

ILBCP-IL Composite Ionomers for High Current Density Performance

FC309

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Team: Yossef Elabd, Anusorn Kongkanand, Kenneth Neyerlin, Maureen Tang

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Overview

Timeline

- Project start date: Oct. 2018
- Project end date: Dec. 2020
- Percent Complete: 7%

Budget

- FY2019 Funding: \$608,029
- Total Project Funding: \$1,244,115
- Cost Share: \$250,380 (20.5%)

Technical Barriers

- O₂ transport through ionomer films
- Ionomer adsorption on catalyst
- Inaccessible catalyst in porous carbon
- Distribution and retention of IL in catalyst layer
- Humidity tolerance at HCD

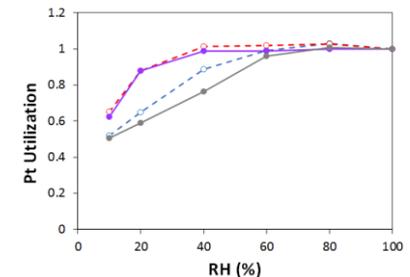
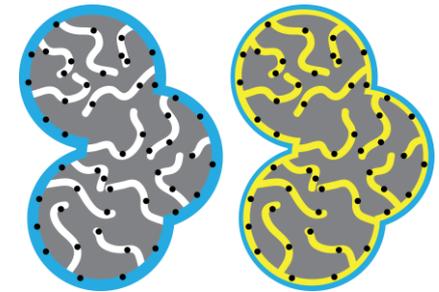
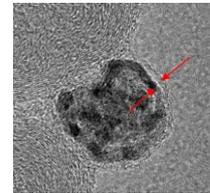
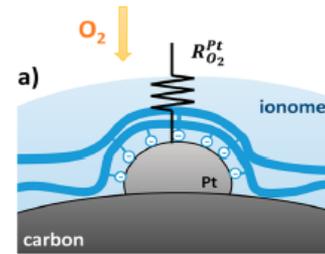
Partners

- Drexel: Maureen Tang
- Texas A&M: Yossef Elabd
- General Motors: Anusorn Kongkanand
- NREL: K.C. Neyerlin

Relevance

Primary Technical Barriers

- ❑ O_2 transport through ionomer thin films
- ❑ Ionomer specific adsorption onto catalyst
- ❑ Inaccessible catalyst in porous carbon supports
- ❑ Distribution and retention of IL in catalyst layers
- ❑ Humidity tolerance at HCD (Pt utilization)



Relevance

Objective:

The goal of this project is to develop a **polymerized ionic liquid block co-polymer/ionic liquid** (PILBCP/IL) composite ionomer to replace traditional PFSA-based ionomers and address their associated limitations. The expected outcomes include: (1) development of a cathode that meets DOE targets for low and high current density, and (2) improved understanding of how interface engineering affects HCD performance

Metric	Units	PtCo/KB	IL-PtCo/KB	DOE 2020 Target	Project Target
PGM total loading (both electrodes)	mg/cm ²	0.125	0.085	<0.125	←
Mass activity @ 900 mV _{iR-free}	A/mg _{PGM}	0.6	0.6	>0.44	←
Loss in catalytic (mass) activity	% loss	30%	-	<40%	←
Performance at 0.8V (150kPa, 80°C)	A/cm ²	0.30	0.31	>0.3	←
Power at rated power (150kPa, 94°C)	W/cm ²	0.80	-	>1.0	←
Power at rated power (250kPa, 94°C)	W/cm ²	1.01	1.05	-	>1.2
PGM utilization (150kPa, 94°C)	kW/g _{PGM}	6.4	-	>8	←
PGM utilization (250kPa, 94°C)	kW/g _{PGM}	8.1	10	-	>9.1
Catalyst cycling (0.6-0.95V, 30k cycles)	mV loss at 0.8A/cm ²	24	-	<30	←



Approach

Task 1:
Development of
PILBCP/IL Ionomer

FY2019 Q1-Q4

- PILBCP synthesis
- IL synthesis and screening
- Nafion and [MTBD][beti] baseline establishment
- In-situ/ex-situ screening of PILBCP/IL thin films
- Create IL property and performance database

Go/No-Go: $>1.0 \text{ W/cm}^2$ at 250 kPa in 25 cm² MEA with two different PILBCP/IL chemistries

Task 2:
MEA Performance
and Durability

FY2020 Q5-Q8

- Catalyst ink formulation and rheology
- Capacitive deposition of IL
- Ex-situ ion and gas transport measurements through PILBCP/IL
- Composite ionomer loading effects
- In-situ Pt utilization: Vulcan vs. HSC
- MEA level ionomer and catalyst durability
- Limiting current for proton and oxygen transport

Project End Goal: $>1.2 \text{ W/cm}^2$ at 250 kPa in 50 cm² MEA, $<10\%$ power loss after AST

Approach

PILBCP-IL Composite Ionomers for High Current Density Fuel Cell Performance DE-FOA-0001874 Topic 3A-4 Ionomer (Control #: 1874-1642)		2019				2020			
		Q1	Q2	Q3	Q4	Q5	Q6	Q7	Q8
Task	Team								
Program Timeline									
Program Start Date									
Quarterly Report and Milestones									
Yearly Go/No-Go Decision									
Annual Program Review									
Final Report									
Phases (Budget Periods)									
Phase 1: PILBCP/Ionic Liquid Composite Ionomer Development						Phase 1 (BP 1)			
Phase 2: High Current Density Performance and Stability with PILBCP/IL Composite Ionomers								Phase 2 (BP 2)	
Task 0 - Program Management and Planning									
0.1 Project Kick-off Meeting	All								
0.2 Project Management, Planning, Review, and Reporting	All								
0.3 Final Report and Review Meeting	All								
Task 1 - Development of PILBCP/IL Composite Ionomer									
1.1 Materials Development									
1.1.1 PILBCP Ionomer Synthesis	TAMU								
1.1.2 IL Screening and Synthesis	Drexel								
1.2 Characterization									
1.2.1 Establish Baseline with Nafion/[MTBD][beti] and Pt	Drexel/GM/NREL								
1.2.2 Ex-situ Screening of PILBCP/IL Composite Thin Films	Drexel/TAMU								
1.2.3 In-situ Characterization	NREL/GM								
Task 2 - Composite PILBCP/IL MEA Performance and Stability									
2.1 Materials Development									
2.1.1 Catalyst Ink Formulations and Rheology	NREL/TAMU								
2.1.2 Capacitive Deposition of IL	Drexel/TAMU								
2.2 Ex-situ Characterization: Transport through PILBCP/IL Composites									
2.3 In-situ Characterization									
2.3.1 PILBCP/IL Loading Effects	NREL/GM								
2.3.2 Pt Utilization: Vulcan vs. High Surface Area Carbon	NREL/GM								
2.3.3 Composite Ionomer and Catalyst Durability at OCV and AST	GM								
2.3.4 Limiting Current for Proton and Oxygen Transport	NREL								



Collaboration



IL development
Half-cell: activity, durability, diagnostics
Thin film transport measurements



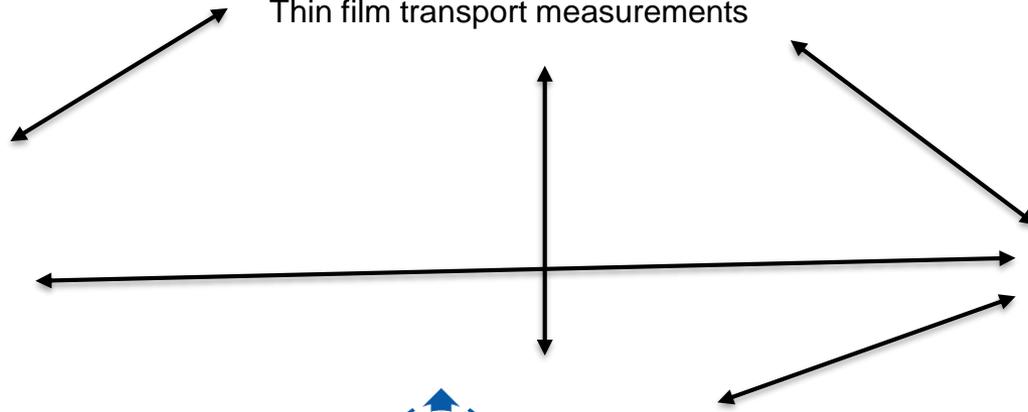
MEA diagnostics
MEA performance testing



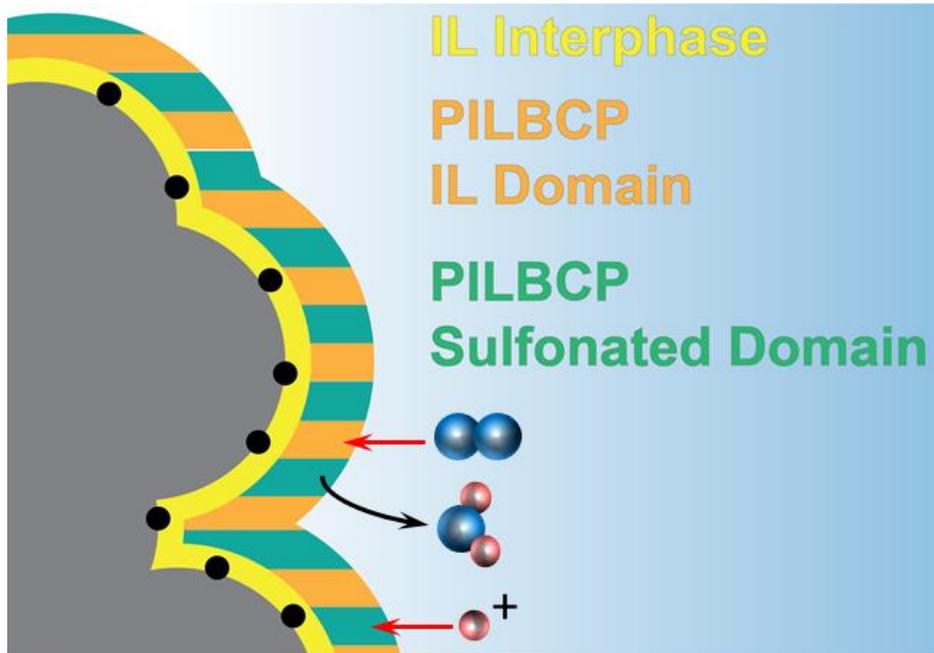
Ink development
MEA diagnostics



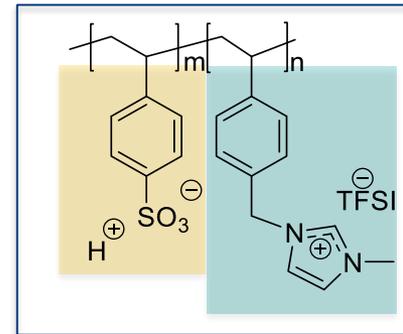
PILBCP synthesis
Ex-situ Ionomer characterization



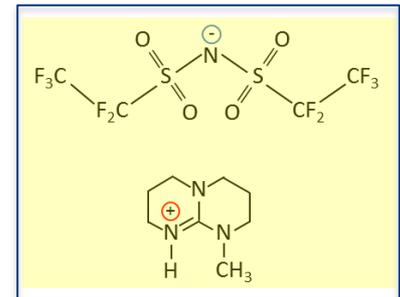
Concept



Polymerized Ionic Liquid Block Copolymer (PILBCP)

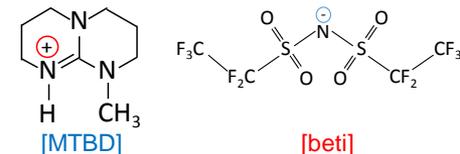


Ionic Liquid (IL)

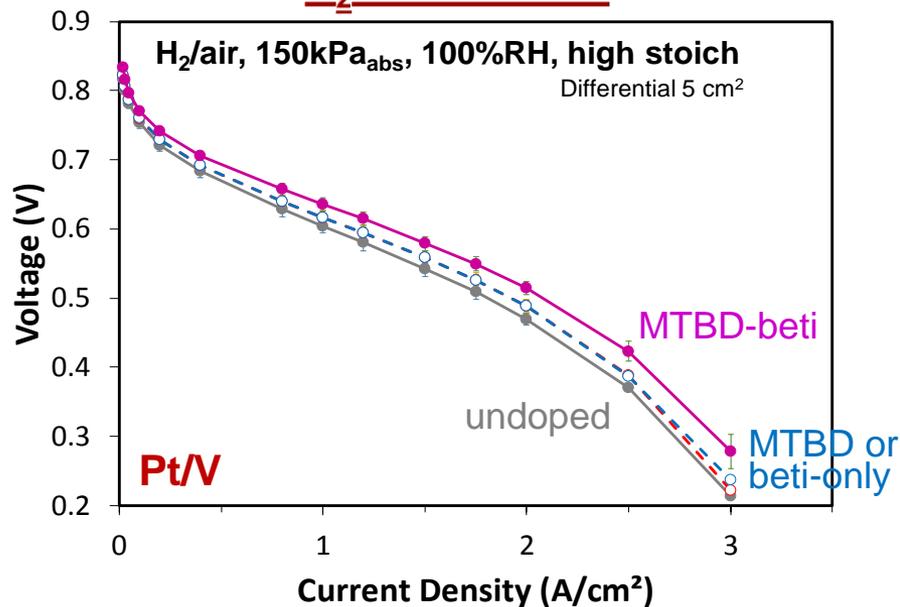


- ❑ IL interphase:
 1. Improved ORR
 2. Low humidity proton conduction
 3. Limited specific adsorption
- ❑ PILBCP polymer:
 1. IL domain improves interaction with IL interphase, decreasing interfacial resistances
 2. Improved retention of IL interphase
 3. Sulfonated domain is H_3O^+ transport block
 4. Domain organization in the absence of PFSA

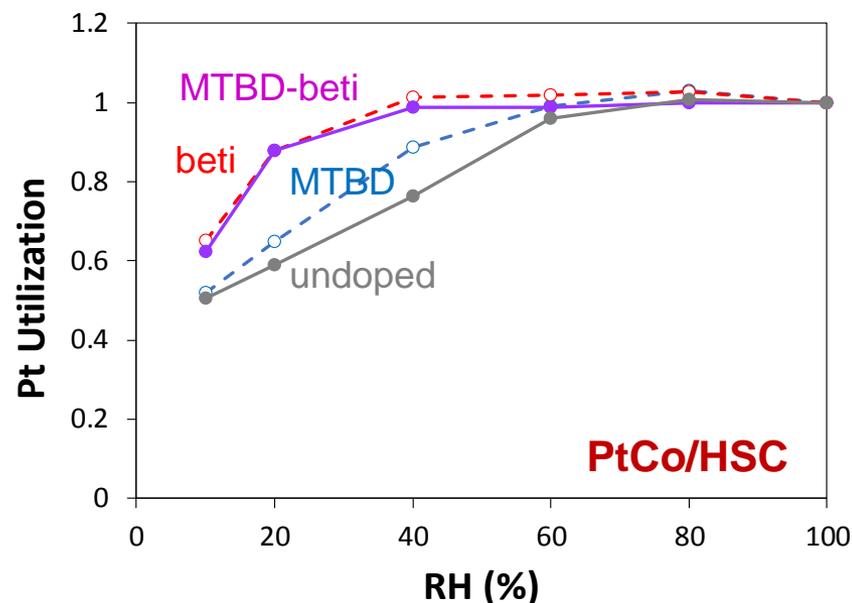
Accomplishments and Progress: Previous EERE Results – FC144



H₂/air I-V curve



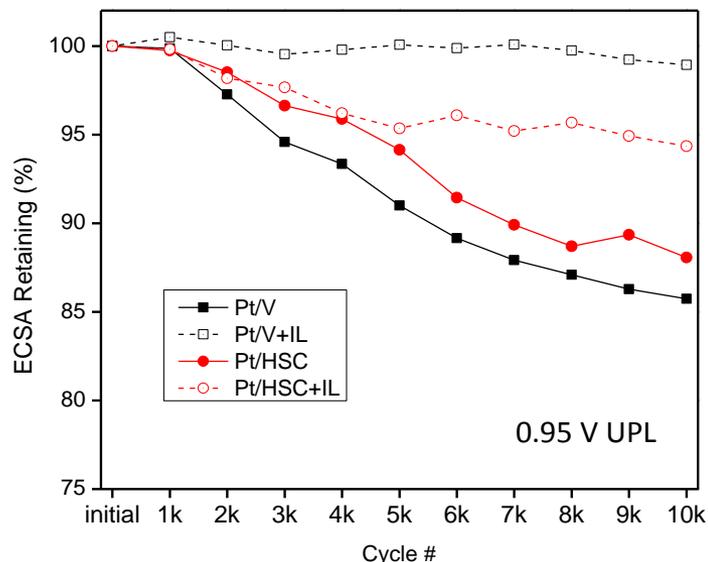
Proton Accessibility



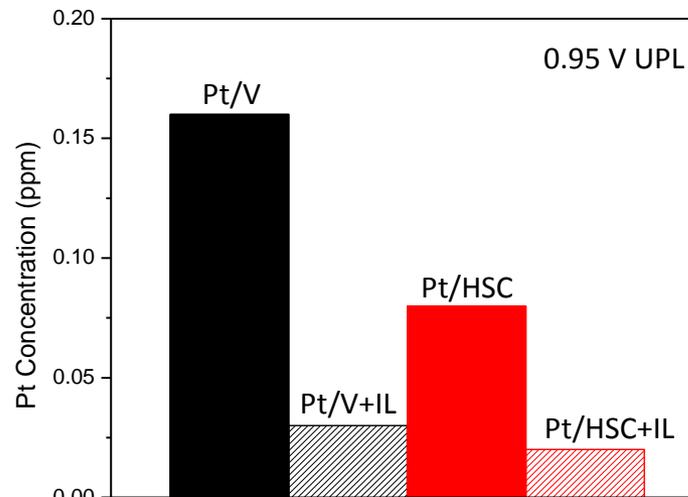
- ❑ MEA performance improvement due primarily to higher ORR activity in presence of [MTBD][beti]
- ❑ Humidity tolerance is improved in presence of protic IL. Utilization of internally located Pt in porous carbons at low humidity is enhanced due to anhydrous protonic conductivity of ILs

Accomplishments and Progress: Previous EERE Results – FC144

ECSA Retained Post RDE-ADT

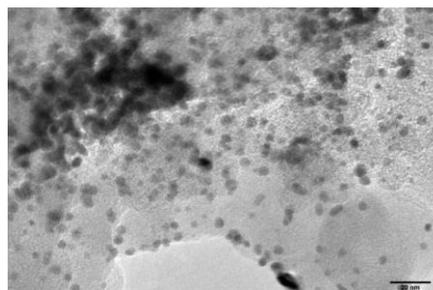


Pt Dissolution from ICP-OES

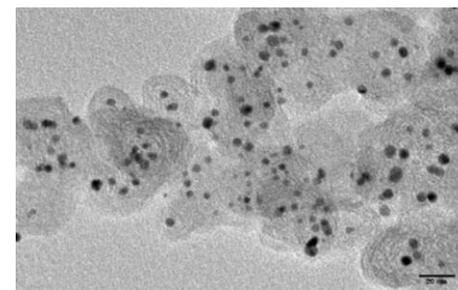


- ❑ Presence of IL thin film on Pt/V and Pt/HSC leads to significant improvements in ECSA retention during RDE AST (0.6-0.95 and 0.6-1.1 V vs. RHE)
- ❑ Hydrophobicity and low metal IL solubility of IL decrease Pt dissolution during RDE AST

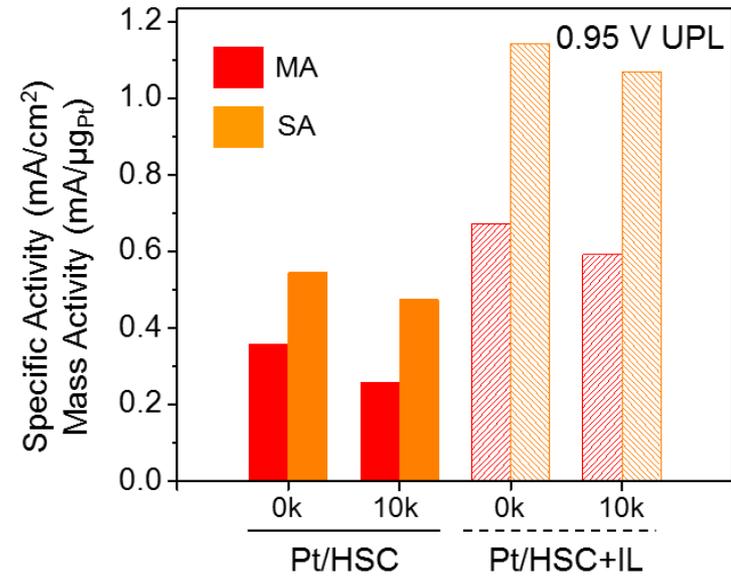
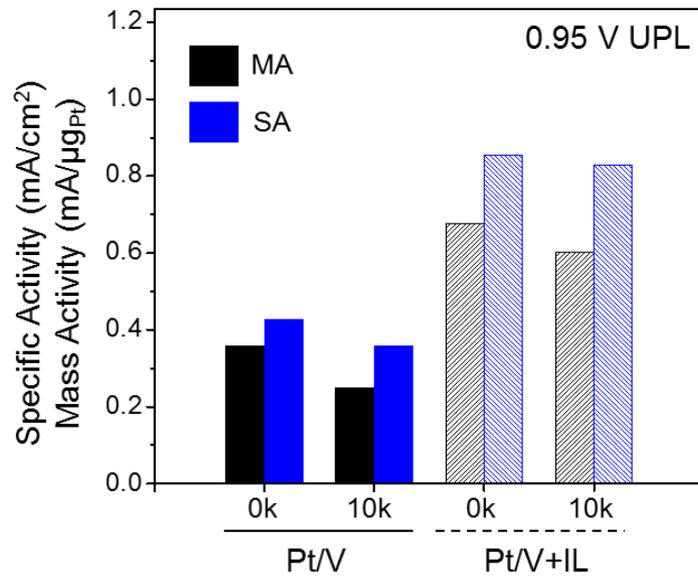
Pt/HSC 10k cycles 0.95 V UPL



Pt/HSC+IL 10k cycles 0.95 V UPL

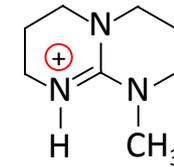
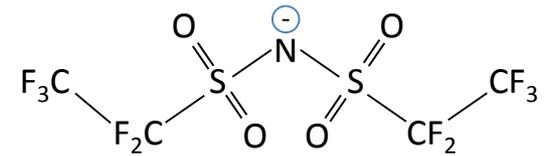
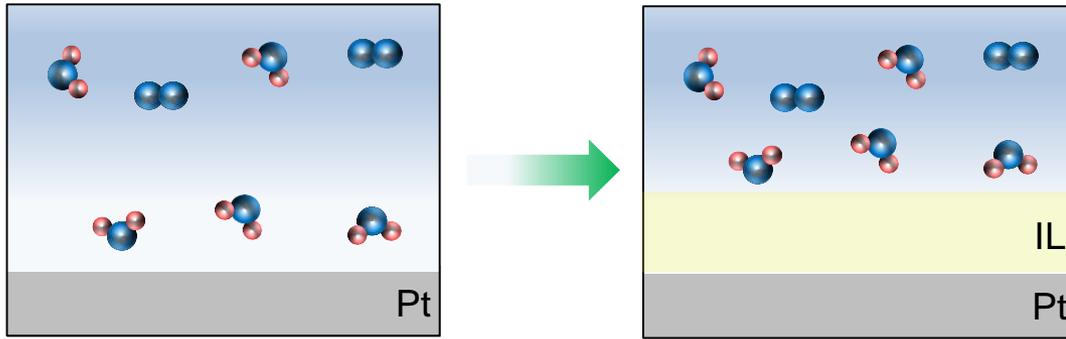


Accomplishments and Progress: Previous EERE Results – FC144

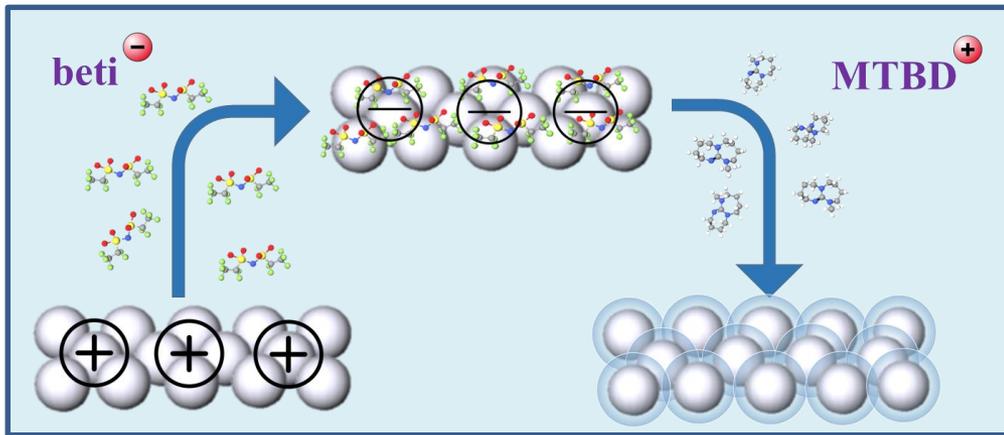


- ❑ IL thin films on Pt/V and Pt/HSC result in significant improvements in intrinsic ORR activity of Pt
- ❑ Specific and mass activity measured at 0.9 V vs. RHE

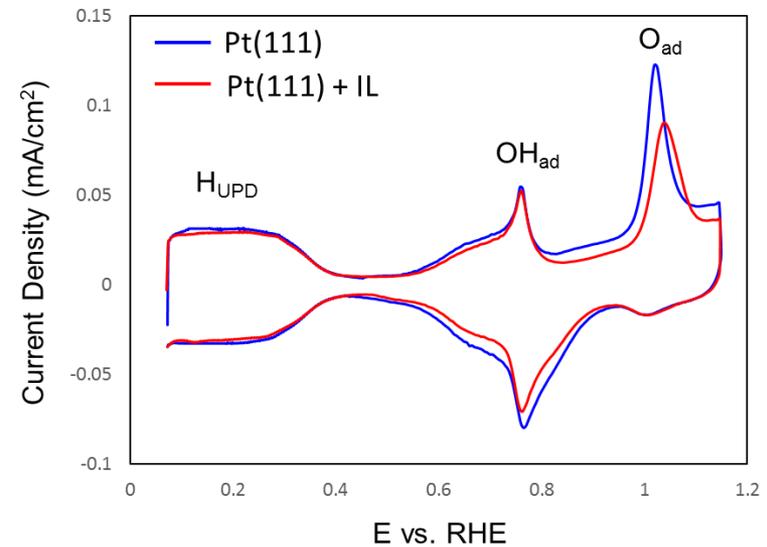
Accomplishments and Progress: Capacitive Deposition of IL



[MTBD][beti]

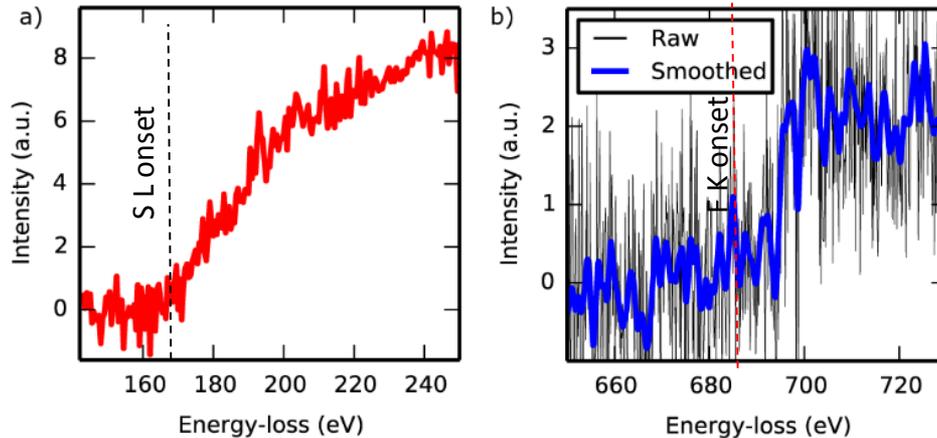


- Alternating potential and electrolyte composition sequentially attracts and condenses IL thin films on conductive electrodes

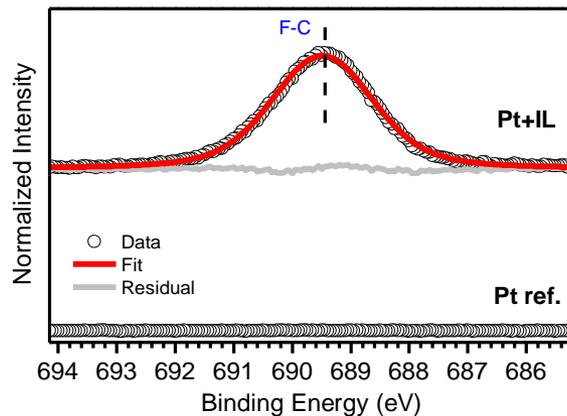


Accomplishments and Progress: Capacitive Deposition of IL

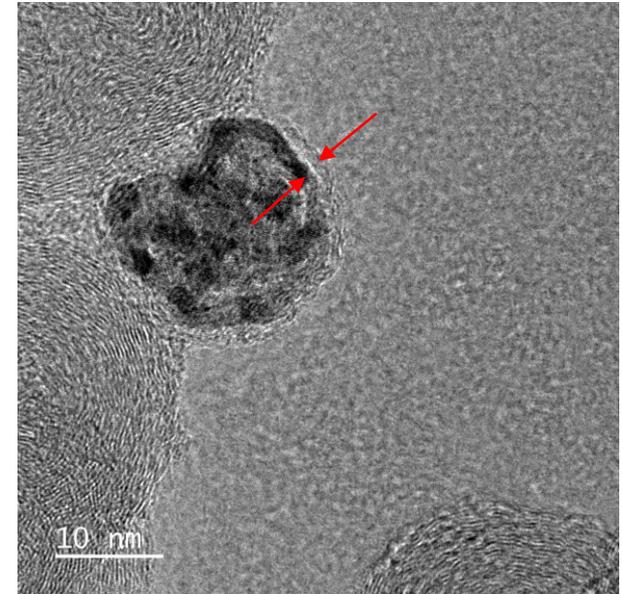
EELS



XPS



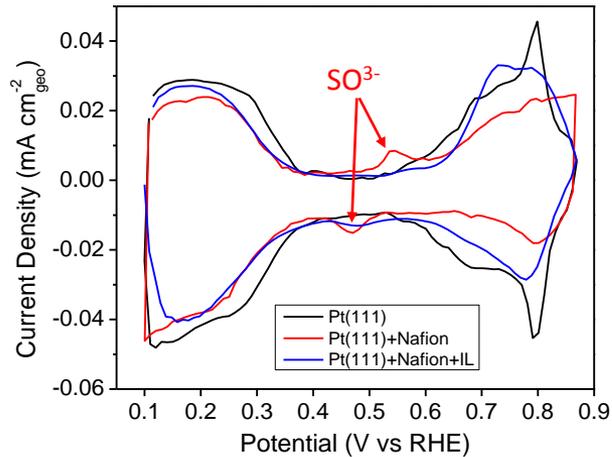
< 2 nm coatings



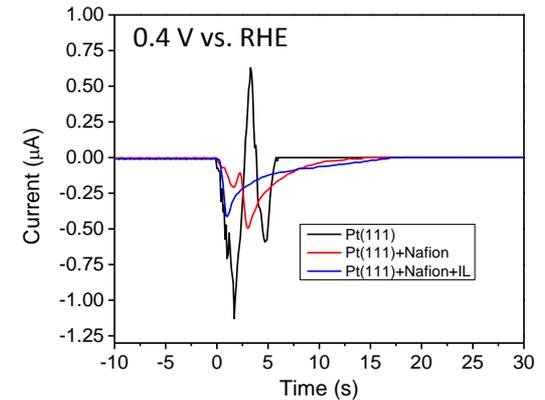
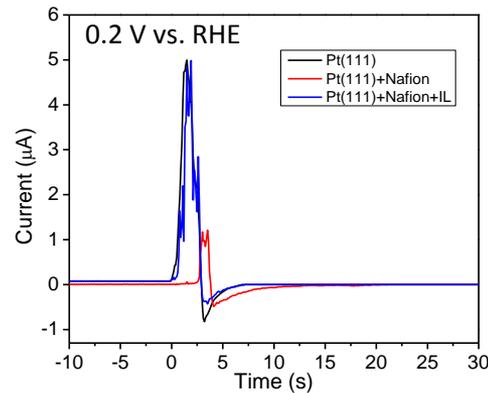
- ❑ Applied potential, immersion time, and electrolyte composition control IL thickness
- ❑ Conformal coating ensures complete coverage in 3D catalyst layers and limits pore blockage, minimizing impact on reactant transport

Accomplishments and Progress: Nafion Specific Adsorption on Pt(111)

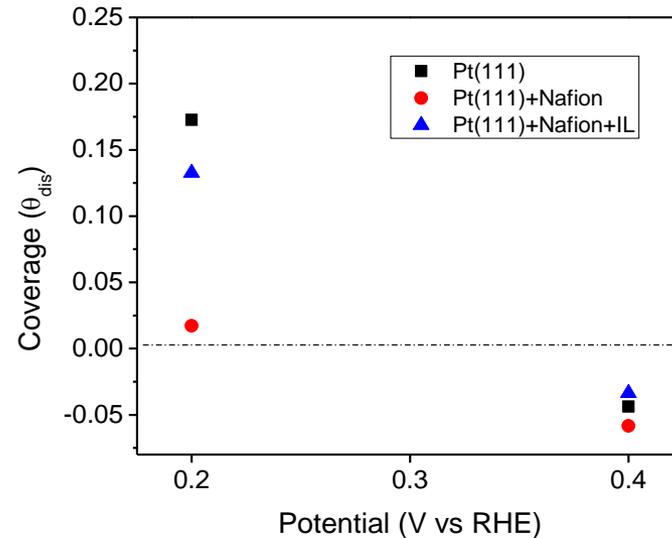
Nafion/IL Thin Films on Pt(111)



CO displacement



- ❑ CO displacement charge at 0.4 V vs. RHE is lower in the presence of IL, indicating decreased anionic species
- ❑ CO displacement below the Pt PZC, < 0.3 V vs. RHE at pH 1, indicates increased H adsorption, approaching that of bare Pt(111), in the presence of IL
- ❑ Intermediary IL thin film both limits ionic species specific adsorption, screening of SO_3^- groups, and lower site blocking from hydrophobic domains of Nafion polymer



Future Work

- ❑ Synthesis and ex-situ/half-cell screening of PILBCP and IL
- ❑ Establish property and performance baseline for Nafion/[MTBD][beti]
- ❑ Create database for ORR performance and general IL properties for a range of IL chemistries
- ❑ Develop testing protocol for ex-situ measurement of gas and ion transport properties of PILBCP/IL composite thin films
- ❑ Further develop methodology for conformal integration of IL thin films into three-dimensional catalyst layers
- ❑ Catalyst ink rheological optimization for non-PFSA based ionomer
- ❑ In-situ MEA testing: performance, diagnostic, durability
- ❑ Ionomer loading and carbon morphology effects

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

Future Work

Task 1: Development of PILBCP/IL Ionomer

Materials Development

Subtask 1.1

M1.2

- PILBCP ionomer synthesis
- IL synthesis and screening

Characterization

Subtask 1.2

M1.1

M1.3

M1.4

- Establish baseline with Nafion/[MTBD][beti]
- Microelectrode screening of PILBCP/IL composite thin films
- In-situ characterization

GNG1:

Demonstrate >1.0 W/cm² at 250 kPa in 25 cm² MEA with two PILBCP/IL chemistries

M1.2: Demonstrate 20% ORR improvement with ILs

M1.1: Demonstrate half-cell and microelectrode testing protocols, establish baseline

M1.3: Identify/characterized three PILBCP/IL chemistries for MEA testing

M1.4: Validate ex-situ O₂ perm and ORR with MEA testing

Future Work

Task 2: MEA Performance and Durability

Materials Development

Subtask 2.1

- Catalyst ink formulation and rheology
- Capacitive IL deposition

M2.2
M2.1

Ex-situ Characterization

Subtask 2.2

- Transport through PILBCP/IL composites

In-situ Characterization

Subtask 2.3

- PILBCP/IL loading
- Pt utilization
- Composite ionomer/catalyst durability

M2.2
M2.3
M2.4

Project end goal:
Demonstrate >1.2
W/cm² at 250 kPa in
50 cm² MEA, $<10\%$
power loss after ADT

M2.1: Demonstrate capacitive deposition reaches ORR activity of Pt/C+IL

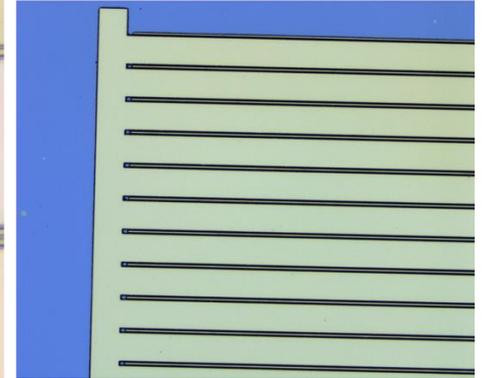
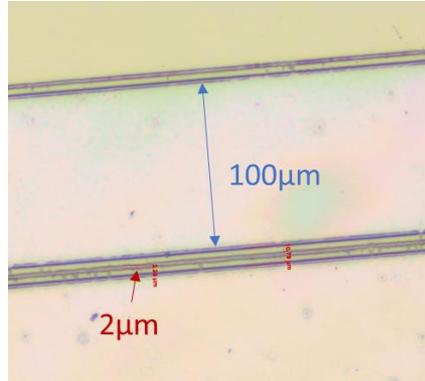
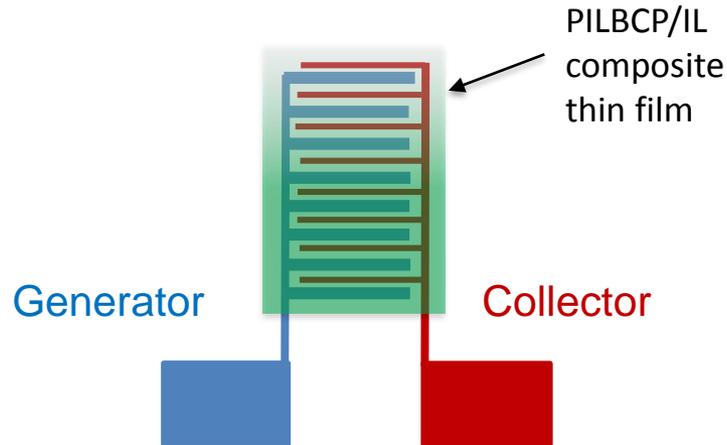
M2.2: Ink formulations and PILBCP/IL loading

M2.3: Demonstrate $>40\%$ Pt utilization at RH $<80\%$

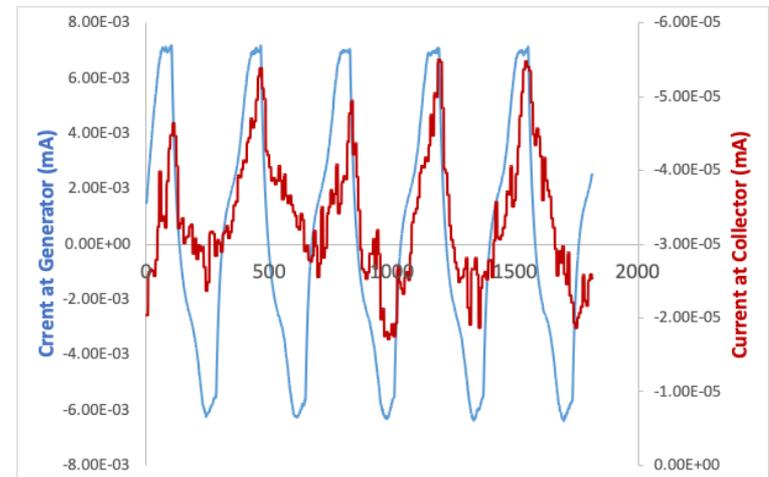
M2.4: Demonstrate catalyst durability with PILBCP/IL at OCV and AST



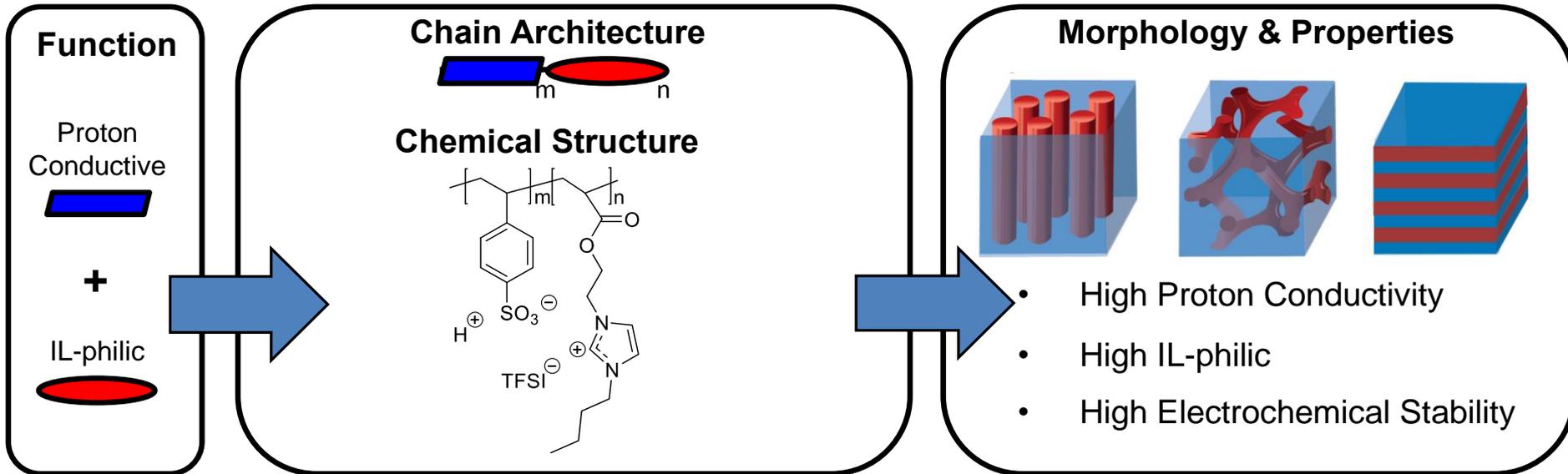
Future Work: Ex-Situ Transport Measurements



- ❑ Separate interfacial kinetics and transport with precise control of electrode geometry
- ❑ Steady-state established at microscale electrodes
- ❑ Measurement of ionic and reactant transport through PILBCP, IL, and PILBCP/IL composite thin films
- ❑ Deconvolution of general and interfacial resistances in composite thin films



Future Work: PILBCP Synthesis

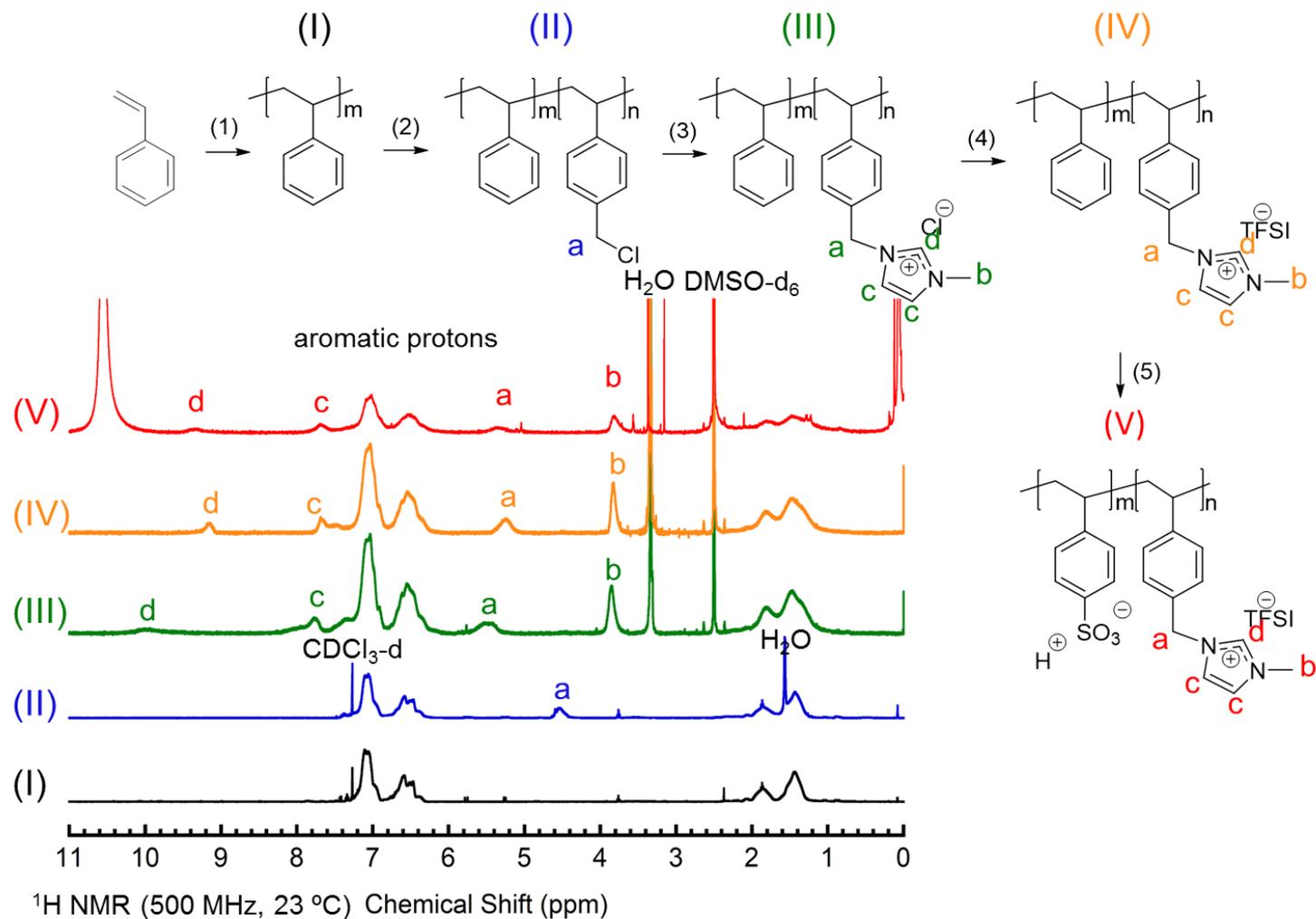


Advantages of PILBCP ionomers

1. High proton conductivity
2. Low degree of swelling
3. Favorable D_{O_2}/C_{O_2}
4. Enhanced humidity tolerance
5. Optimal interface with IL interlayer
6. Broad library of IL chemistries

Future Work:

PILBCP Synthesis



Summary

❑ PILBCP Composite Ionomers

1. Improved ORR
2. Low humidity proton conduction
3. Limited specific adsorption
4. IL domain improves interaction with IL interphase, decreasing interfacial resistances
5. Improved retention of IL interphase
6. Sulfonated domain is H_3O^+ transport block
7. Domain organization in the absence of PFSA

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Acknowledgements

DOE

- Greg Kleen
- Thomas Nucci
- Dan Berteletti
- Nicholas Oscarsson

GM

- Anusorn Kongkanand

Texas A&M

- Yossef Elabd

NREL

- Kenneth Neyerlin

Drexel

- Maureen Tang

