Novel Fluorinated Ionomer for PEM Fuel Cells

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Newton, MA

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Project ID# FC185

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

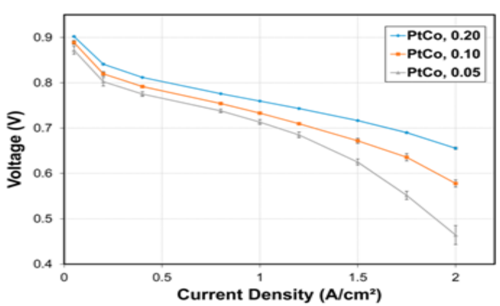
Design and synthesize novel fluorinated ionomer for PEM fuel cell cathodes to lower local transport loss

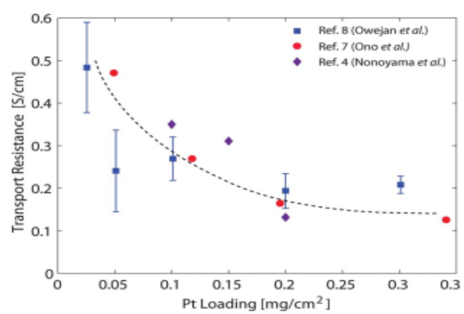
- Design fluorinated Ionomer exclusively for PEM fuel cell electrodes
- Evaluate fuel cell performance and local transport resistance using developed ionomer, under low Pt and high power operation

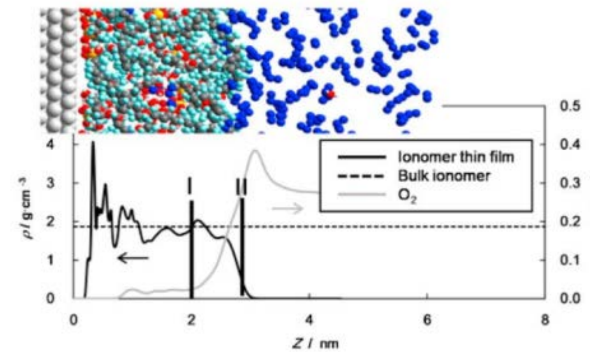
Relevance:

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$_{iR\text{-}free}$	>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]







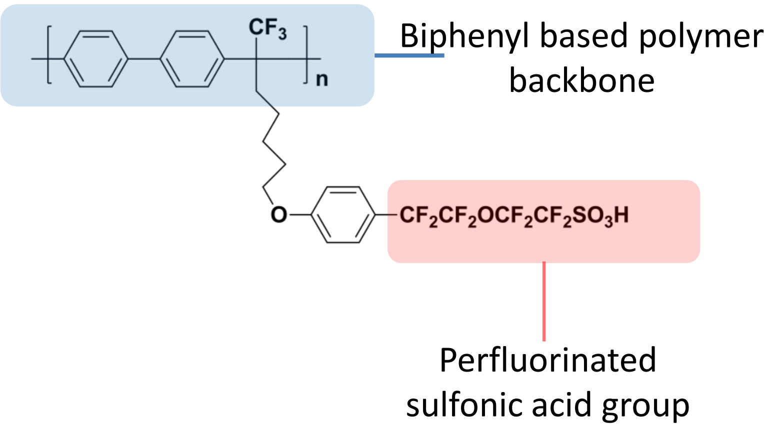
Kongkanand and Mathias, J. Phys. Chem. Lett. **7**, 1127 (2016); Easterman et al, Macronolecules, **45**, 7920 (2012)

- ❑ 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

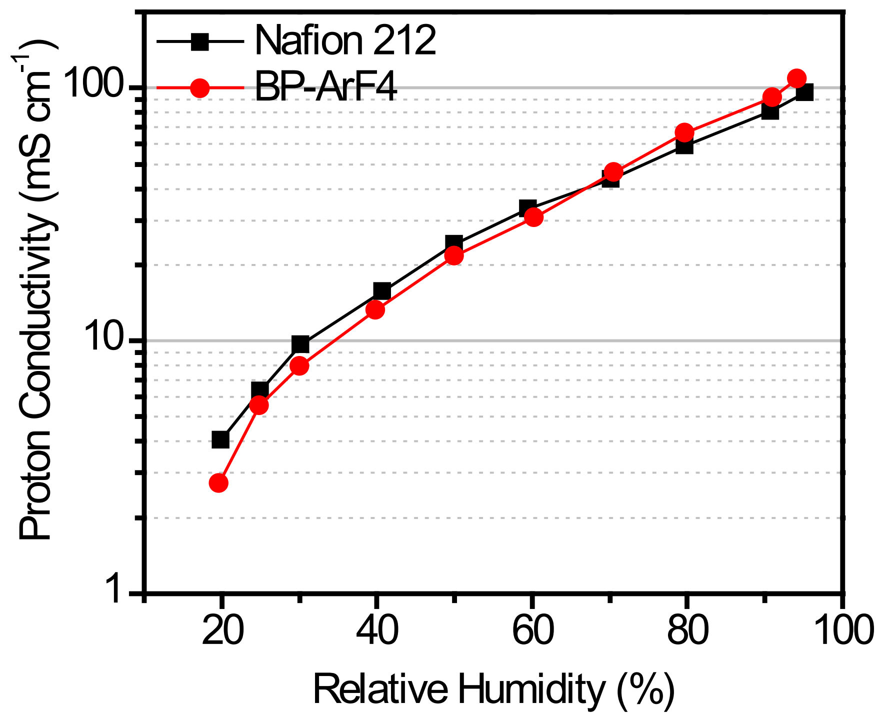
BP-ArF4

Preliminary ionomer



IEC: 1.4 (mequiv. g^{-1})

Proton conductivity (@ 80 °C)

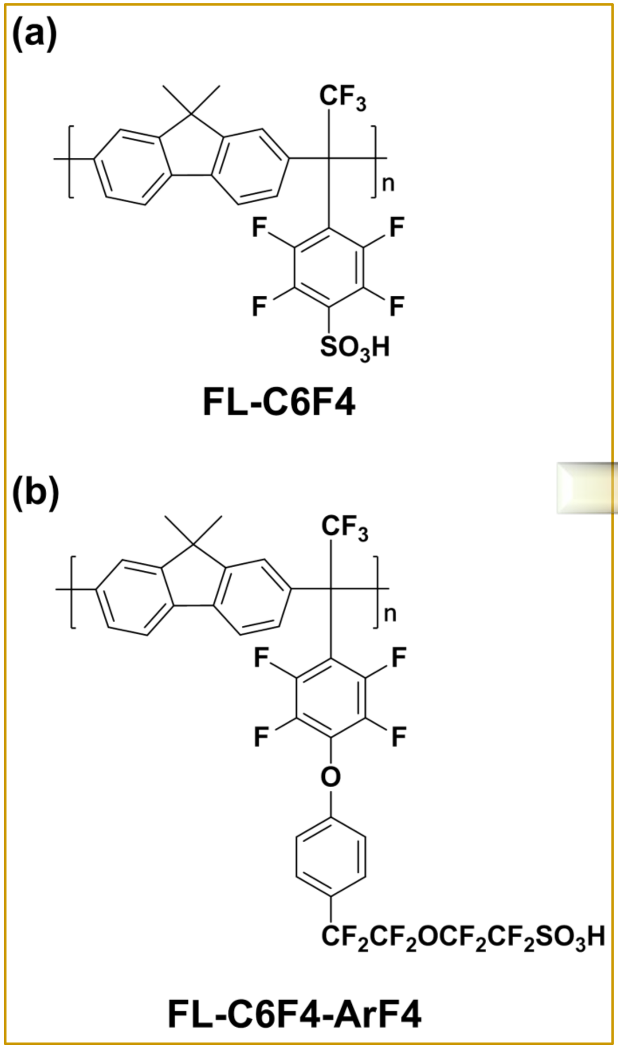


Solubility test

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

Proposed Ionomers

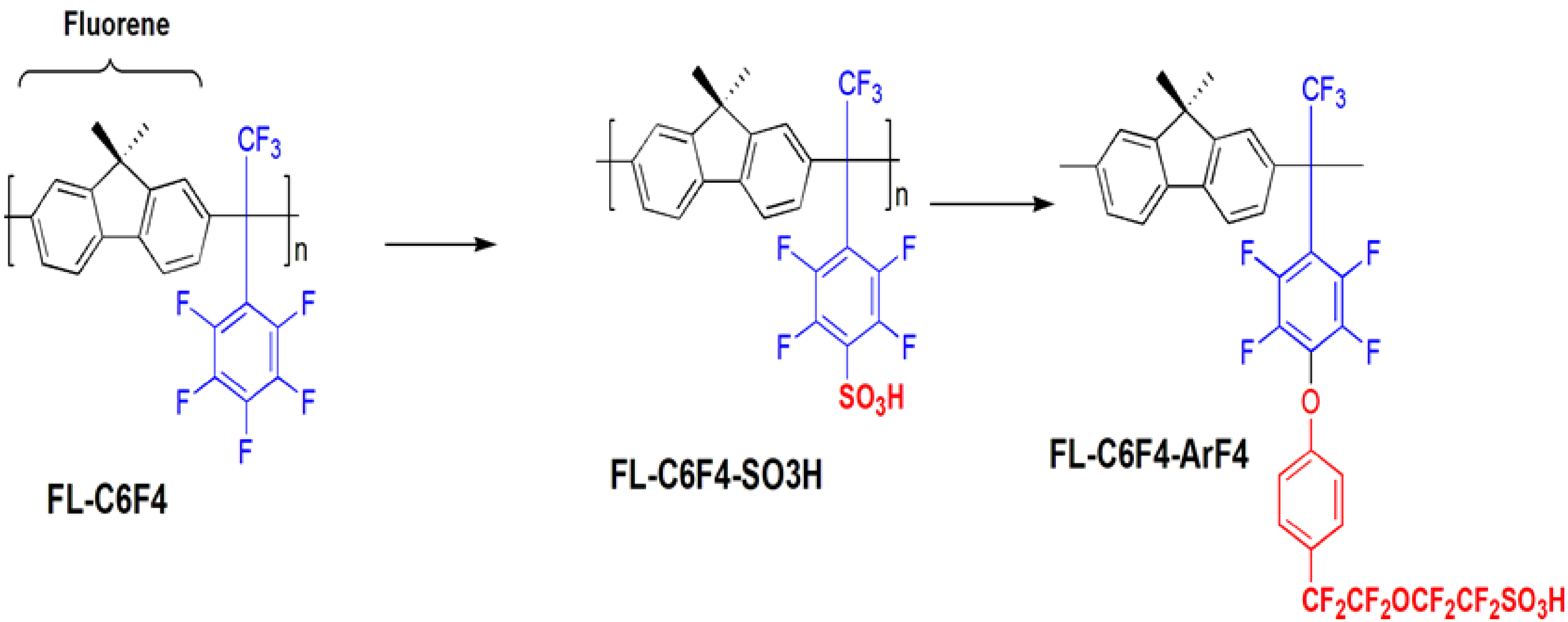


- Good proton conductivity in a range of temperature and humidity conditions
  - ➢ **Multiple fluorine moieties in both ionomers increase the acidity of sulfonic acid groups.**
- Good compatibility with PFSA membranes enabling low resistance at the membrane-catalyst layer interface
  - ➢ **Multiple fluorine 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 O_2, H_2
  - ➢ **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 affords 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

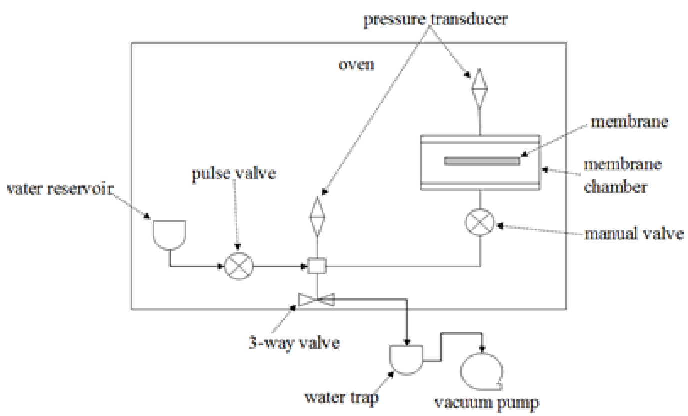
Task 1: Synthesize Ionomer

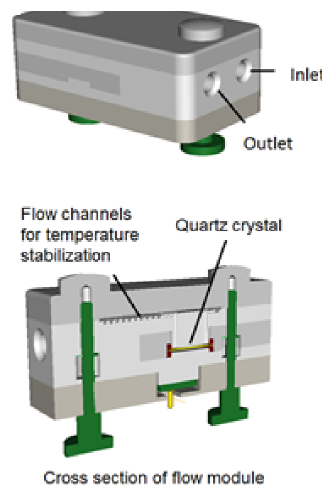


- Both FL-C6F4-SO_3H and FL-C6F4-ArF4 potentially have high chemical durability because the backbone of these polymers are composed of all C–C bonds without heteroatoms.
- The multiple fluorine-substituted benzene ring can effectively shield the ether linkage (-O-) from the reactive radicals by the strong electron-withdrawing effect of fluorine.

Task 2: Fabricate and characterize Ionomer thin films

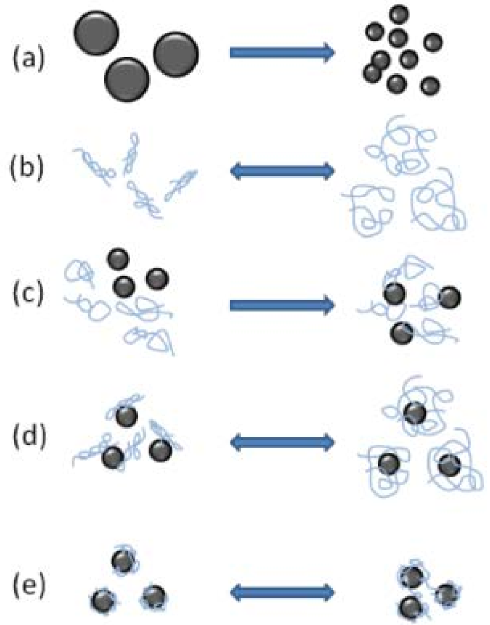
Fundamental Properties
Simultaneous water uptake and diffusivity
Electro-osmotic drag coefficient
Gas permeability
Membrane conductivity
Mechanical properties





- ❑ 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

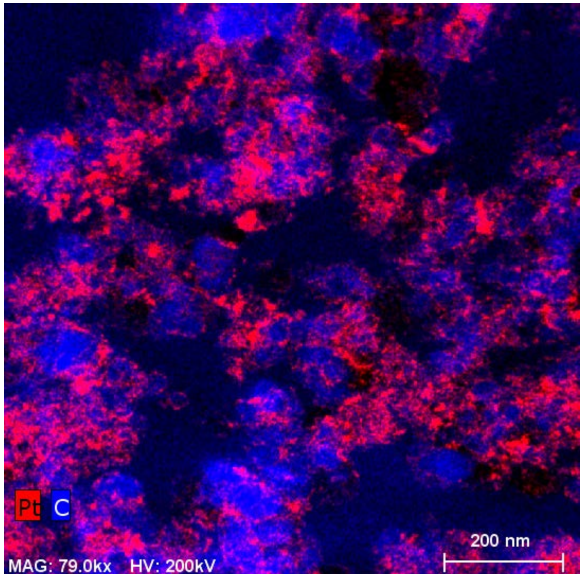
Task 3: Design and characterize fuel cell electrodes using proposed ionomers



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

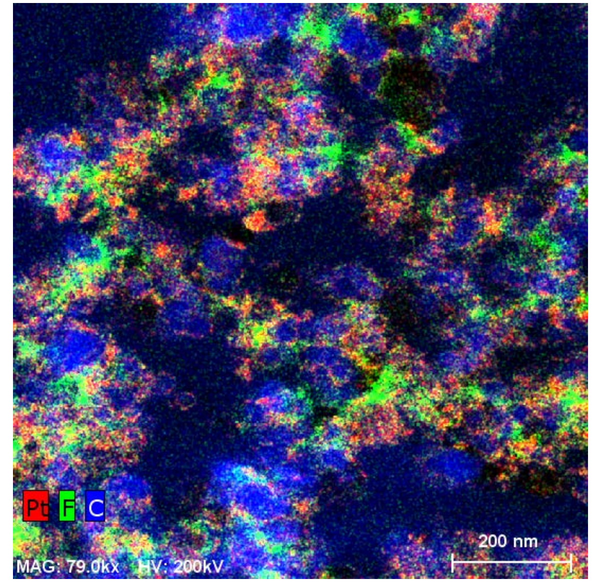
Interaction of Carbon, Pt and Ionomer

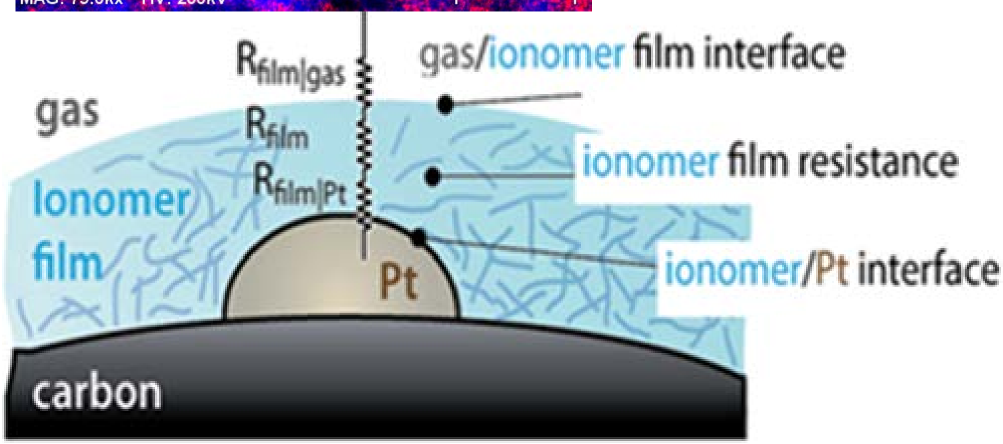


F Fluorine

Pt Platinum

C Carbon

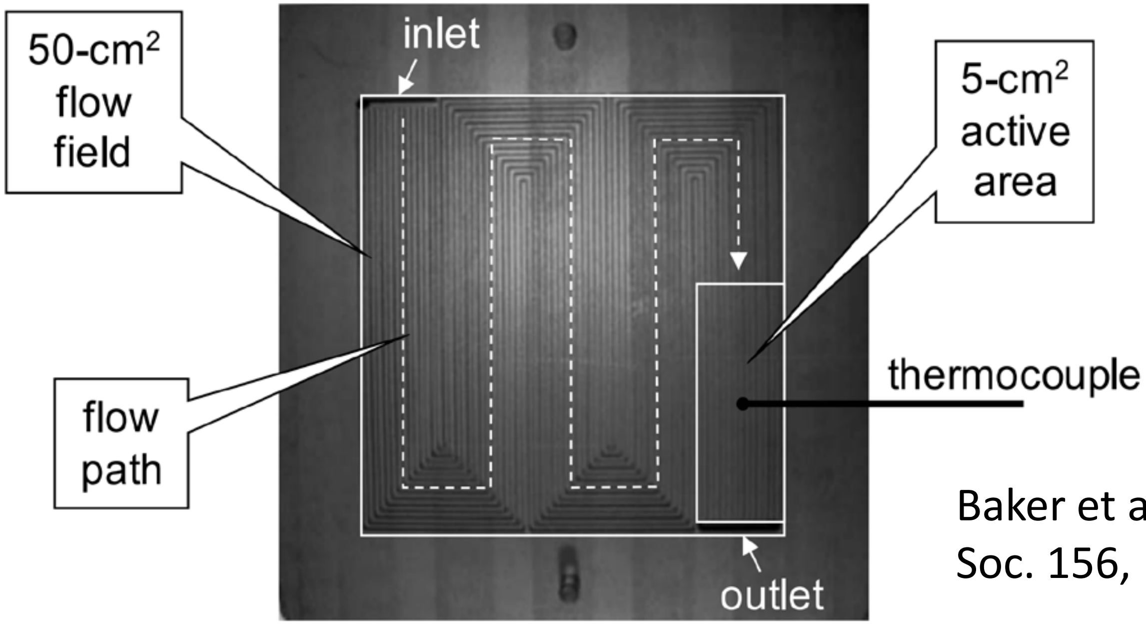




Weber and Kusoglu, . Mater. Chem., **2**, 17207 (2014)

- ❑ 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. $R_T = R\text{ch} + R_{DM} + R_{MPL} + R_{other}$

- ❑ 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 ℃: 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 O_2 transport resistance: at least 30% decrease compared to Nafion 1100EW ionomer

Team Collaboration

Institutions	Roles
Giner Inc. (Giner) 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 O_2, H_2
  - 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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- Collaborators
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  - Prof. Jasna Jankovic (Univ. of Connecticut)

- Giner Personnel
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  - Chao Lei
  - Corky Mittelsteadt