



Rensselaer

Novel Fluorinated Ionomer for PEM Fuel Cells

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This presentation does not contain any proprietary or confidential information

Project Overview

Timeline

- Project Start Date: 4/9/2018
Project End Date: 1/8/2019

Budget

- Total Project Value:
\$150 K

Collaborator

- Prof. Chulsung Bae (RPI)

Barriers Addressed

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

Technical Targets

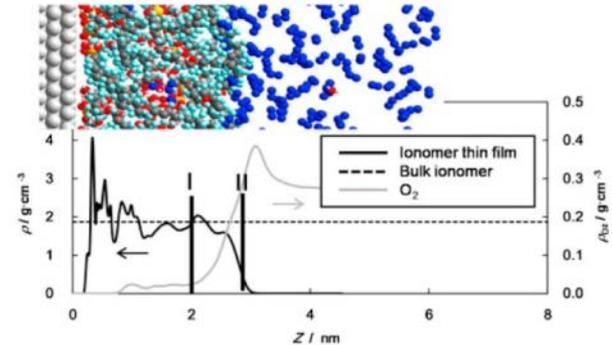
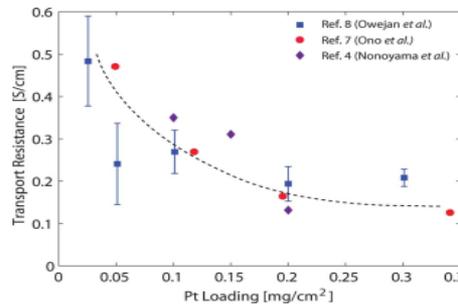
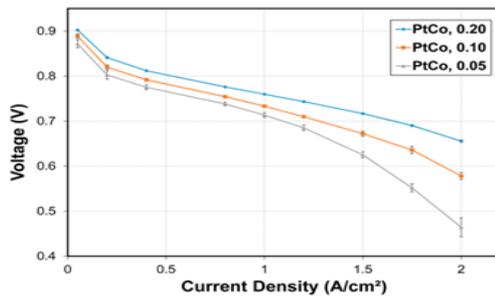
Design and synthesize novel fluorinated ionomer for PEM fuel cell cathodes to lower local transport loss

- Design fluorinated Ionomer exclusively for PEM fuel cell electrodes
- Evaluate fuel cell performance and local transport resistance using developed ionomer, under low Pt and high power operation

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-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-free}	0.016 ⁱ	>0.044 ^j

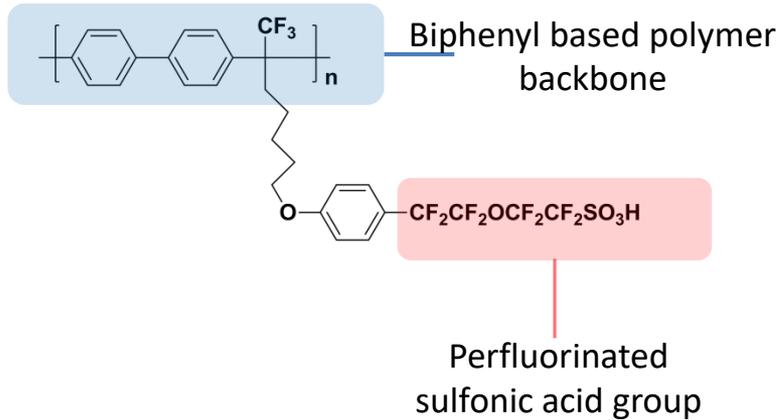


Kongkanand and Mathias, *J. Phys. Chem. Lett.* **7**, 1127 (2016); Easterman et al, *Macromolecules*, **45**, 7920 (2012)

- Thin ionomer film formed in ultra-low Pt electrodes
- Large local oxygen transport due to thin ionomer film surrounding Pt particles
- Inferior performance at low-Pt loading due to local oxygen transport resistance

Technical Approaches

BP-ArF4



IEC: 1.4 (mequiv. g⁻¹)

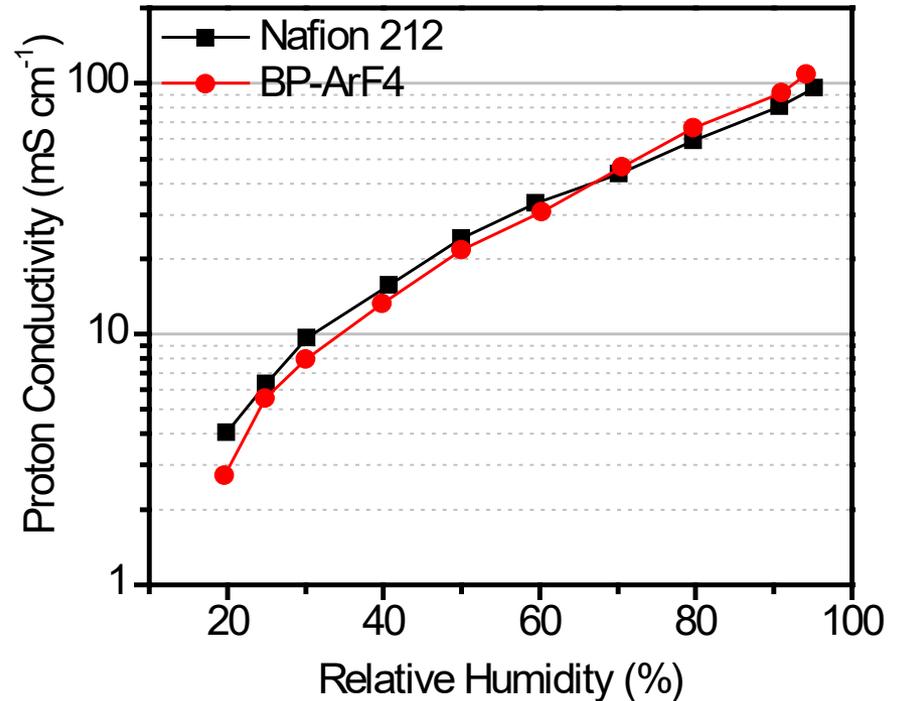
Solubility test

Membranes	MeOH	EtOH	1-ProH	THF	DMF	DMAc	DMSO	Water
BP-ArF4	+	+	+	±	++	++	++	-

++, soluble at room temp.; +, soluble at heating; ± partially soluble at heating; -, insoluble even at heating

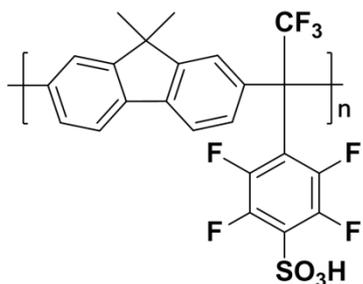
Preliminary ionomer

Proton conductivity (@ 80 °C)



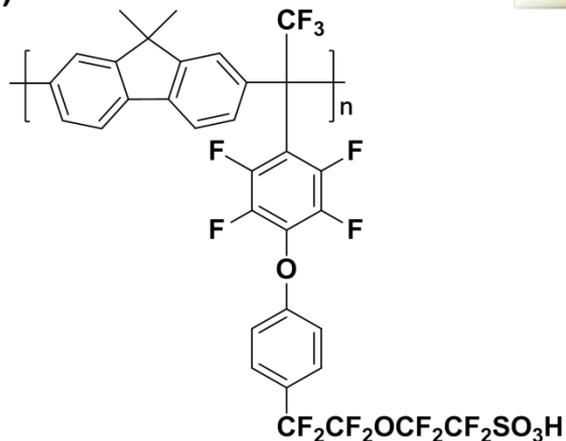
Proposed Ionomers

(a)



FL-C6F4

(b)



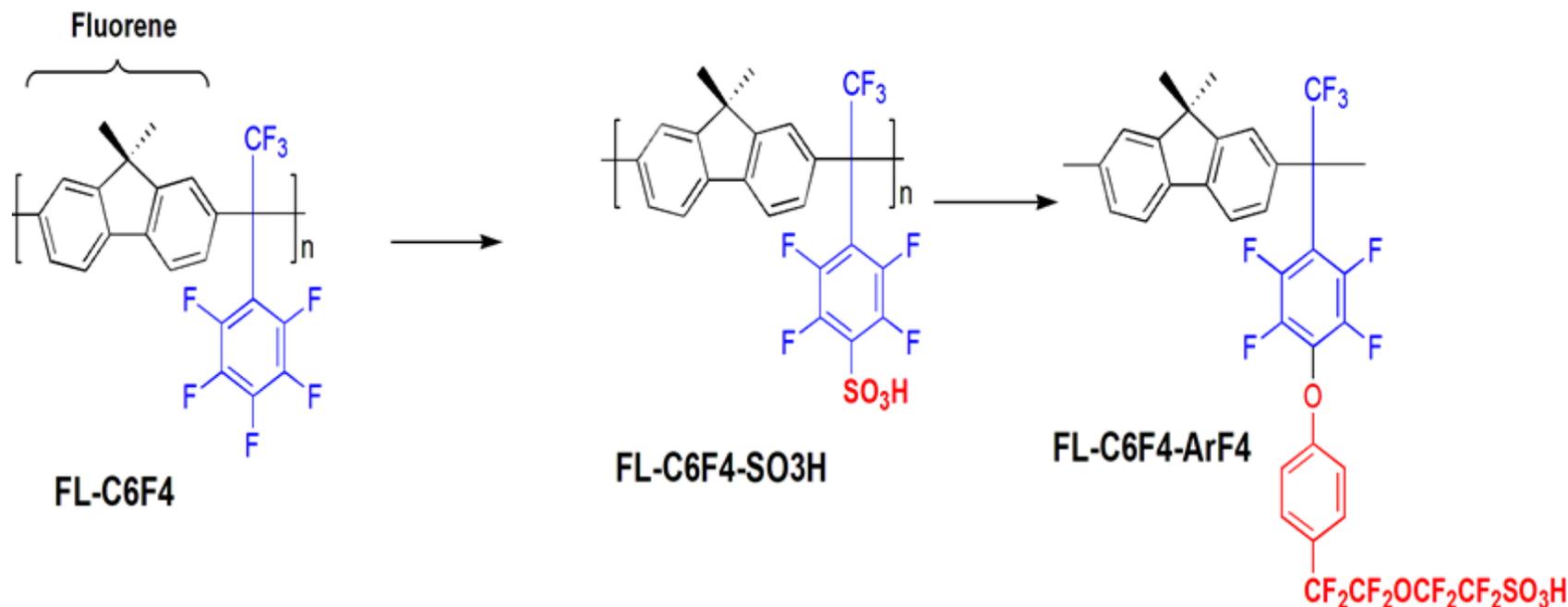
FL-C6F4-ArF4

- Good proton conductivity in a range of temperature and humidity conditions
- **Multiple fluorine moieties in both ionomers increase the acidity of sulfonic acid groups.**
- Good compatibility with PFSA membranes enabling low resistance at the membrane-catalyst layer interface
- **Multiple fluorine moieties in both ionomers can decrease the resistance originating from the different molecular component between the ionomers and PFSA membranes.**
- High permeability to gases, including O₂, H₂
- **High concentration of fluorine in both ionomers can enhance the gas permeation. [1].**
- Low or no anion adsorption on Pt
- **Rigid main back bones of both ionomers can effectively decrease the adsorption of sulfonate anion groups on Pt [2].**
- Chemical durability sufficient to pass the accelerated stress tests in the DOE MYRD&D plan
- **Main backbones of both ionomers are composed of chemically stable C-C bond without heterogeneous atoms which can afford good chemical stability even under rigorous operating conditions.**

Proposed Tasks

Task	% Time	Month								
		1	2	3	4	5	6	7	8	9
1. Synthesize Ionomer	25	■	■	■						
2. Fabricate and characterize Ionomer thin films	20		■	■	■					
3. Design and characterize fuel cell electrodes	30			■	■	■	■			
4. Evaluate fuel cell performance and transport resistance	35					■	■	■	■	■
Project Management		■	■	■	■	■	■	■	■	■
Report				X			X			X

Task 1: Synthesize Ionomer



- ❑ Both FL-C6F4-SO₃H and FL-C6F4-ArF4 potentially have high chemical durability because the backbone of these polymers are composed of all C–C bonds without heteroatoms.
- ❑ The multiple fluorine-substituted benzene ring can effectively shield the ether linkage (-O-) from the reactive radicals by the strong electron-withdrawing effect of fluorine.

Task 2: Fabricate and characterize Ionomer thin films

Fundamental Properties

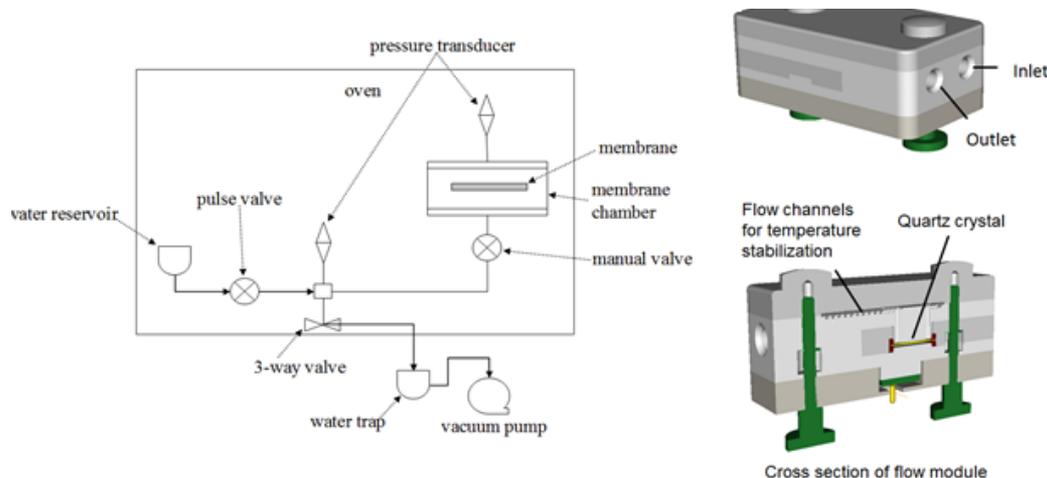
Simultaneous water uptake and diffusivity

Electro-osmotic drag coefficient

Gas permeability

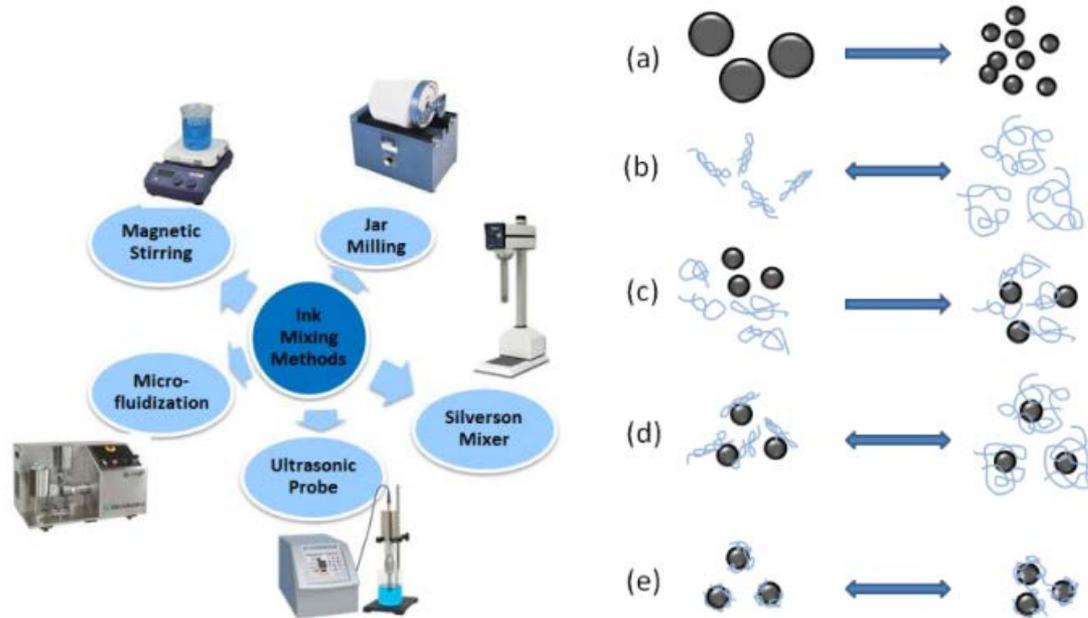
Membrane conductivity

Mechanical properties



- Silicon or platinum will be used as substrates
- Thin-films will be spun-cast from ionomer solutions to the substrate
- Thin films will be characterized in terms of water uptake, diffusivity and gas permeability

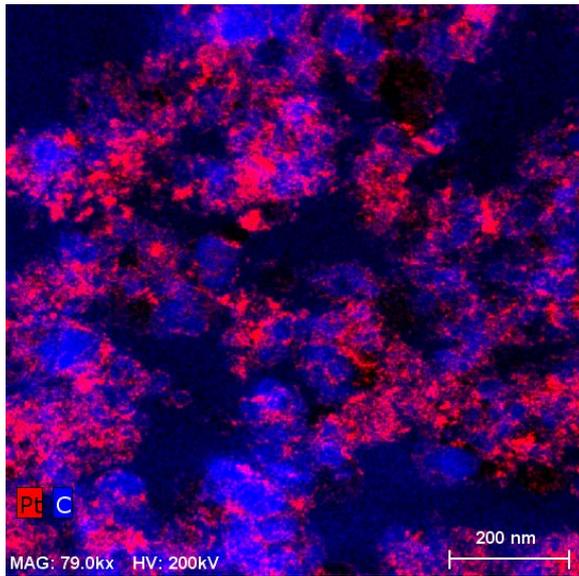
Task 3: Design and characterize fuel cell electrodes using proposed ionomers



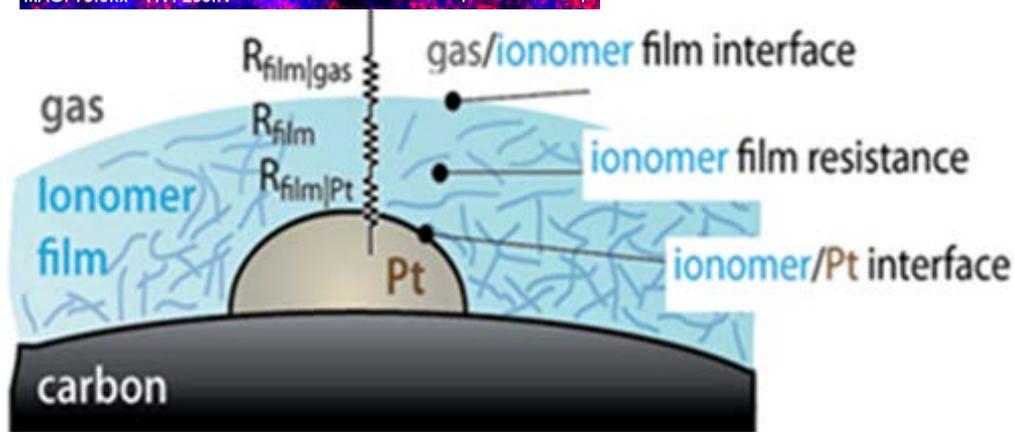
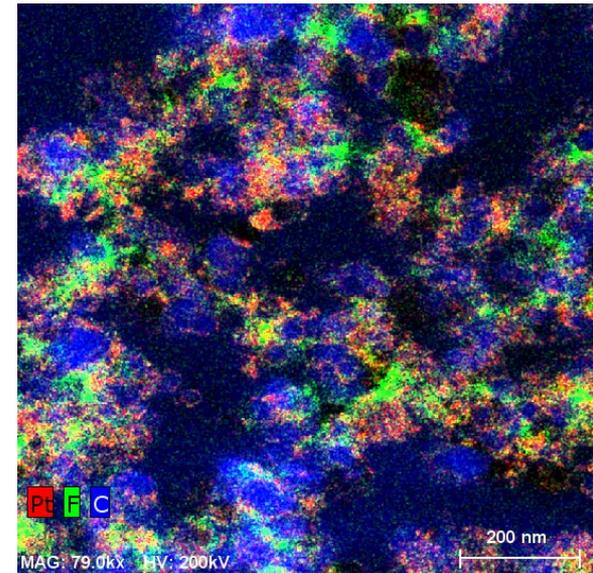
Catalyst ink fabrication and complex interactions

- (a) break-down of core catalyst agglomeration,
- (b) ionomer re-conformation in various solvent blends
- (c) ionomer adsorption onto catalyst particle surface
- (d) ionomer re-conformation on particle surface
- (e) formation and breaking-up of flocculation

Interaction of Carbon, Pt and Ionomer



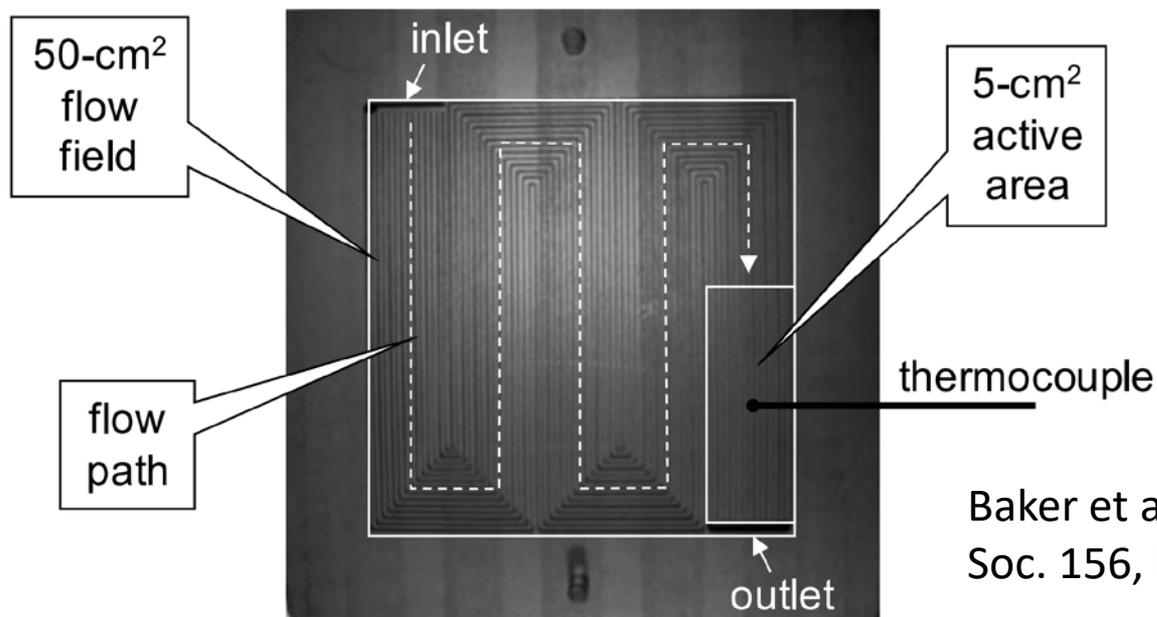
F Fluorine
Pt Platinum
C Carbon



Weber and Kusoglu, .
Mater. Chem., 2,
17207 (2014)

- ❑ Complicated interaction of carbon, Pt and developed ionomer will be investigated by TEM and modeling

Task 4: Evaluate fuel cell performance and transport resistance



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

- ❑ A limiting current approach will be used to measure the transport resistance. $R_T = R_{ch} + R_{DM} + R_{MPL} + R_{other}$
- ❑ Oxygen balanced with helium and variety in oxygen partial pressure will be performed to analyze the transport resistance from various sources.

Milestones

- ❑ Delivery 10 g ionomer of each category
- ❑ Proton conductivity at 80 °C: 20 mS/cm at 50% RH and 90 mS/cm at 98% RH
- ❑ Gas permeability: at least 2X increase compared to Nafion 1100EW ionomer
- ❑ Local O₂ transport resistance: at least 30% decrease compared to Nafion 1100EW ionomer

Team Collaboration

Institutions	Roles
<u>Giner Inc. (Giner)</u> Hui Xu (PI)	Prime, oversees the project; MEA design and fabrication; performance test and data analysis
Rensselaer Polytechnic Institute (RPI): Prof. Chulsung Bae	Subcontractor, fluorinated hydrocarbon ionomer design, synthesis and scale-up

Biweekly meeting

Quarter report/project review

Summary

- ❑ A novel fluorinated hydrocarbon ionomer has been proposed for PEM fuel cell cathode with anticipated properties
 - High permeability to gases, including O₂, H₂
 - Low or no anion adsorption on Pt

- ❑ Thin-films derived from the ionomer will be fabricated and their water uptake and gas permeability properties will be compared to those of bulk membranes

- ❑ The ionomer will be implemented to fuel cell electrodes to improve low-Pt and high-power operations
 - Interaction of carbon, Pt and ionomer will be investigated
 - Local oxygen transport resistance due to ionomer thin film will be characterized

Acknowledgments

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 - Jason Willey
 - Chao Lei
 - Corky Mittelsteadt