Novel Fluorinated Ionomer for PEM Fuel Cells

Hui Xu (PI)

Team: N. Macauley, M. Spinetta, S. Zhong, F. Yang, D. Lousenberg,
H. Murnen, J. Jankovic, S. Pedram, I. Zenyuk, Y. Qi

Giner Inc.
Newton, MA

Project ID #
FC328

Project Overview

Timeline

- Project Start Date: 5/28/2019
- Project End Date: 5/27/2021

Budget

- Total Project Value: $ 1 Million
- Spent: $ 394k

Collaborators

- Compact Membrane Systems, Inc.
- University of Connecticut
- University of California Irvine

Barriers Addressed

- PEM fuel cell transport loss at low Pt and high power

Technical Targets

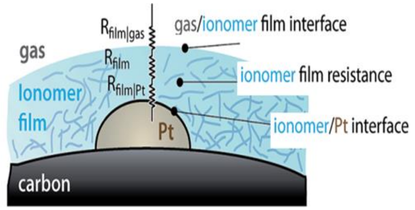
Develop next generation of fluorinated ionomers for PEM fuel cell cathodes to reduce local transport loss

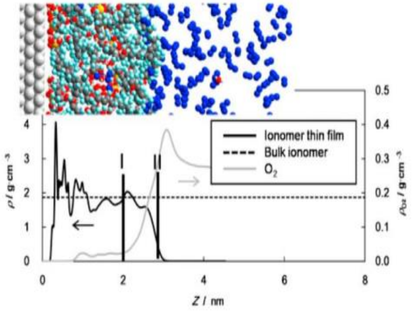
- Improve O_2 permeability by 5x
- Increase polymerization scale by 10x per batch
- Evaluate fuel cell performance, durability and local transport resistance

Relevance

DOE Fuel Cell Catalyst Technical Targets

Characteristic	Units	2015 Status	2020 Targets
Platinum group metal total content (both electrodes)[a]	g / kW (rated,[b] gross) @ 150 kPa (abs)	0.16[c,d]	0.125
Platinum group metal (pgm) total loading (both electrodes)[a]	mg PGM / cm^2 electrode area	0.13[c]	0.125
Mass activity[e]	A / mg PGM @ 900 $mV_{iR\text{-}free}$	>0.5[f]	0.44
Loss in initial catalytic activity[e]	% mass activity loss	66[c]	<40
Loss in performance at 0.8 A/cm^2[e]	mV	13[c]	<30
Electrocatalyst support stability[g]	% mass activity loss	41[h]	<40
Loss in performance at 1.5 A/cm^2[g]	mV	65[h]	<30
PGM-free catalyst activity	A / cm^2 @ 0.9 $V_{IR\text{-}free}$	0.016[i]	>0.044[j]



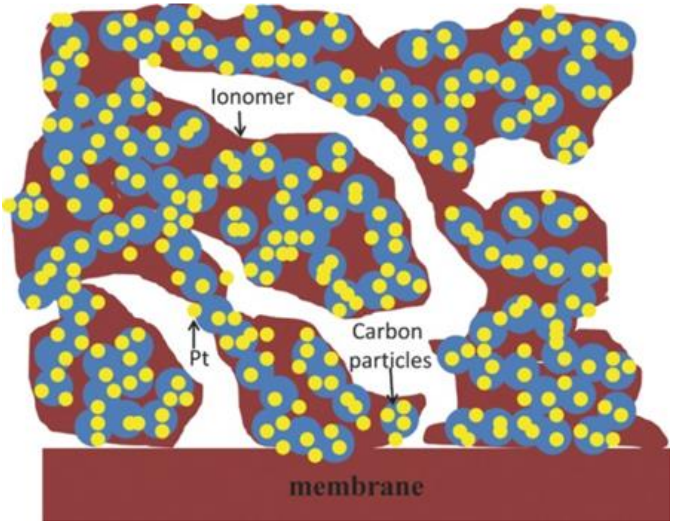


- **Electrode design is crucial to maximize the catalyst performance**
- Thin ionomer film formed in ultra-low Pt electrodes
- High local oxygen transport resistance due to thin ionomer film surrounding Pt particles
- Inferior performance at low-Pt loading due to local oxygen transport resistance

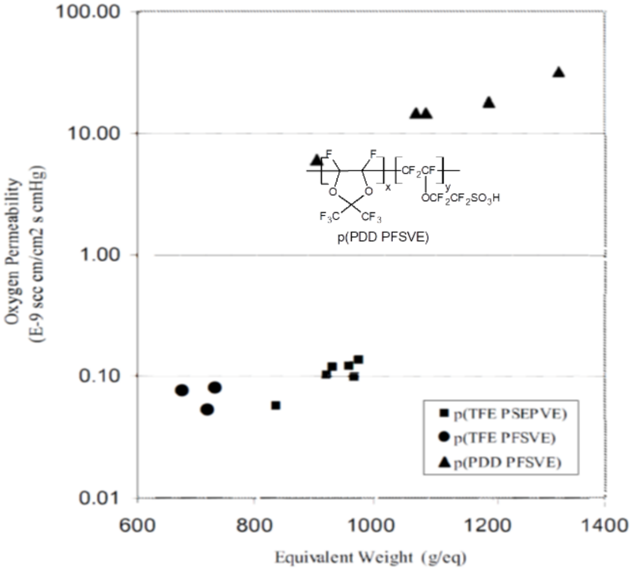
GOAL: Increase ionomer permeability to reduce local oxygen transport resistance

Kongkanand and Mathias, J. Phys. Chem. Lett. 7, 1127 (2016); Easterman et al, Macromolecules, 45, 7920 (2012)

Approach



Cathode with ionomer layer



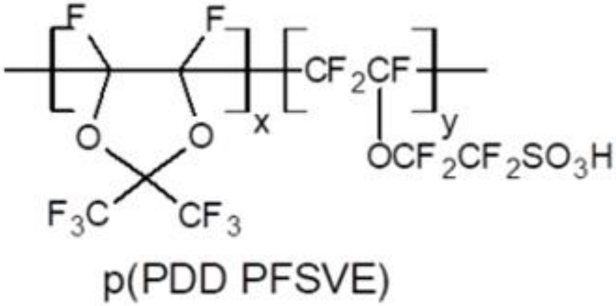
Dry O_2 permeability of PDD copolymers vs. p(TFE PSEPVE) "Nafion®" or p(TFE PFSVE) "Aquivion®"

Amorphous ionomers (fluoropolymers) that are highly conductive like Nafion® but also have higher free volume may enhance oxygen permeance to the PGM catalyst and improve overall PEMFC cathode kinetics

Accomplishment: Develop Ionomer and Scale-up

GOAL: Higher ionomer oxygen permeability at lower equivalent weight

Fluoro-ionomers comprising perfluoro-2,2-dimethyl-1,3-dioxole (PDD) were known to have higher **dry** O_2 permeability from increased free volume imparted by the PDD repeat unit.

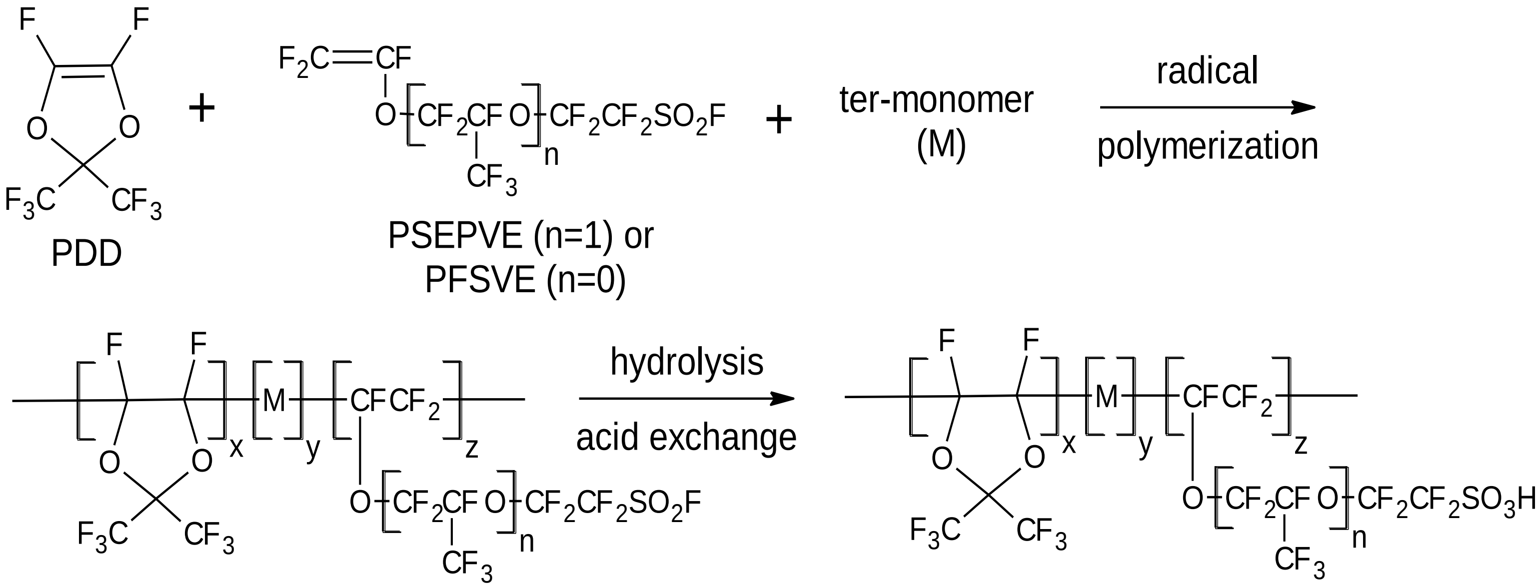


- Synthesize and characterize new fluorinated amorphous ionomers with varied composition, EW, and molecular weight
    - Measure humidified oxygen permeability
    - Measure ionomer conductivity
    - Perform fuel cell testing

- Scale up the most promising high-PDD content ionomer

R. L. Perry, M. G. Roelofs, R. C. Wheland, R. M. Aten, Ionomers and Ionically Conductive Compositions. *United States Patent Application 20130245219 A1* **2013**

Ionomer Synthesis Route

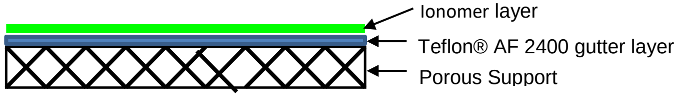


Copolymerization of PDD, PFSVE (or PSEPVE), **and** a ter-monomer (M) for higher molecular weight (intrinsic viscosity) and better film-forming properties at low equivalent weight (EW)

Oxygen Permeability Measurement

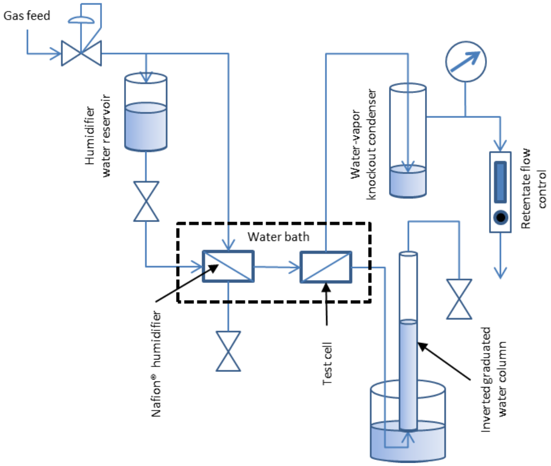
O_2 permeability from dilute solution casting on a high-permeance support to form a thin ionomer layer

- Thin ionomer layers (<5-µm) have realistically measurable gas fluxes over practical and manageable areas
- Gravimetric and helium permeability estimation of ionomer layer thicknesses
- Support + gutter layer resistance << ionomer layer resistance



Permeance testing design features

- Temperature-controlled water bath for consistent humidification (≥95% RH) and cell temperature
- Graduated and inverted water column for very low permeate-flow measurement by displacement



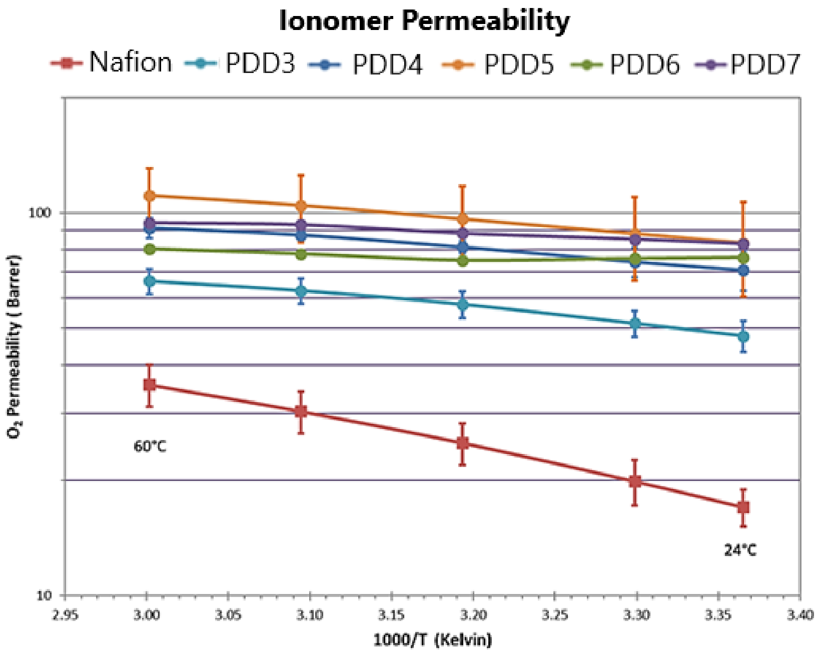
Ionomers Comprising PDD

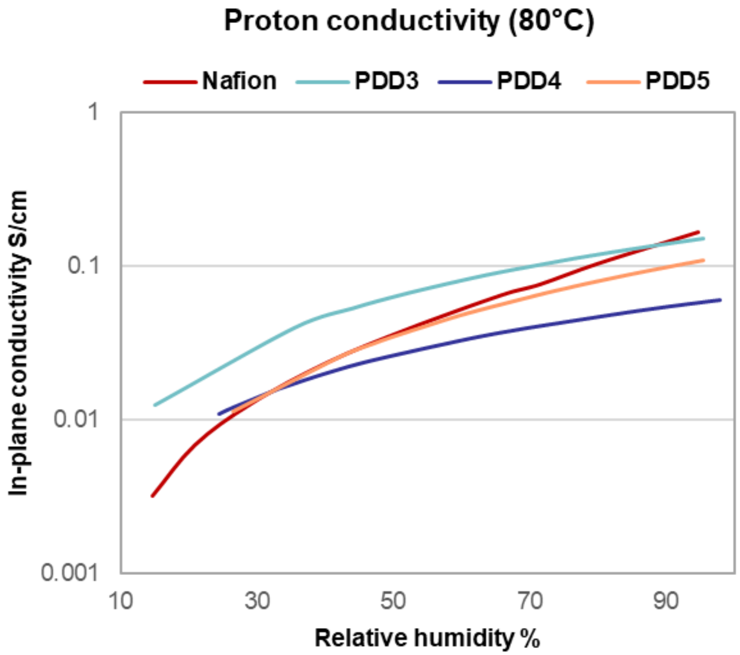
- Explored multiple variations of PDD content and equivalent weight
- Relative molecular weight (M_v) characterization through intrinsic viscosity (η) of copolymers prior to hydrolysis ($\eta \sim M_v^{0.5}$ in theta solvent systems)
- Equivalent weight measurement by titration after hydrolysis

Ionomer	Composition	Estimated PDD content (mole%)	EW (g/mole)	Intrinsic Viscosity (dL/g)	O_2 Permeability (Barrer)	
					24°C	60°C
PDD3	PDD/PFSVE/M	62 – 68	754	0.20	48	66
PDD4	PDD/PFSVE/M	67 – 73	863	0.31	71	91
PDD5	PDD/PFSVE/M	67 – 73	859	0.31	84	111
PDD6	PDD/PFSVE/M	70 – 76	953	0.20	77	81
PDD7	PDD/PFSVE/M	70 – 76	951	0.38	85	94
Nafion™ (control)	PSEPVE/TFE	0	930	n/a	17	36

High PDD content (low M) required for O_2 permeability significantly higher than Nafion™

O_2 Permeability and Proton Conductivity


Ionomer Permeability

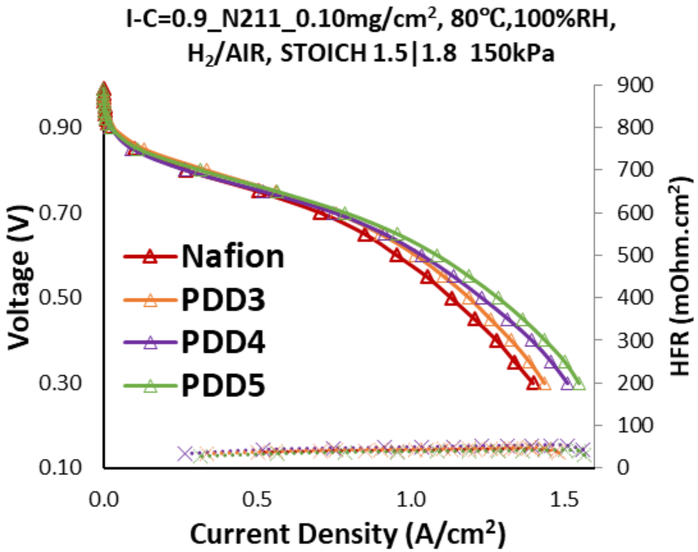

Proton conductivity (80°C)

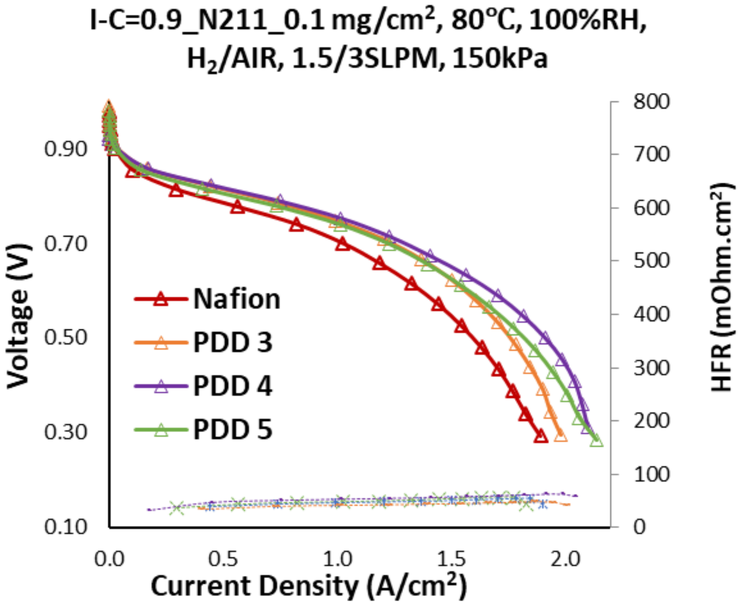
Permeability improvement vs Nafion

T (°C)	PDD 3	PDD 4	PDD 5	PDD6	PDD7
24	3x	**4x**	**5x**	**5x**	**5x**
60	2x	3x	3x	2x	3x

- PDD5, PDD6 and PDD7 display **5x** the permeability of Nafion
- PDD3 has higher conductivity than Nafion
  - Lowest equivalent weight

Accomplishment: PtCo/HSC Performance

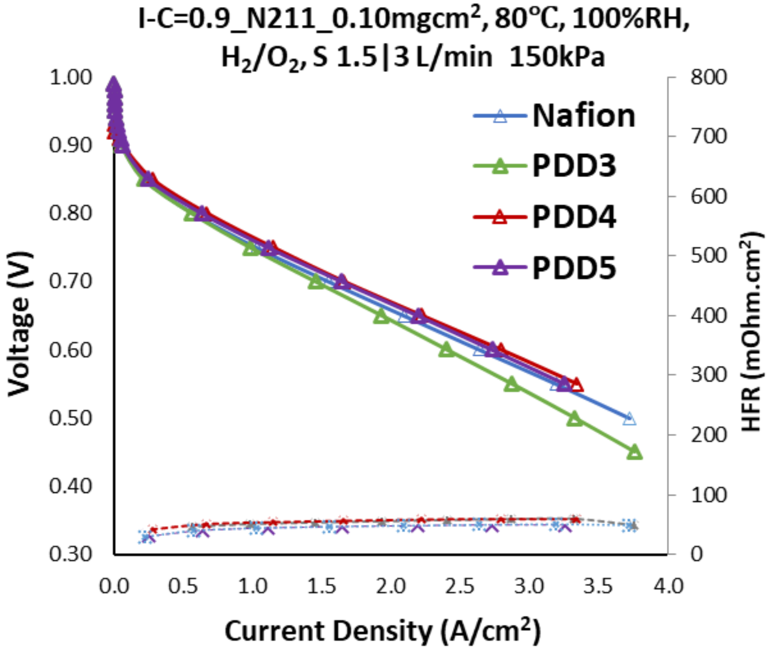

I-C=0.9_N211_0.10mg/cm², 80°C,100%RH, H_2/AIR, STOICH 1.5|1.8 150kPa

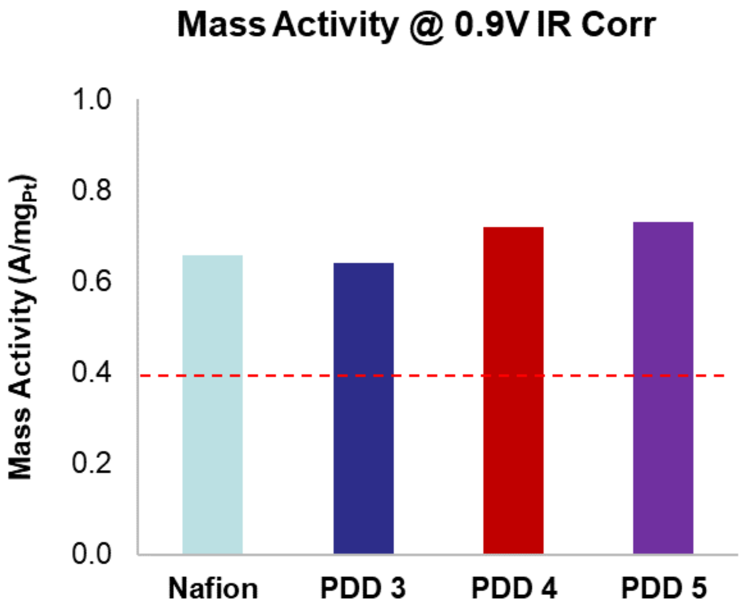

I-C=0.9_N211_0.1 mg/cm², 80°C, 100%RH, H_2/AIR, 1.5/3SLPM, 150kPa

- All PDD MEAs outperform Nafion in the high current density region in good agreement with ionomer permeability values at 60°C
- MEA PDD5 has highest performance with stoichiometric flows; PDD5 has higher permeability & conductivity than PDD4
- MEA PDD4 shows highest performance with fixed flows; may be correlated with 10% higher secondary porosity
- MEA PDD3 has low high current density performance due to low EW = more SO_3^- groups attract water making ionomer swell and causing mass transport resistance

PtCo/HSC H_2/O_2 Performance and Mass Activity

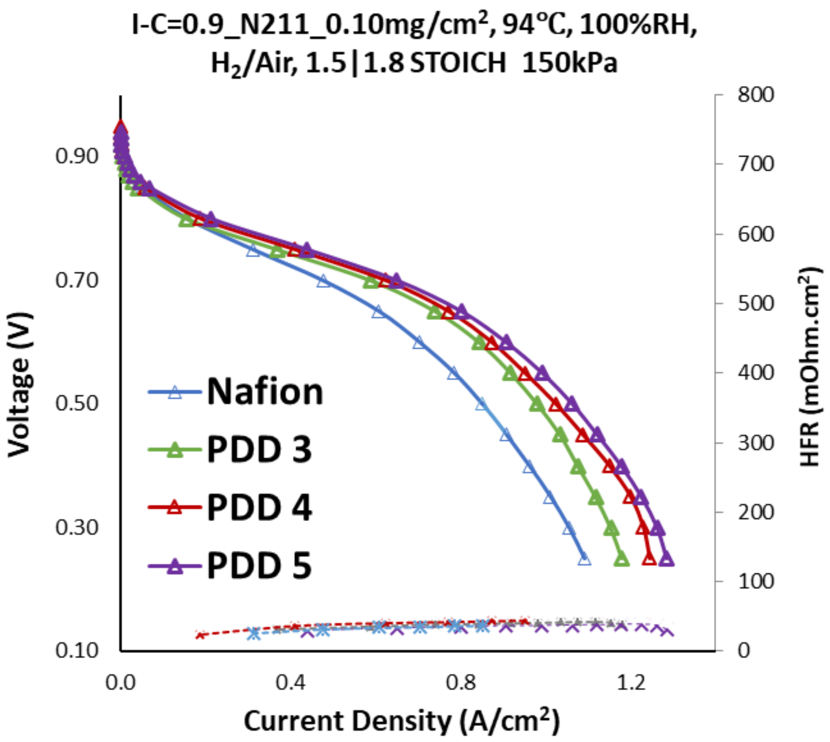
25 cm^2 and 29BC SGL GDL





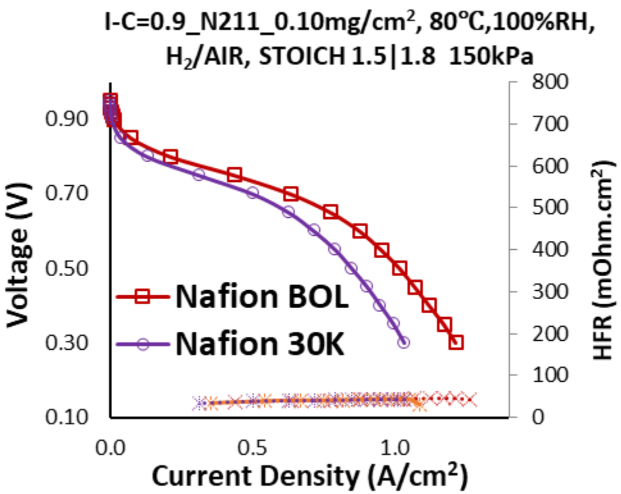
- MEAs **PDD4** and **PDD5** show improved performance in oxygen and higher mass activity vs. Nafion
- Differences in the triple phase boundaries, and Pt accessibility for O_2
- MEA **PDD3** has lowest MA and oxygen performance

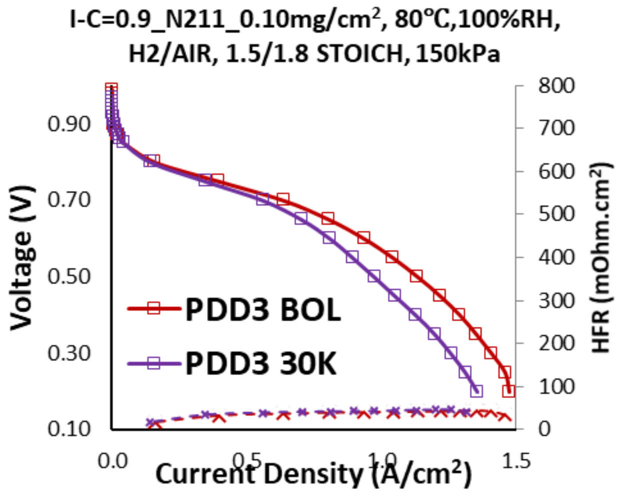
PtCo/HSC 94℃ 100% RH Performance

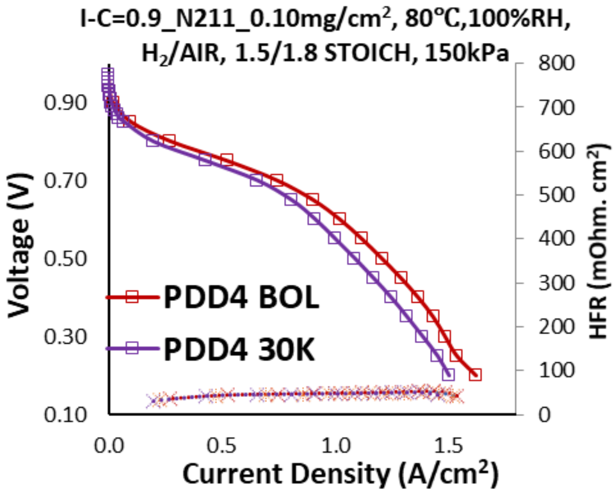


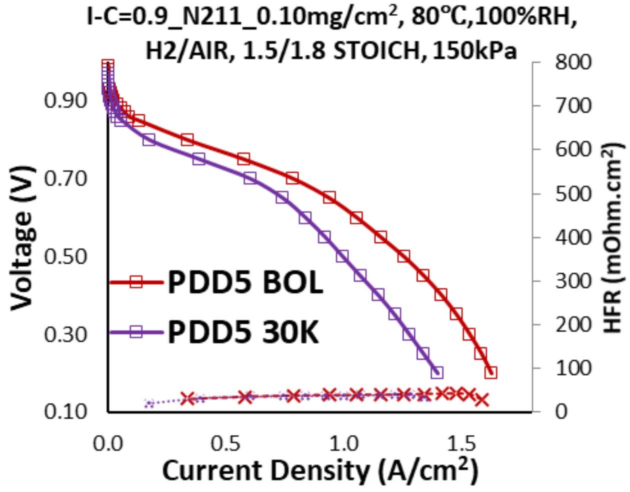
- MEA performance is worse at 94 °C than at 80 °C for all MEAs
  - Ionomers may have different water uptake capability in ionomer film at 94 °C than at 80 °C
- All PDD MEAs outperform Nafion MEA
  - PDD structure with bulky molecule in the backbone poses an advantage at high temperatures leading to even better performance of PDD MEAs vs Nafion MEA at 94 °C
  - PDD ionomers may hold more water due to lower EW
- At 94 °C MEA PDD5 performs better than MEA PDD4
  - Produced in different solvent (NPA vs IPA)
  - NPA dries faster than IPA
  - May have slightly different pore structure

PtCo/HSC Durability in 30K Square Wave AST


I-C=0.9_N211_0.10mg/cm², 80℃,100%RH, H₂/AIR, STOICH 1.5|1.8 150kPa

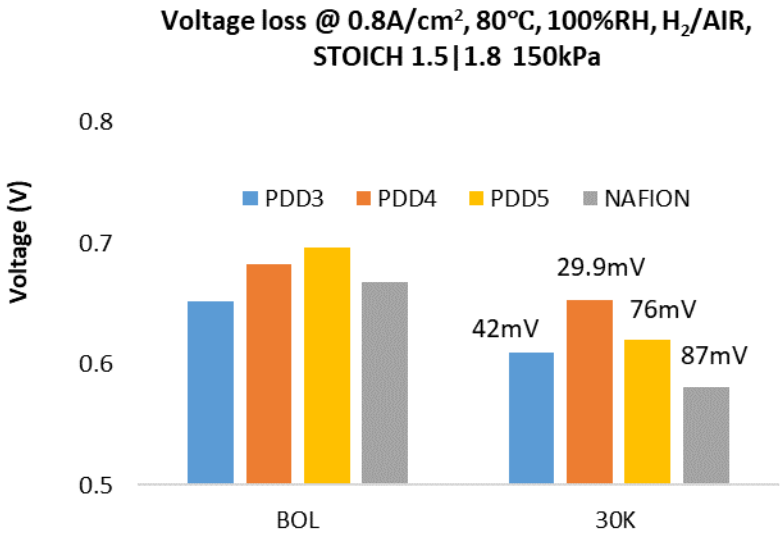

I-C=0.9_N211_0.10mg/cm², 80℃,100%RH, H2/AIR, 1.5/1.8 STOICH, 150kPa

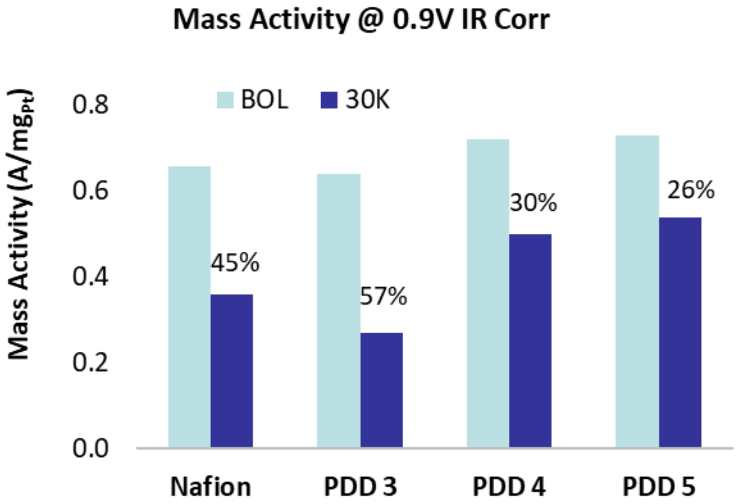

I-C=0.9_N211_0.10mg/cm², 80℃,100%RH, H₂/AIR, 1.5/1.8 STOICH, 150kPa


I-C=0.9_N211_0.10mg/cm², 80℃,100%RH, H2/AIR, 1.5/1.8 STOICH, 150kPa

- **PDD4** MEA displays best durability
- MEA **PDD3** shows performance loss high current density region
- MEA **PDD5** shows performance loss in low and high current density region

PtCo/HSC Durability w Nafion vs PDD

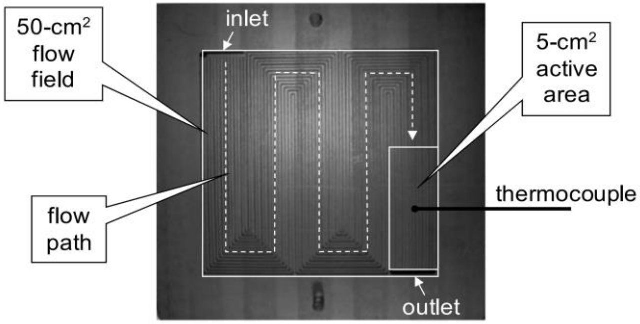

Voltage loss @ 0.8A/cm^2, 80℃, 100%RH, H_2/AIR, STOICH 1.5|1.8 150kPa

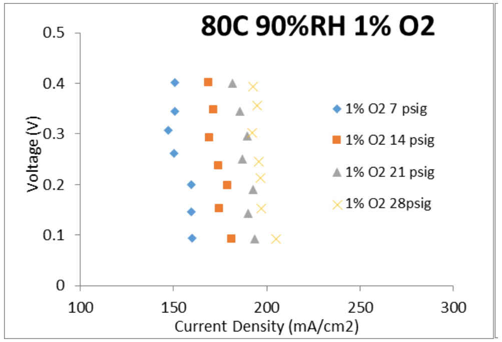

Mass Activity @ 0.9V IR Corr

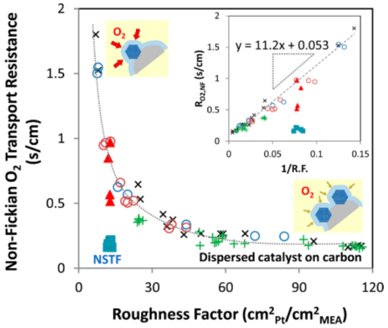
- MEA **PDD**4 displays **30 mV** performance loss 0.8 A/cm^2 meeting DOE durability target
- MEAs **PDD4** and **PDD5** meet DOE mass activity durability target < 40%
- MEA **PDD4** lost 86 mV at 1.5 A/cm^2 not meeting DOE target of < 30mV yet

Accomplishment: Isolate Local O_2 Transport Resistance

$5cm^2$ GM Differential cell







Baker et al, J. Electrochem. Soc. 156, B991 (2014)

- A limiting current approach was used to measure the transport resistance.

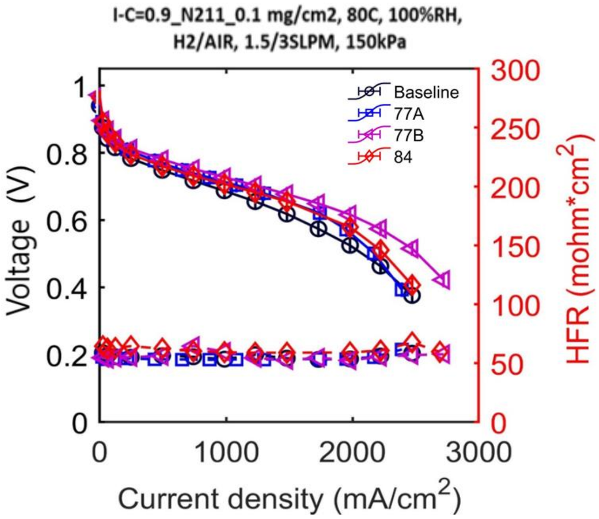
$$R_T = Rch + R_{DM} + R_{MPL} + R_{other}$$

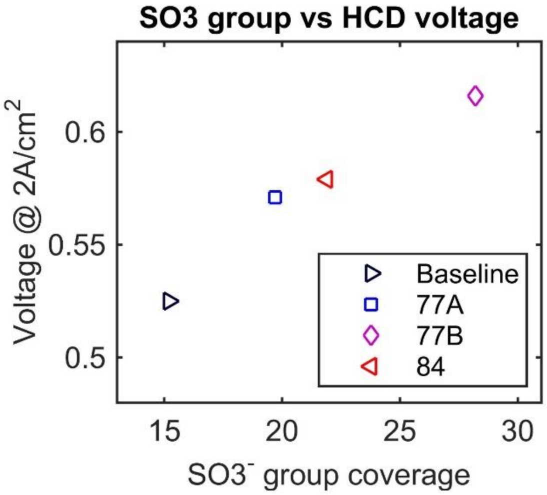
- 1%, 2% and 4% O_2 balanced with helium and variety in oxygen partial pressure was used to analyze the transport resistance from various sources
- Current densities at 0.2 V were used for local oxygen transport analysis

Pt/Vulcan	Nafion	PDD4
RO_2 NF BOL (s/cm)	0.2096	0.0913

- **PDD4** has **2x lower local O_2** resistance than Nafion
- Bulky PDD molecule may create void space for O_2 transport
- Absence of micropores in the carbon

Accomplishment: SO_3^- Group Coverage





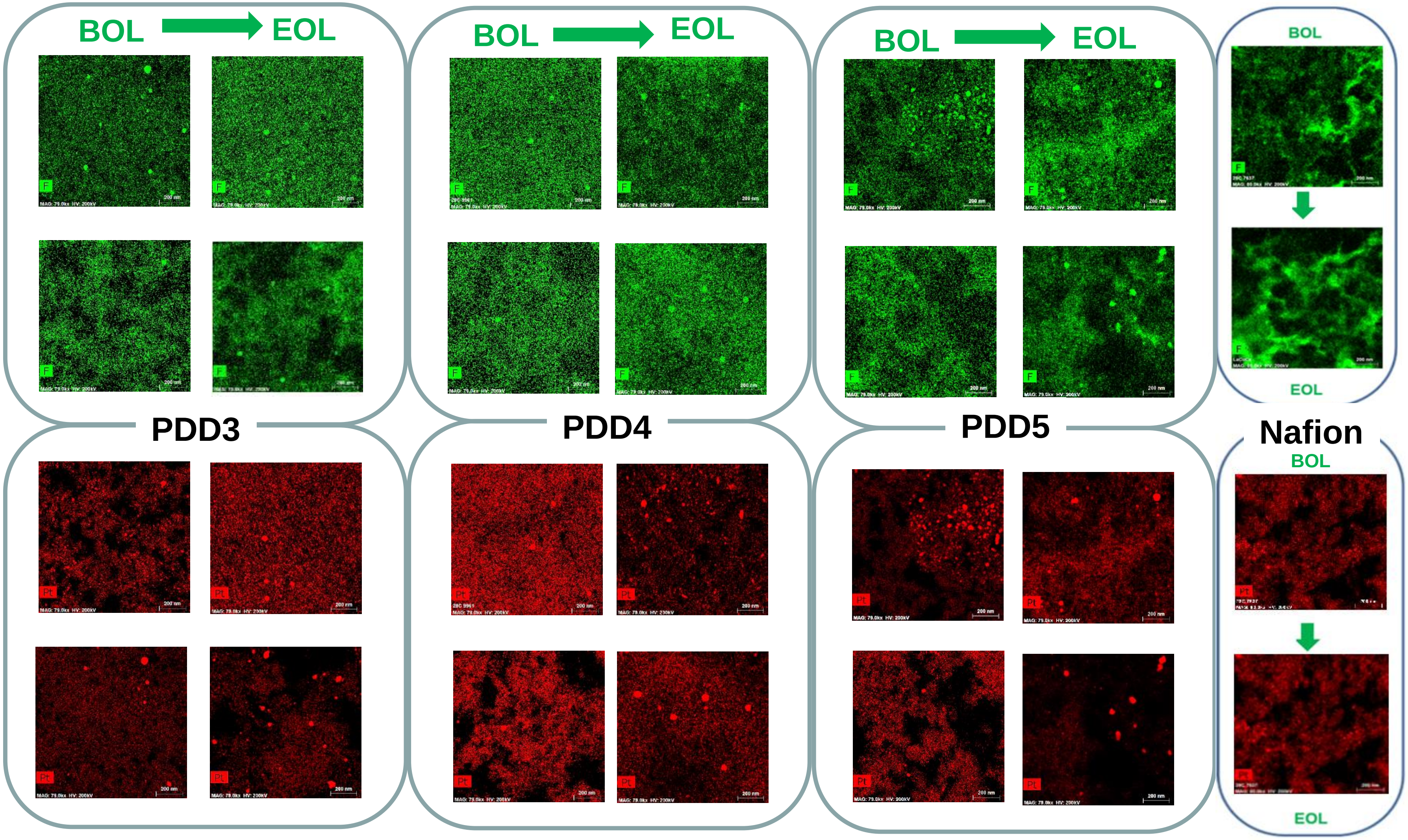
- Calculated using charge transfer theory which is based on CO replacing the SO_3^- groups adsorbed on Pt particles

$$\theta_{SO\_3^-} = \frac{2*displacement\ charge}{Stripping\ charge} * 100\%$$

- SO_3^- group coverage should correlate with RO_2 local – ionomer backbone near Pt surface can block O_2 transport – also depends on number of mesopores vs micropores vs macropores because ionomer cannot enter micropores smaller than 2 nm …. Relevant for high surface area carbon
- Increasing SO_3^- group coverage correlated well with high current density performance – linked to RO_2 transport & hydration
- Nafion has higher EW than both PDD4 and PDD5 and therefore lower SO_3^- group coverage

Accomplishment: Ionomer and Pt Distribution

BOL = Beginning of Life **EOL = End of Life**



- All MEAs have regions with non-uniform ionomer distributions at BOL and EOL
- Ionomer and Pt distributions become more agglomerated and non-uniform at EOL
- **PDD3** and **PDD5** display more visible agglomeration at BOL

MEA Microstructure Comparison

Sample ID	Primary porosity	Secondary porosity	Total porosity	Pt loading (mg/cm^2)	Pt/Co Atomic	Average Particle size (nm)	Co count
PDD3 BOL	37%	47%	84%	0.08	7.91	3.13±1.07	0.008
PDD3 EOL	37%	45%	82%	0.05	14.48	4.63±1.15 **(+48%)**	0.005 (-37%)
PDD4 BOL	25%	**64%**	89%	0.07	8.43	3.98±1.25	0.007
PDD4 EOL	36%	47%	83%	0.05	16.99	4.43±1.04 (+11%)	0.004 (-43%)
PDD5 BOL	28%	53%	81%	0.06	5.73	3.69±1.31	0.01
PDD5 EOL	24%	44%	69%	0.05	14.11	4.72±1.17 (+28%)	0.005 (-50%)
Nafion BOL	39%	45%	85%	0.1	6.3	6.25±1.86	0.0326
Nafion EOL	39%	44%	83%	0.06	19.5	9.04±3.93 (+45%)	0.015 **(-53%)**

- MEA **PDD4** has the highest secondary porosity of 64% and best performance
- MEA **PDD5** has the highest porosity loss
- MEA **PDD3** has the highest particle size growth and highest mass activity loss of 57%
- MEA **PDD4** has the smallest particle size growth and lowest mass activity and performance loss
- Cobalt leaching is evident from the increase in Pt/Co atomic ratio after degradation
- Nafion MEA lost the most cobalt from catalyst layer of 53% and has of 82 mV at 0.8 A/cm^2

Collaboration and Coordination

Giner (Lead): Hui Xu, Natalia Macauley, and Shirley Zhong: Oversee the project direction and progression. Electrode design and data analysis, and MEA commercialization.

CMS (Subcontractor)**:** Dan Lousenberg. Synthesize ionomer samples and provide ionomer permeability data.

UCI (Subcontractor): Iryna Zenyuk**.** Analyze ionomer and SO_3^- group coverage, and O_2 transport resistance.

UConn (Subcontractor): Jasna Jankovic. Perform microstructure analysis with SEM and TEM.

Responses to Previous Year Reviewers' Comments

This project was not reviewed in 2019

Summary

- ☐ Novel PDD ionomers with 2-5x higher O_2 permeability than Nafion have been synthesized
- ☐ PDD ionomers show fuel cell performance and durability improvement compared to Nafion
- ☐ PDD ionomers show 2x lower local transport resistance than Nafion
  - DOE Mass Activity and Durability targets met with PDD Ionomers
- ☐ PDD ionomers in catalyst layers has more SO_3^- groups in contact with Pt than Nafion
- ☐ Microstructural analysis is in agreement with performance and durability results in porosity changes, Pt and Co loss

Future Direction

- ☐ **Performance Improvement**
  - Use higher quality membranes from 3M
    - 15 µm supported membrane with doped Ce
    - 20 µm unsupported membrane
  - Further optimize I/C ratio to better suit PDD ionomer
  - Adopt advanced flow field and GDL
- ☐ **Understanding ionomer durability**
  - Detect fluoride emission rate from ionomer during AST with ion chromatography by use of hydrocarbon membrane
  - NMR: Fenton's test to identify ionomer breakage point
- ☐ **Evaluate MEAs by OEMs and FC-PAD**
  - Send 50-100 cm^2 MEAs with best ionomer
  - Extensive and harsh FC vehicle operation conditions (Transients, Sub-freezing operations)
  - FC-PAD for ionomer/MEA evaluation
- ☐ **Commercialization Strategies**
  - License ionomer technology to provide products to fuel cell and other community
  - Utilize CMS ionomer for Giner's products

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

Acknowledgments

- Financial support from DOE SBIR/STTR Program under award DE-SC001859

- Technical Manager
  - Dr. Dimitrios Papageorgopoulos

- Collaborators
  - Jasna Jankovic (Univ. of Connecticut)
  - Iryna Zenyuk (Univ. of California, Irvine)
  - Hannah Murnen and Dan Lousenberg (CMS)
  - General Motors (flow field to measure local O_2 transport resistance)