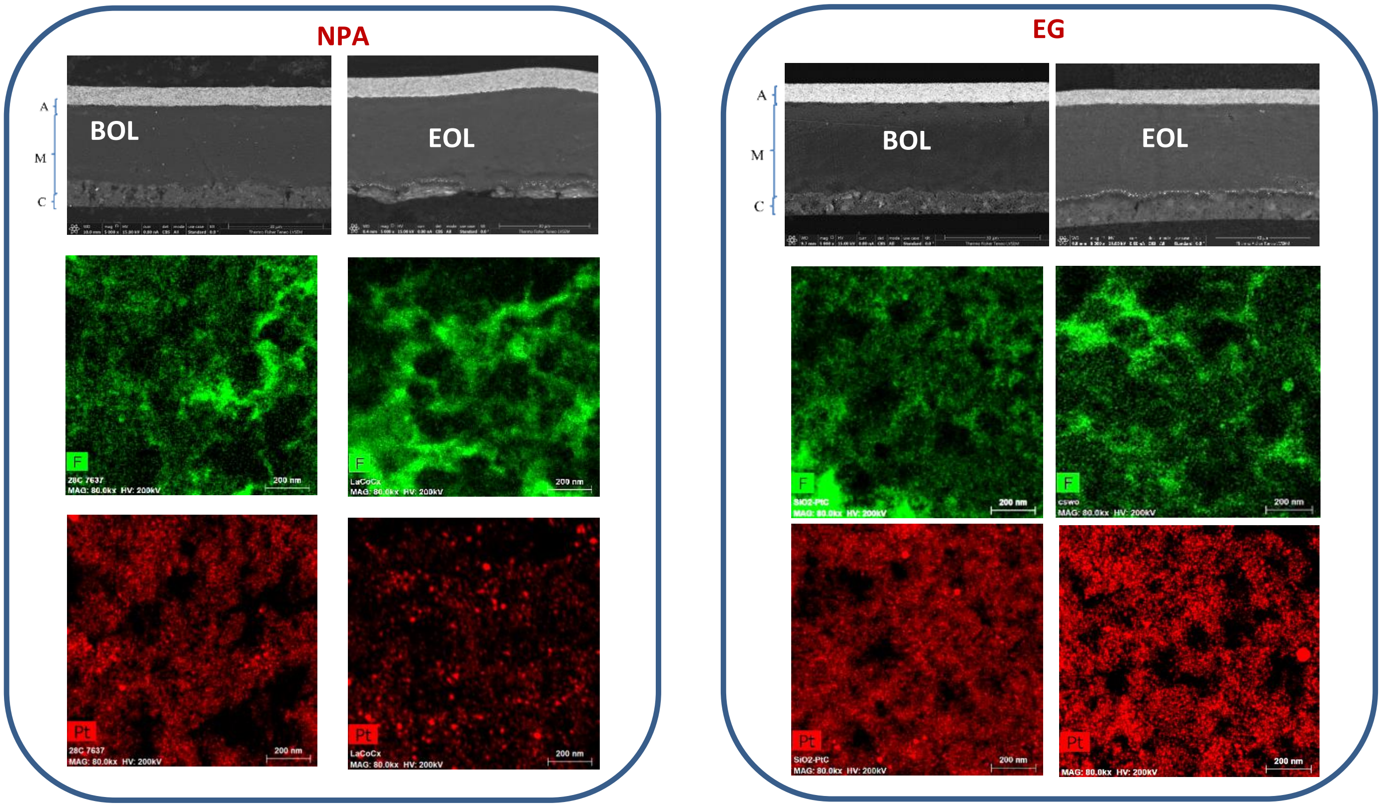
30,000 cycle 0.6-0.95 V Square Wave Accelerated Stress Test (30K SW AST)





- EG with Nafion overspray lost 40% of performance after 30k SWAST similar to NPA durability – testing methanol based Nafion overspray
- EG without Nafion overspray meets DOE mass activity durability target of a loss < 40%
- Sheet resistance of the NPA cathode increases from 0.135 Ω.cm^2 to 0.162 Ω.cm^2
- EG cathode has lower sheet resistance than NPA cathode: increases from 0.088 Ω.cm^2 to 0.096 Ω.cm^2

Accomplishment: Microstructural Analysis



- No thinning or structural damage observed in the EG catalyst layer
- NPA catalyst layer thins from 7.02±2.52 µm to 5.74±1.39 µm, i.e. 18% thinner
- Ionomer and platinum aggregation seen in both MEAs

Microstructural Analysis

	BOL Primary porosity	EOL Primary porosity	BOL Secondary porosity	EOL Secondary porosity	BOL PtCo Particle size (nm)	EOL PtCo Particle size (nm)	BOL Cobalt	EOL Cobalt
PtCo/NPA	39%	39%	46%	44%	6.25±1.86	9.04±3.93	0.0326	0.0151
PtCo/EG, without spray	55%	29%	24%	62%	3.42±1.10	5.58±1.83	0.0187	0.0129
PtCo/EG, with spray	54%	24%	30%	67%	3.30±1.09	5.50±1.67	0.0252	0.0110

- EG cathode’s lower secondary porosity may lead to higher mass transport losses
- Higher loss in primary porosity for EG cathode after durability test
- Significant porosity changes in EG cathodes vs no change in NPA cathode
- Similar particle size growth in all cathodes after durability test
- Lowest Cobalt loss of 30% in EG MEA without Nafion Overspray vs 53% for NPA MEA and 56% for EG MEA with Nafion Overspray

Accomplishment: Coating GDL with EG Ink

- Shifting from CCM to GDE for commercialization
- Tested on various GDL: 29 BC SGL, 22BB SGL and Freudenberg H23C8
- Variability in GDL hydrophobicity
- Variability in ionomer batch
- Ways to improve GDL coating
  - Mix NPA:EG to improve coating – poor performance
  - Air plasma GDL surface modification
  - Heat ink to 60 ℃
  - Treat GDL with NPA

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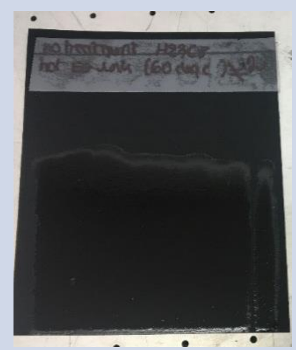
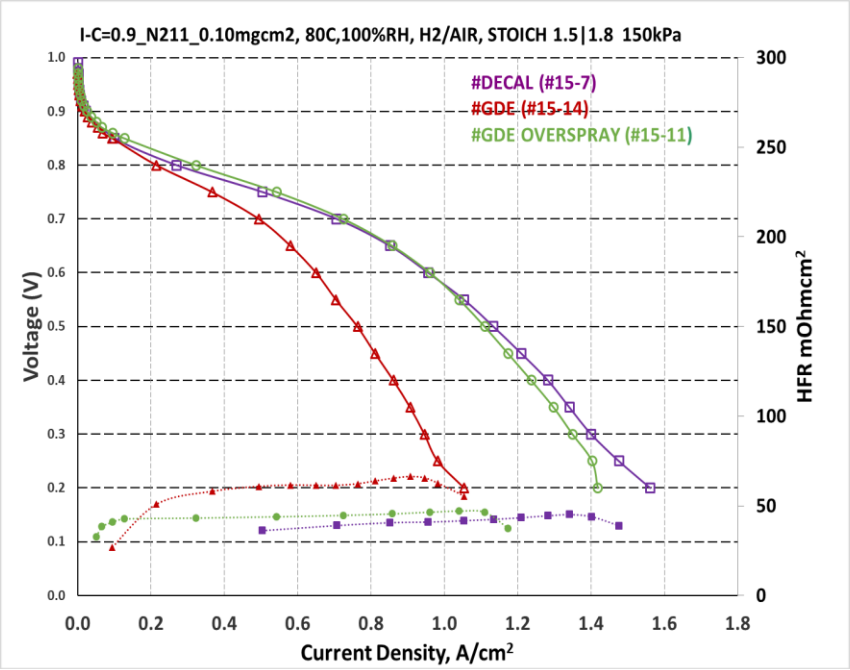
Coating Approaches on GDL H23C8

	NO treatment	GDL Plasma treatment	GDL NPA treatment	Heated ink (60 ℃)	Cooled ink from 60 ℃ to 25 ℃ (ambient)
Comment	H23C8 is not treated and EG ink is coated	Plasma treatment is applied prior to coating	NPA deposit on the GDL, drying for a few minutes at 60°C prior to coating	Ink is heated at 60°C during a few minutes and then coatde, **H23C8 is not treated**	Ink is heated to 60°C and then cooled down to 25°C prior to coating, **H23C8 is not treated**
Result	X Failed (no coating possible)	√ worked	√ worked	√ worked	√ worked
Pictures					

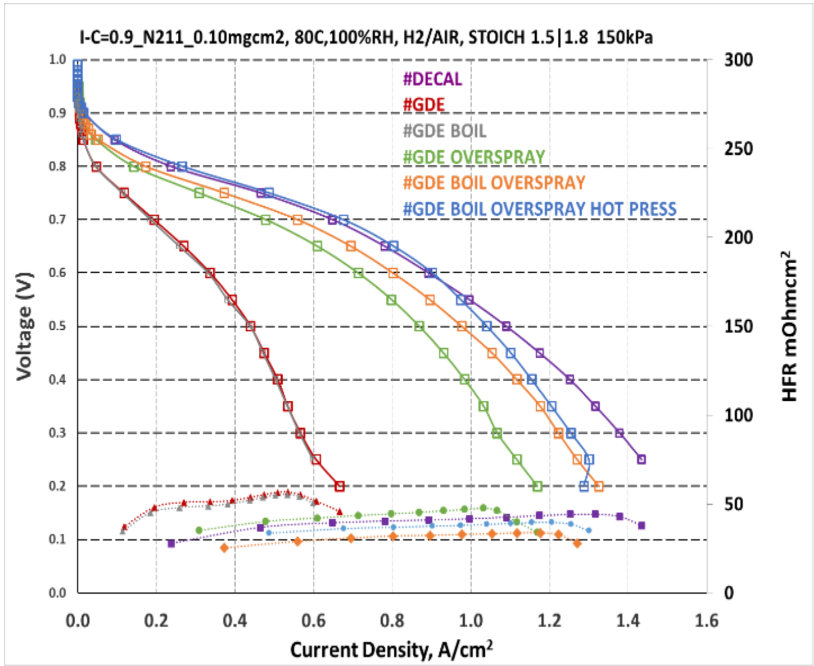
CCM vs GDE Performance

0.1 mg/cm² PtCo, 29 BC SGL, 25 cm²

NPA



EG NPA based Nafion Overspray



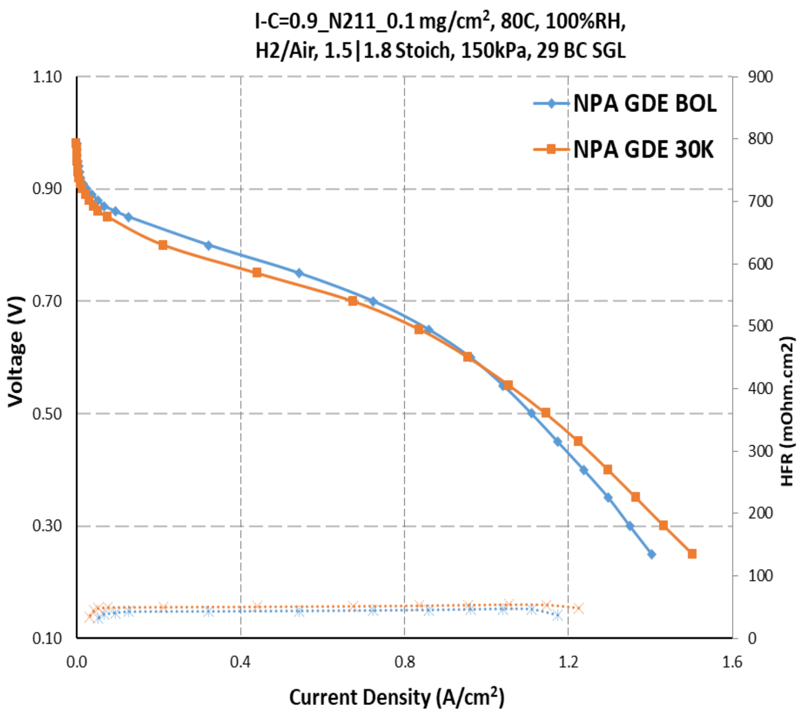
GDE proof of concept necessary for R2R production:

- NPA GDE performs similar to decal with just Nafion overspray
- EG GDE requires multi step process to match decal performance
  - Boiling + Nafion overspray + Hot pressing

R2R: GDE Durability

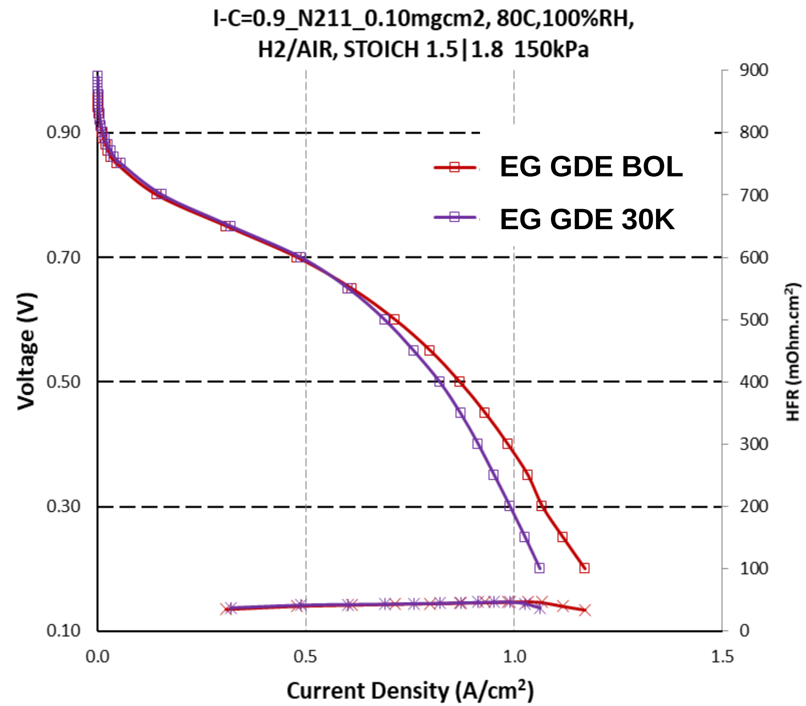
0.1 mg/cm^2 PtCo, 29 BC SGL, 25 cm^2

NPA



EG

NPA based Nafion Overspray

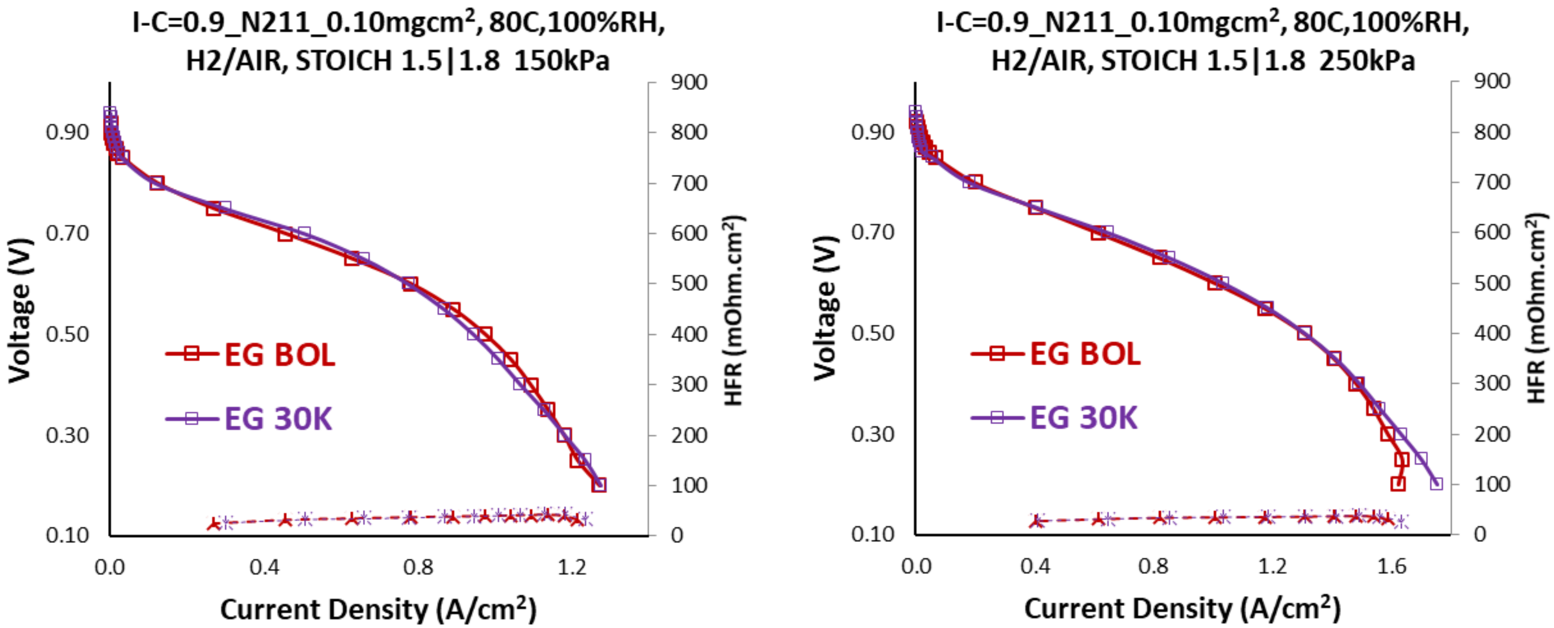


- GDE durability is different from decals: lower overall performance losses
- NPA MEA has higher losses at 0.8 V
- NPA GDE has higher sheet resistance than EG GDE, 0.26 Ω.cm^2 vs 0.21 Ω.cm^2

R2R: GDE Durability

0.1 mg/cm^2 PtCo, H23C8, 25 cm^2

EG <u>Methanol</u> based Nafion Overspray



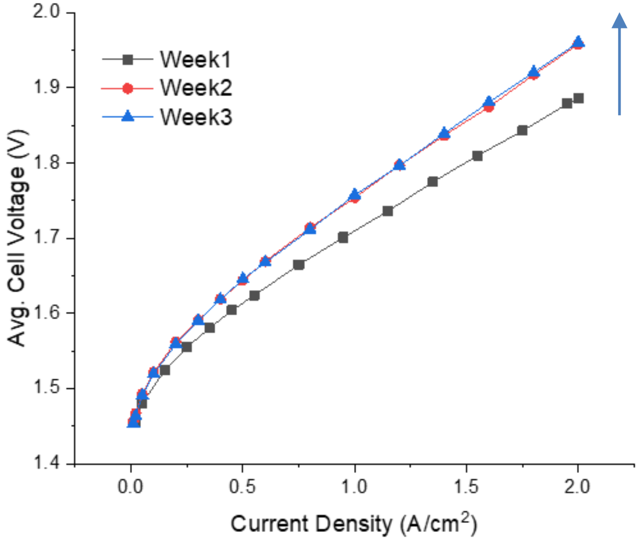
Freudenberg H23C8 with plasma treatment

- GDE durability is better than with NPA based Nafion overspray
- Almost no performance degradation at all
- Hot pressed half CCM and then mild hot pressing of GDE to half CCM

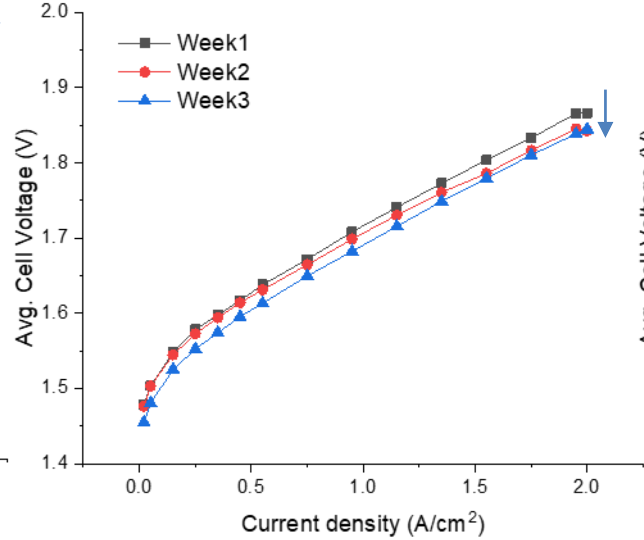
Accomplishment: Electrolyzer Performance

1 mg/cm² Ir Anode, 0.2 mg/cm² Pt/XC72 Cathode, 50cm²

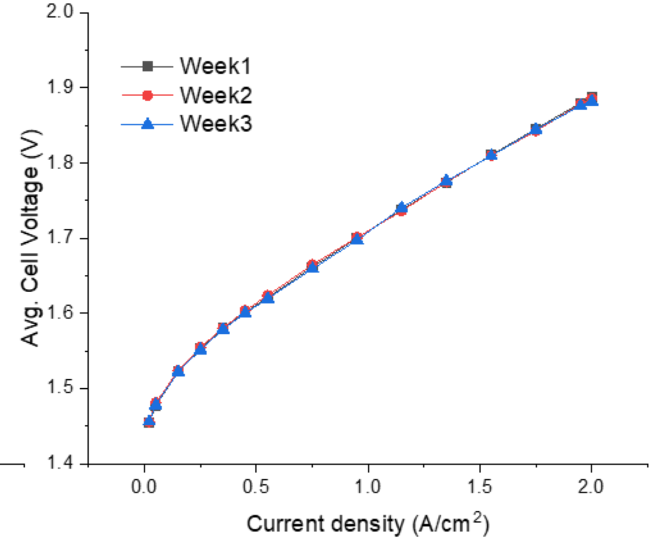
EG



H2O Rich



NPA Rich

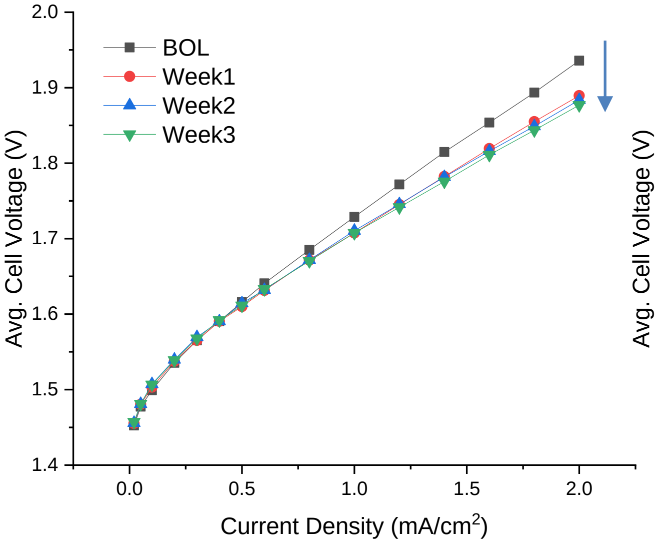


- 3 weeks at 3 A/cm² caused performance changes similar to conditioning
- No change was seen for the **NPA rich anode**
- Water rich anode improved; EG anode performance decreased

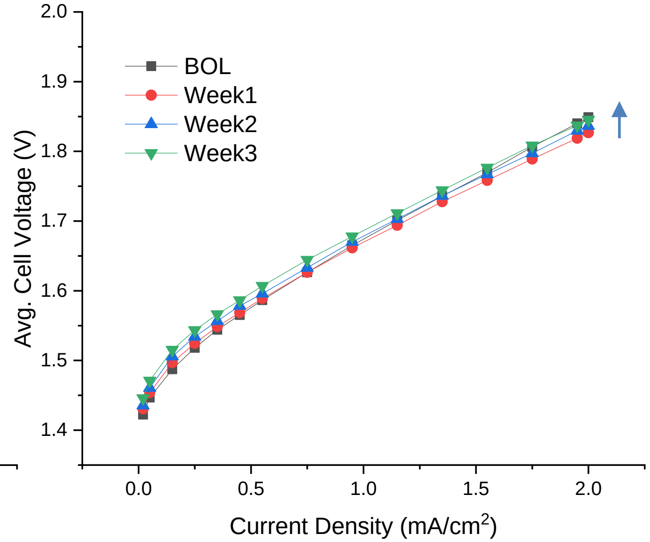
Electrolyzer Performance

1 mg/cm² IrOx Anode, 0.2 mg/cm² Pt/XC72 Cathode, 50cm²

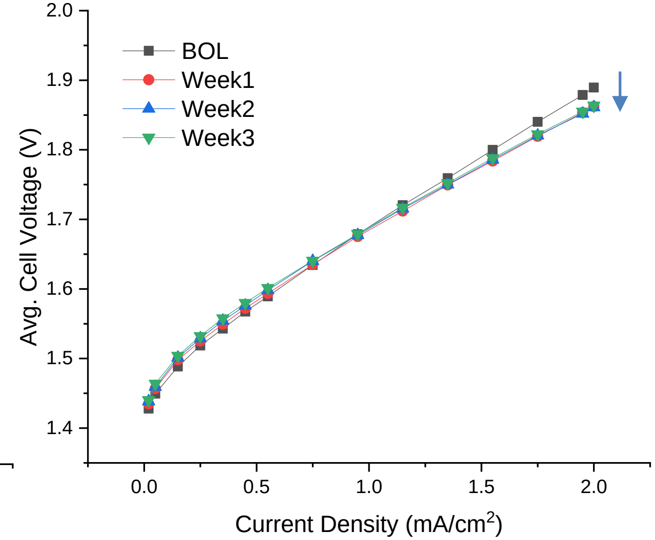
EG



H2O Rich



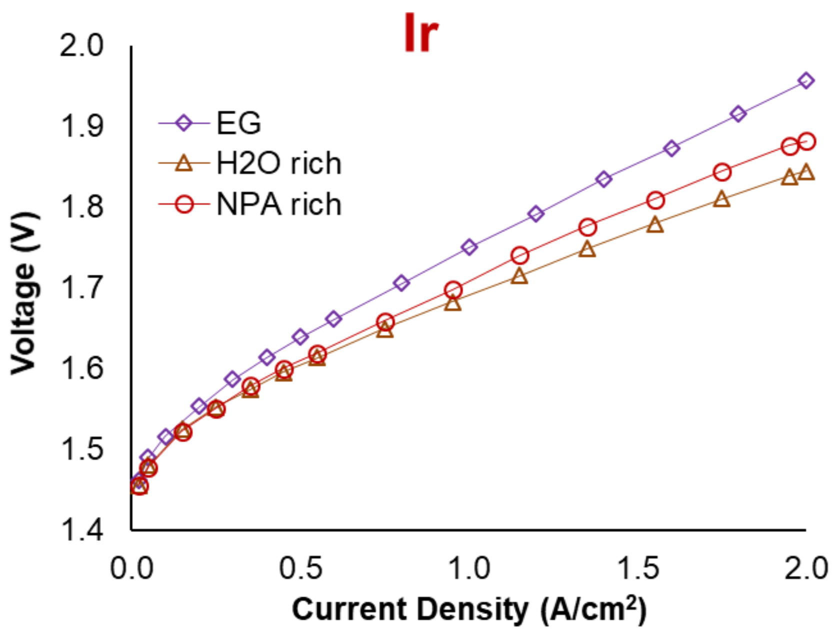
NPA Rich

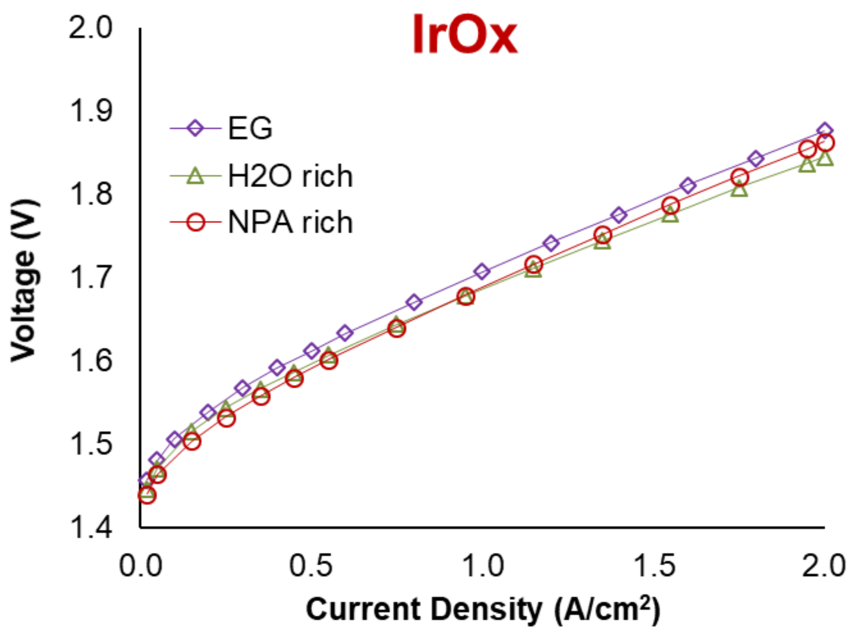


- 3 weeks at 3 A/cm² caused performance changes similar to conditioning
- NPA rich anode shows improvement
- Water rich anode improved but then decayed
- EG anode performance improves

Ir vs. IrOx Comparison

1 mg/cm² IrOx Anode, 0.2 mg/cm² Pt/XC72 Cathode, 50cm²





- Initial performance of IrOx samples are better than Ir black
- Performance: H_2O rich > NPA rich > EG
- For durability: move to lower loading of 0.1 mg/cm² Ir

R2R Plan with NREL

- Address EG's high boiling point
- Identify R2R parameters for EG ink
- NREL's experience with coating battery anodes made with NMP will help guide EG ink R2R fabrication process
  - Similar boiling point to EG
  - Use of 2 ovens: Prebake + Bake

Ink Formulation (**Giner**): send premixed ink and substrate material to NREL

Small scale trials (**NREL**)

– rod coating, SEM

Roll-to-Roll Coating (**NREL**)

- Corona treatment of GDL
- Tuning of coating speed and flow rate
- Variations in ink formulation & drying process
- Inspection of coating quality – optical or SEM

Send **1 m^2** coated GDE from NREL to Giner for in-situ testing

NREL
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Collaboration and Coordination

- **Giner (Lead):** Hui Xu, Natalia Macauley, Magali Spinetta, and Shirley Zhong. Oversee the entire project management, catalyst ink rheology, electrode design and scale-up, and MEA commercialization
- **LANL (Subcontractor):** Yu Seung Kim. Provide ionomer dispersions in EG and Methanol, and SANS measurements of Nafion
- **NREL (Subcontractor):** Scott Mauger. Optimize R2R conditions for GDE fabrication
- **UConn (Collaborator):** Jasna Jankovic. Perform microstructure analysis with SEM and TEM: ionomer, Pt, Co distributions and particle size changes from BOL to EOL

Responses to Previous Year Reviewers' Comments

This project was not reviewed in 2019

Conclusions

- Rheology, zeta potential and laser diffraction was used to characterize catalyst inks for ink quality
- Average performance of EG MEA without Nafion overspray is similar to NPA baseline MEA performance
- EG MEA with Nafion overspray outperforms NPA Baseline MEA
- Durability of EG MEA without Nafion overspray is better than that of NPA
- Better MEA durability of EG GDE compared to NPA GDE seen at low voltages
- Methanol based Nafion overspray results in highly stable EG MEA
- Catalyst microstructure agrees with observed performance in PtCo catalysts with NPA vs EG solvents
- NPA based electrolyzer anodes perform better than EG based anode
  - Non uniform microstructure of EG based Ir anode in good agreement with observed performance

Future Work

Fuel Cell

- Establish performance and durability of EG vs NPA GDEs on H23C8
- Finalize TSA with NREL and send EG ink for initial coating tests
- Local oxygen resistance of EG vs NPA GDEs
- Evaluate microstructure difference between GDEs in NPA vs EG solvent

Electrolyzer

- Perform electrolyzer durability test on 0.1 mg/cm^2 Ir NPA rich and EG MEA to evaluate EG's durability advantage
  - 1.45 – 2.0 V square wave with 30s dwell time
- Microstructure analysis on degradation process of low loaded anodes
- Follow iridium dissolution during AST using ion chromatography

Acknowledgements

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  - Ms. Donna Ho
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- Dr. Jasna Jankovic at UConn