PILBCP-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: March 2021
- Percent Complete: 50%

Technical Barriers

- O_2 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

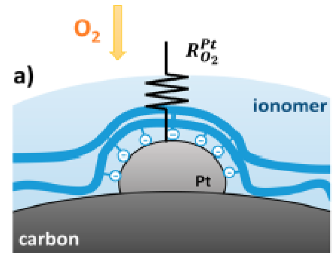
Budget

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

Partners

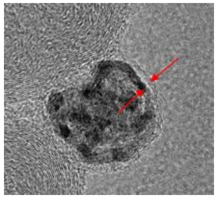
- Drexel: Maureen Tang
- Texas A&M: Yossef Elabd
- General Motors: Anusorn Kongkanand
- NREL: K.C. Neyerlin

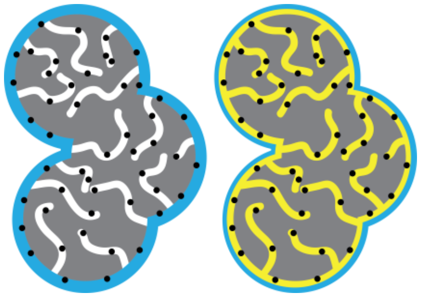
Relevance

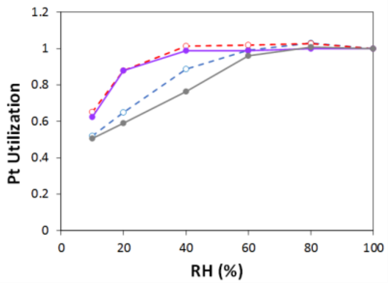


Primary Technical Barriers

- ❑ 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 $mV_{iR\text{-}free}$	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 W/cm^2 at 250 kPa in 25 cm^2 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 W/cm^2 at 250 kPa in 50 cm^2 MEA, <10% power loss after AST

Approach

Focus of Past Year

- PILBCP synthesis
- IL synthesis and screening
- Nafion and [MTBD][beti] baseline establishment
- In-situ/ex-situ screening of PILBCP/IL thin films
- Catalyst ink formulation and rheology
- Capacitive deposition of IL

TASK 1 - Development of PILBCP Ionomer

Go/No-go: >1.0 W/cm^2 at 250 kPa in 25 cm^2 MEA with two different PILBCP/IL chemistries

- Standardize half-cell and microelectorde testing protocols to establish baseline 100%
- Demonstrate 20% ORR improvement in RDE with ILs matching chemistry of PILBCP ionomers 100%
- Identify three PILBCP, IL candidate combinations matching or bettering half-cell performance metrics 75%
- Validate ex-situ O_2 permeability and ORR activity measurements with in-situ testing 70%

Collaboration

Drexel University

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

GM

MEA diagnostics
MEA performance testing

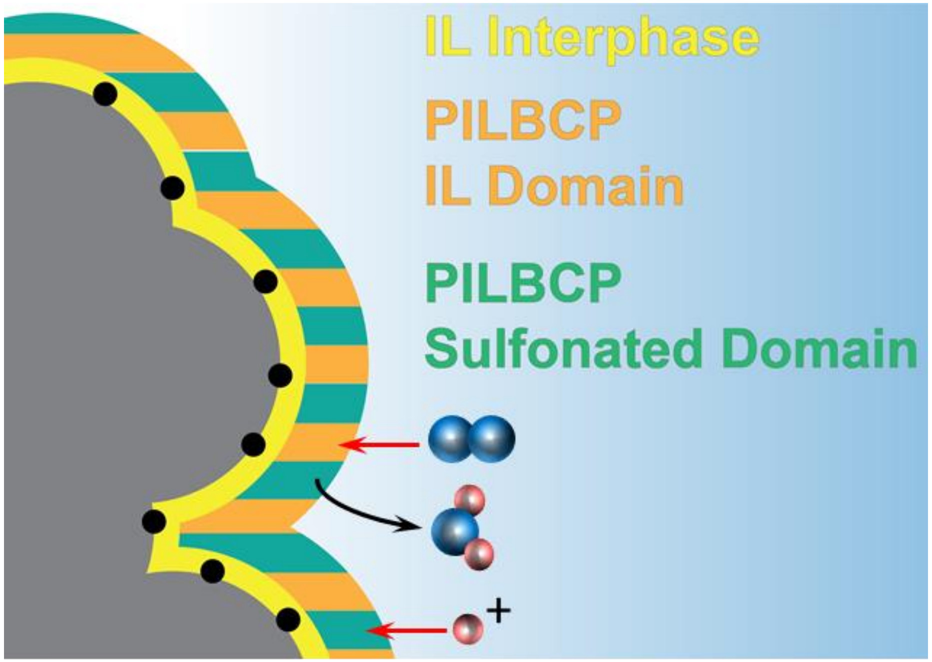
NREL

Ink development
MEA diagnostics

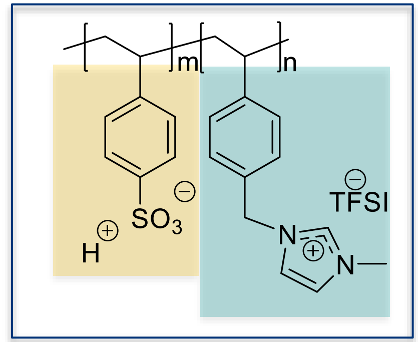
Texas A&M

PILBCP synthesis
Ex-situ Ionomer characterization

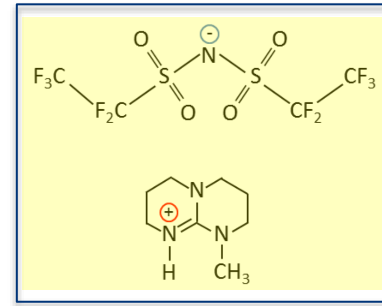
Concept



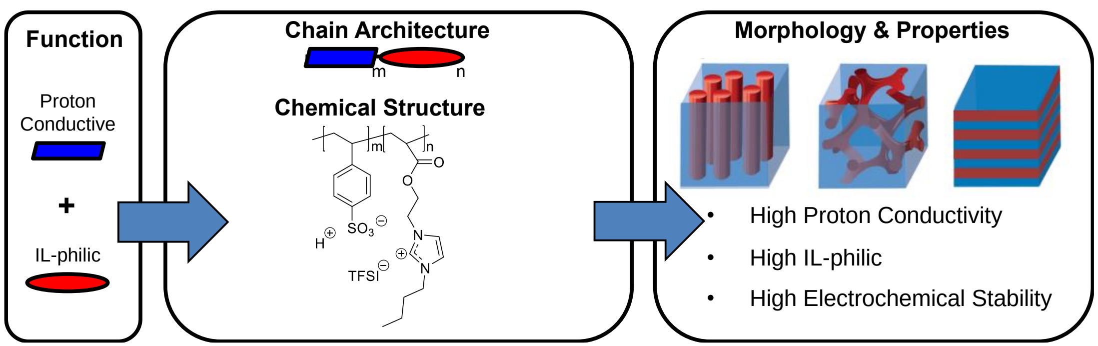
Polymerized Ionic Liquid Block Copolymer (PILBCP)



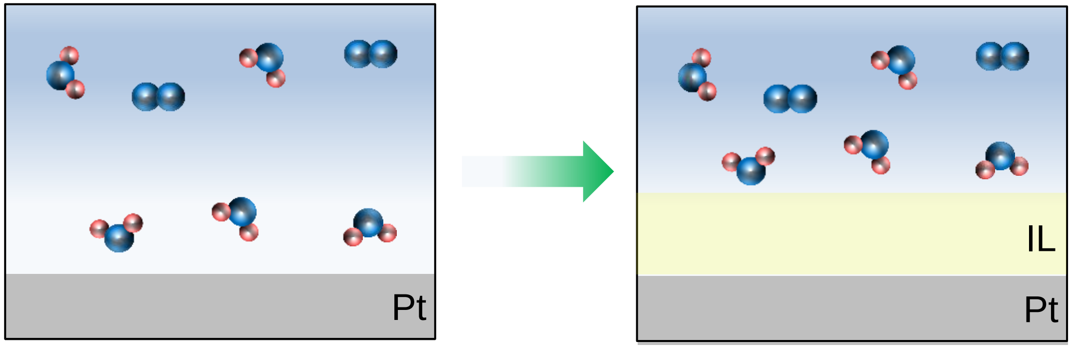
Ionic Liquid (IL)

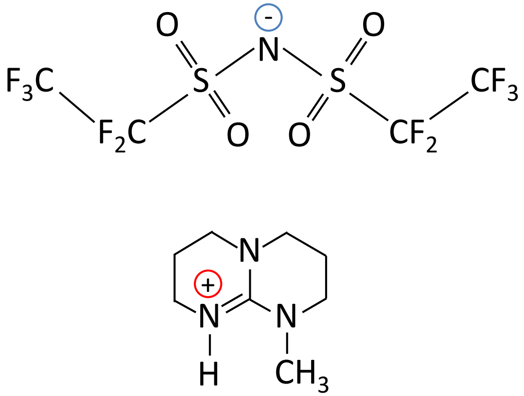


- IL interphase:
  1. Improved ORR
  2. Low humidity proton conduction
  3. Limited specific adsorption
- PILBCP polymer:
  1. IL domain improves interaction with IL interphase, decreasing interfacial resistances
  2. Improved retention of IL interphase
  3. Sulfonated domain is H_3O^+ transport block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

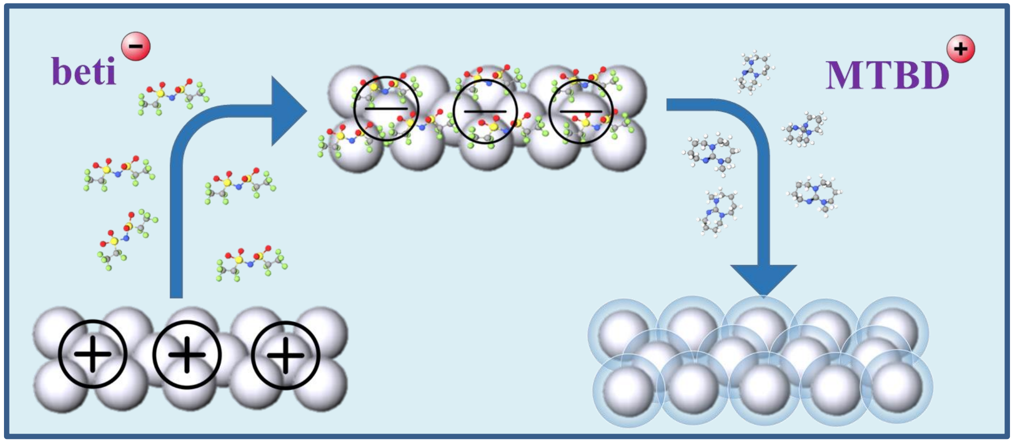


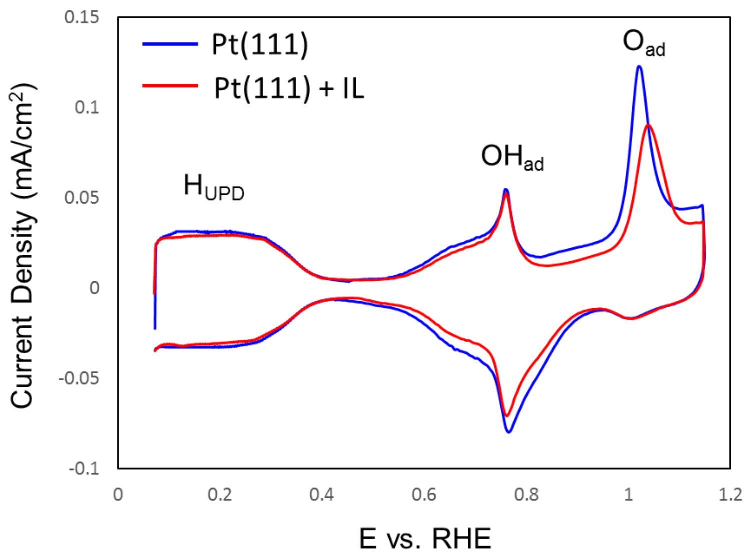
Accomplishments and Progress: Capacitive Deposition of IL





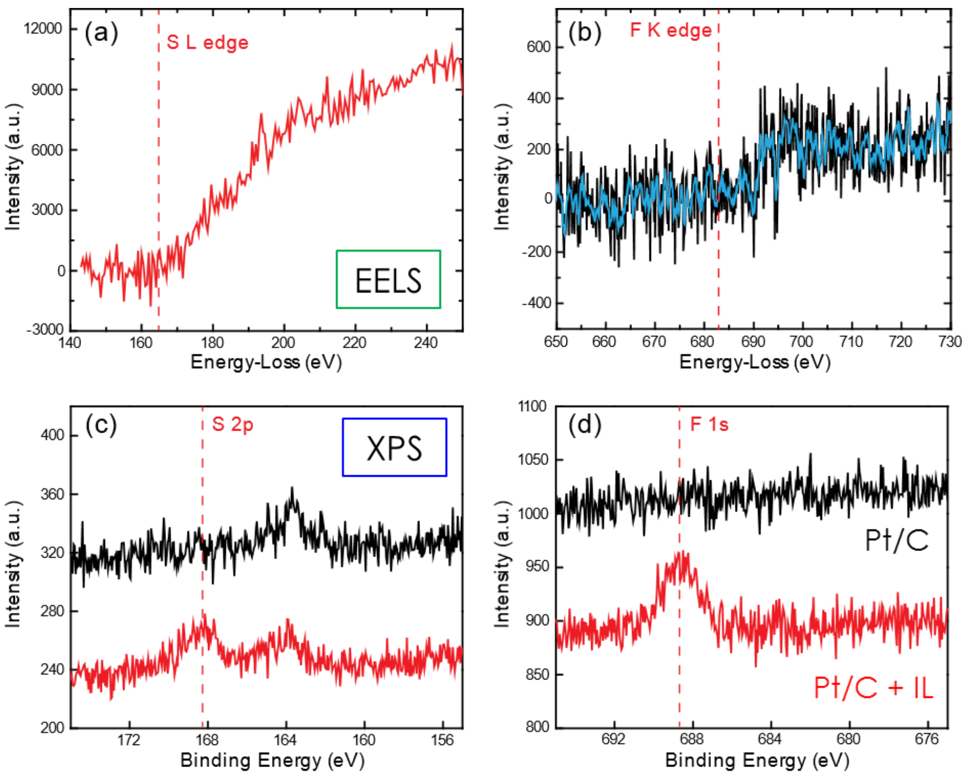
[MTBD][beti]



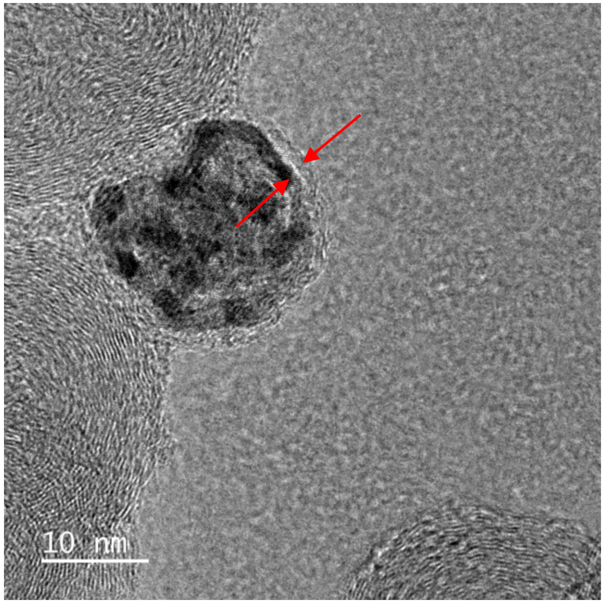


- Alternating potential and electrolyte composition sequentially attracts and condenses IL thin films on conductive electrodes

Accomplishments and Progress: Capacitive Deposition of IL

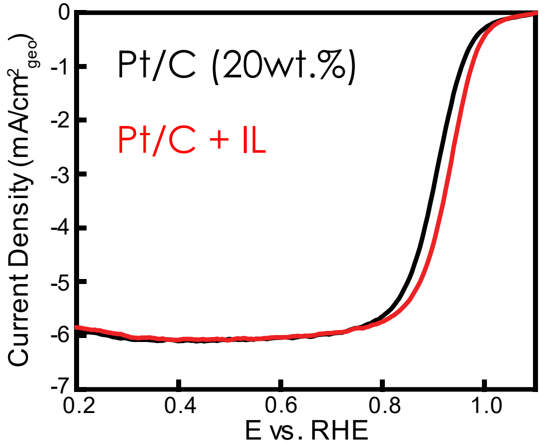


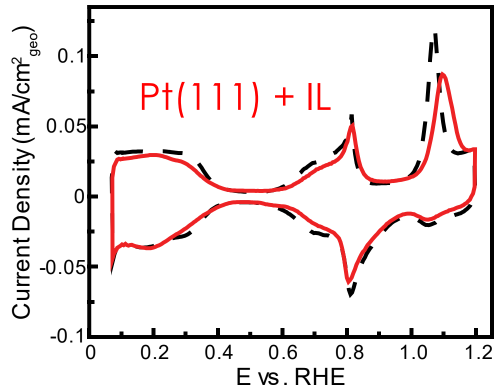
< 2 nm coatings

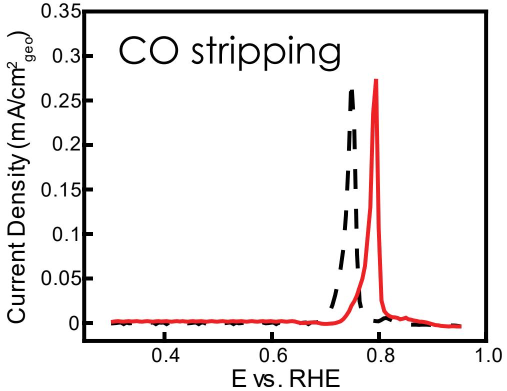


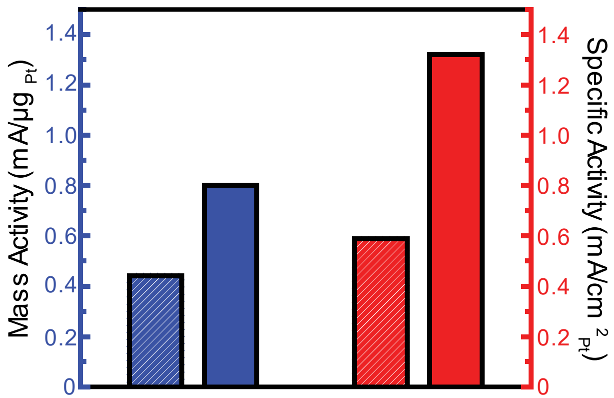
- Applied potential, immersion time, and electrolyte composition control IL thickness
- Conformal coating ensures complete coverage in 3D catalyst layers and limits pore blockage, minimizing impact on reactant transport

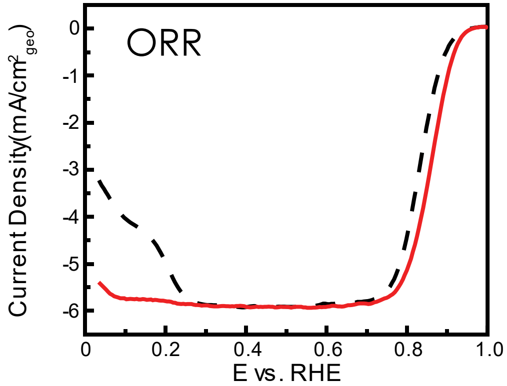
Accomplishments and Progress: Capacitive Deposition of IL











- ~2X improvement in mass and specific activity in the presence of the capacitively loaded IL thin film

SCD yields reproducible effect on planar surfaces and nanocatalysts. IL thin film reduces oxide coverage

Potential for IL thin film growth in 3D MEA catalyst layers

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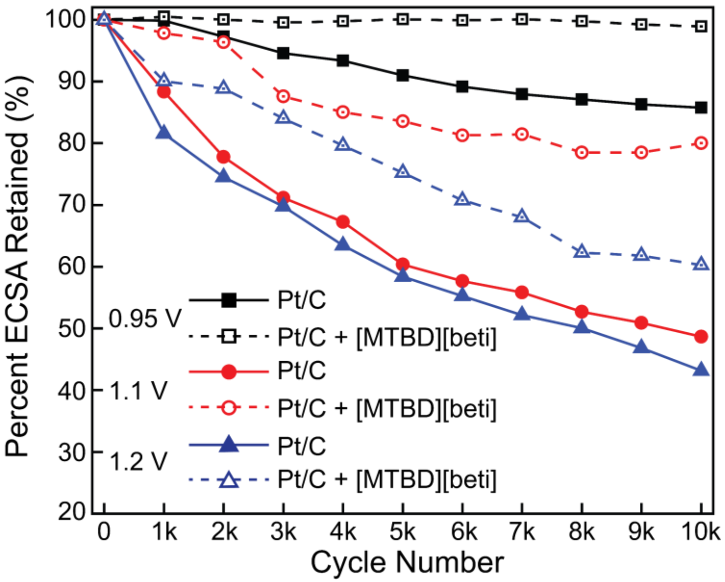
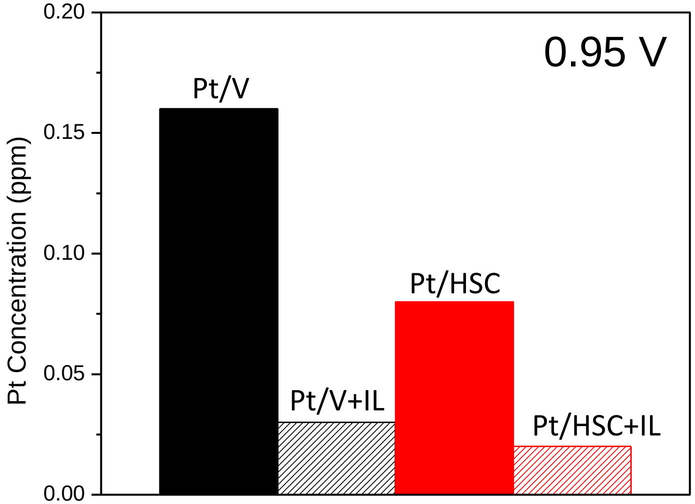
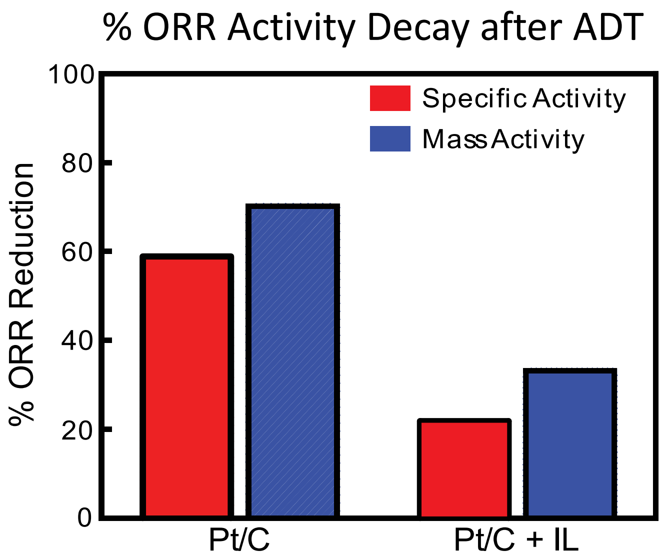
Accomplishments and Progress: Capacitive Deposition of IL

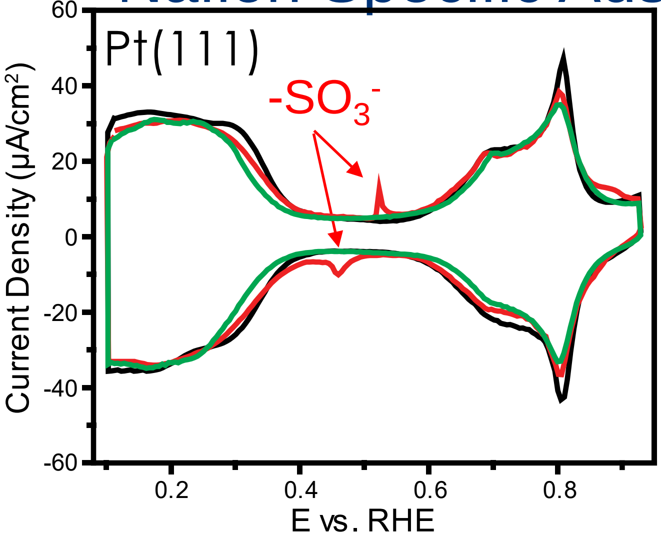


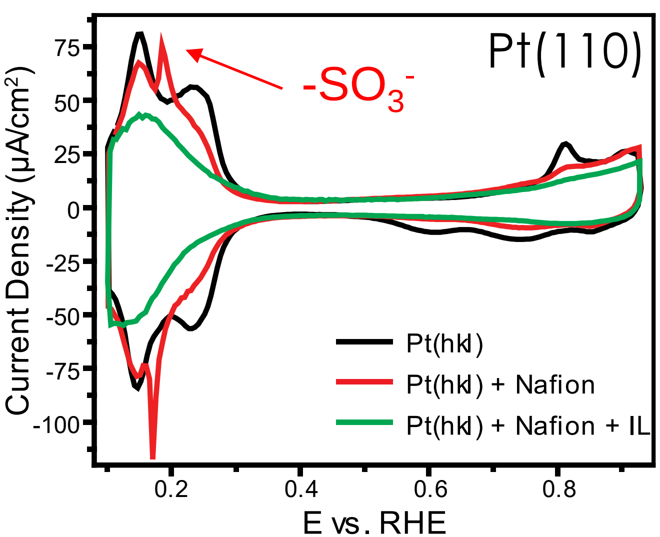


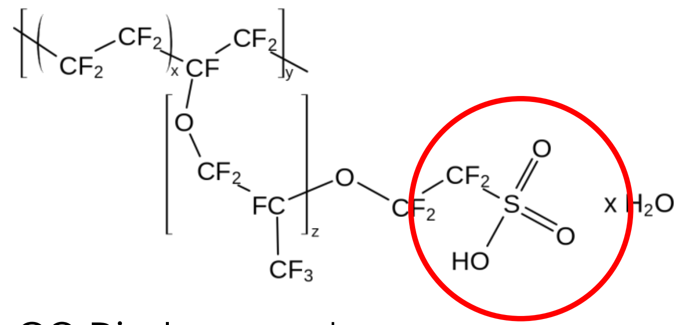


- ❑ Presence of IL thin film on Pt/V and Pt/HSC leads to significant improvements in ECSA retention during RDE AST (0.6-0.95 and 0.6-1.1 V vs. RHE)
- ❑ Hydrophobicity and low metal IL solubility of IL decrease Pt dissolution during RDE AST

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

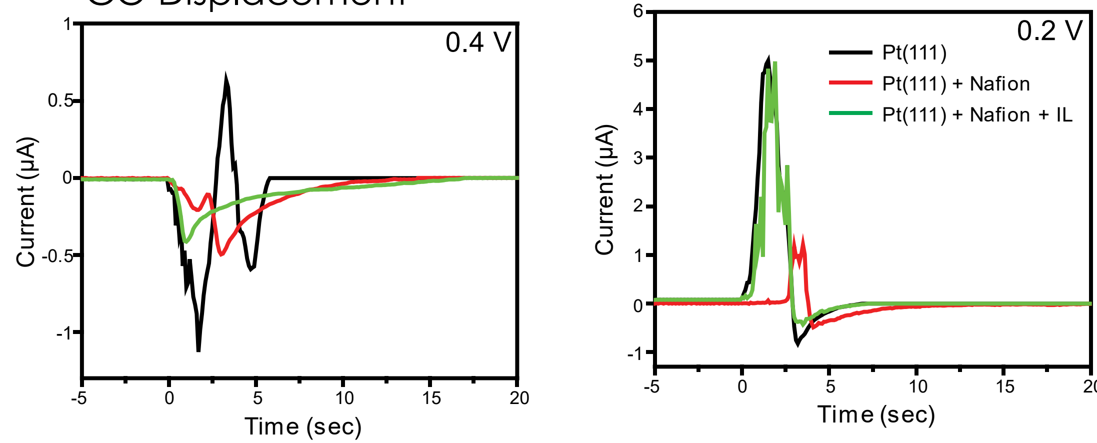






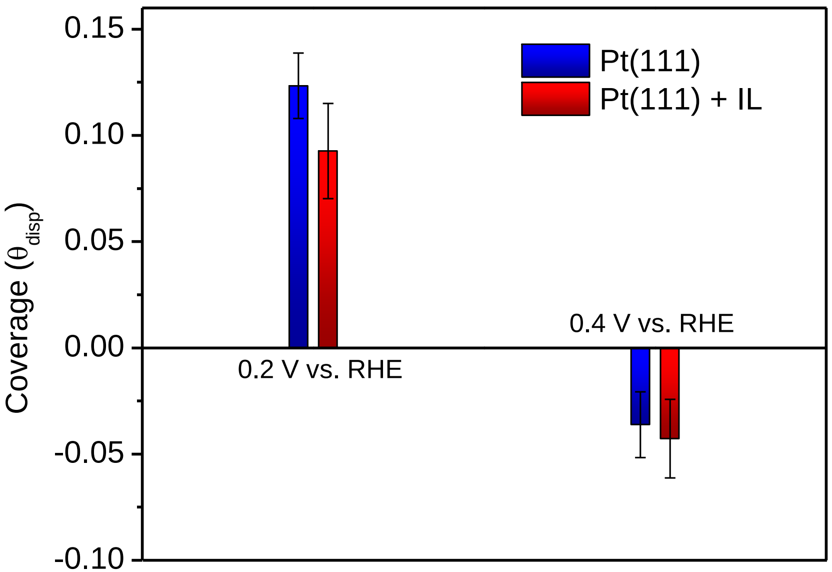
Nafion

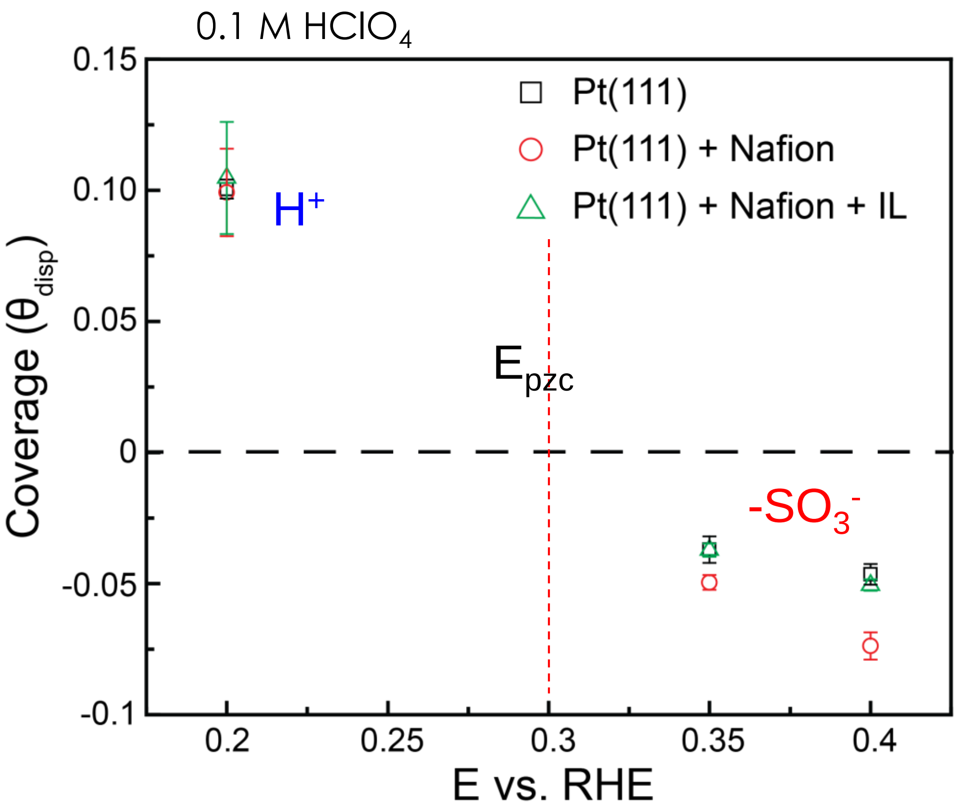
CO Displacement



- ❑ Presence of IL at the Pt surface prevents sulfonate specific adsorption either through physical blocking or charge screening
- ❑ IL also results in a reduction in OH_{ad}/O_{ad} coverage

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

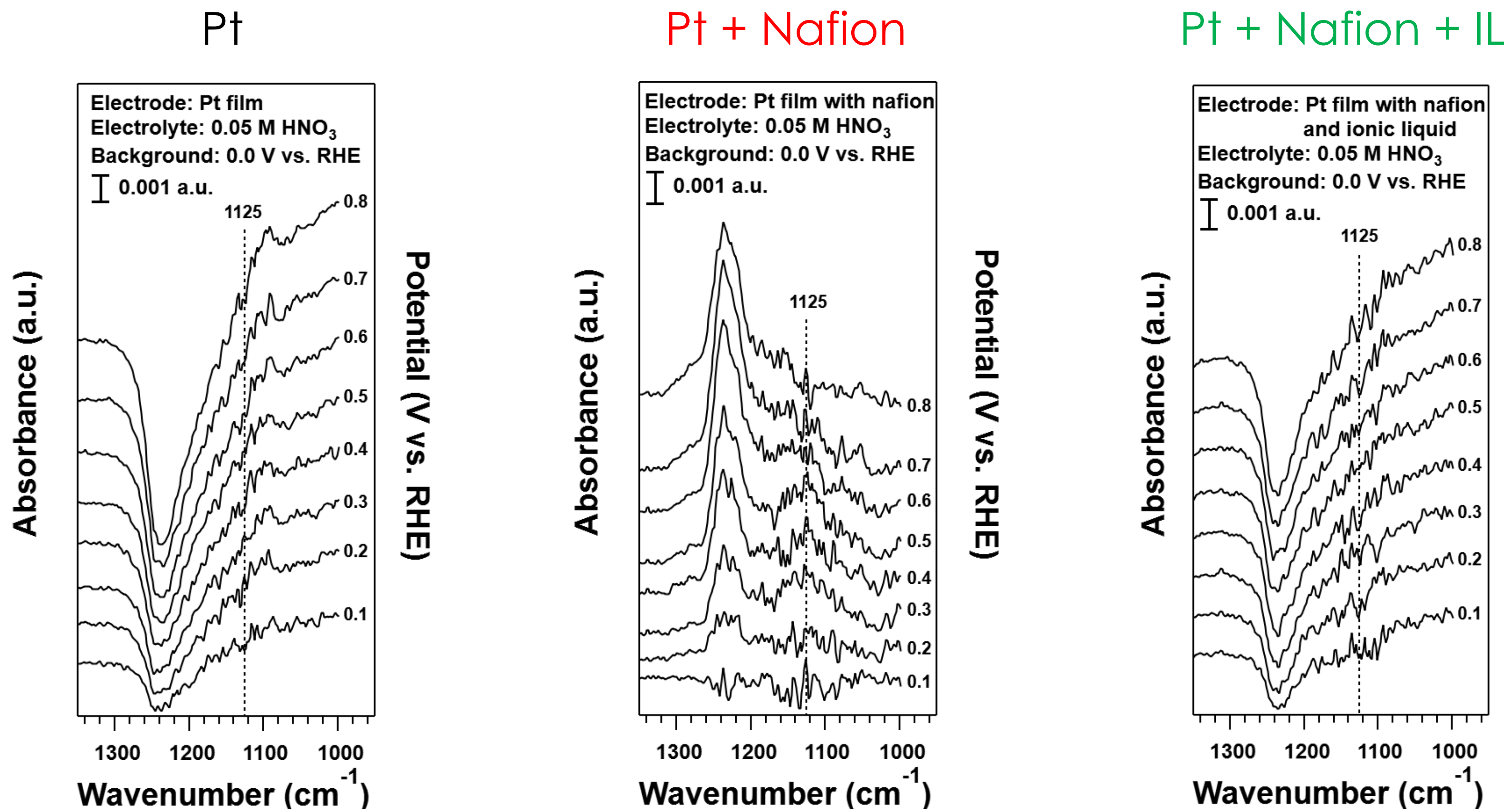




- ❑ IL moieties are sterically hindered from specific adsorption
- ❑ No statistically relevant difference in displacement charge on Pt(111) with and without IL thin film

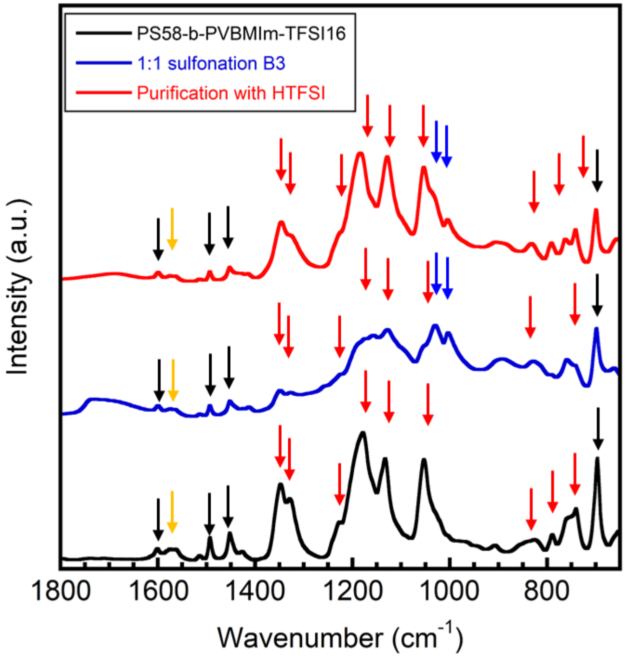
- ❑ Statistically relevant decrease in sulfonate coverage in the presence of IL

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



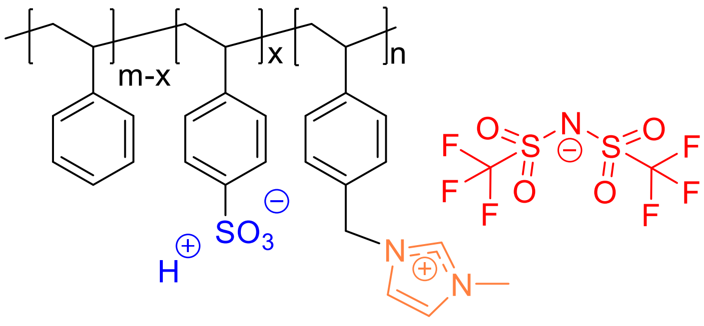
- Strong potential dependence of sulfonate adsorption (1125 cm^{-1}) for Nafion thin film
- No signals attributed to Nafion visible in the presence of IL

Accomplishments and Progress: PILBCP Synthesis



- Synthesized ~2 gram scale batches of first generation of the sulfonated polymerized ionic liquid block copolymer
- poly(SS-H-b-VBMIm-TFSI)

Generation 1 PILBCP Ionomer



- 1600, 1492, 1451 and 694 cm^{-1}

Imidazolium cation

- 1574 and 1564 cm^{-1}: imidazole ring stretching

TFSI anion

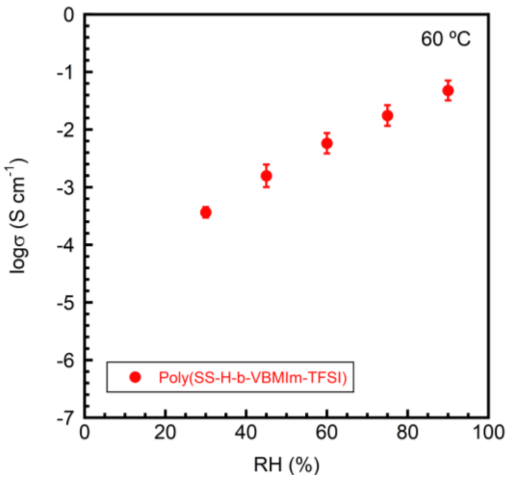
- 1348 and 1328 cm^{-1}: SO_2 antisymmetric stretching
- 1226 and 1180 cm^{-1}: CF_3 stretching
- 1133 cm^{-1}: SO_2 symmetric stretching
- 1053 cm^{-1}: N-S-N antisymmetric stretching

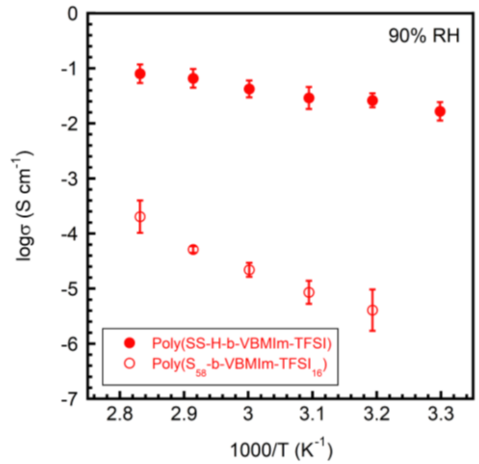
Sulfonic acid

- 1006 cm^{-1} : in-plane bending vibrations of the aromatic ring (in styrene) para-substituted with the sulfonate group
- 1034 cm^{-1}: symmetric stretching of SO_3-

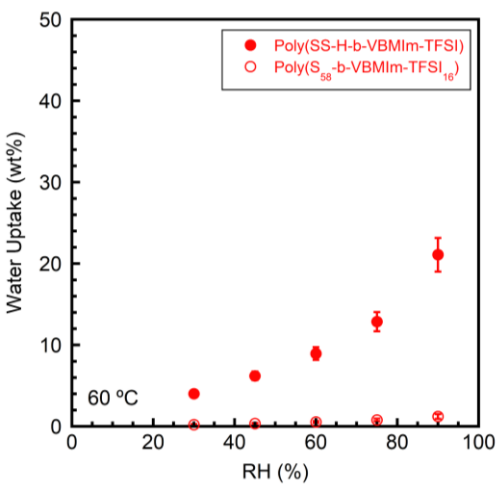
Accomplishments and Progress: PILBCP Synthesis

Poly(SS-H-b-VBMIm-TFSI)





- ❑ Ionic conductivities are comparable to Nafion
- ❑ Water uptake and conductivity decrease in the absence of sulfonated block. This indicates that the sulfonated block accounts for nearly all of the protonic conductivity



	Poly(S_{58}-b-VBMIm-$TFSI_{16}$)	Poly(SS-H-b-VBMIm-TFSI)	Nafion 212 (our lab)	Nafion 212 (Barique, M. A., et al)	Nafion 117 (Chen, L., et al)
$\sigma_{60\,°C,\,90\%\,RH}$ (mS cm^{-1})	0.022	42	106	104	133
$\sigma_{80\,°C,\,90\%\,RH}$ (mS cm^{-1})	0.20	80	151	136	144
Activation energy (KJ/mol)	91	28	-	-	10 ± 2
$WU_{60\,°C,\,90\%\,RH}$ (%)	1.2	21.1	-	-	-

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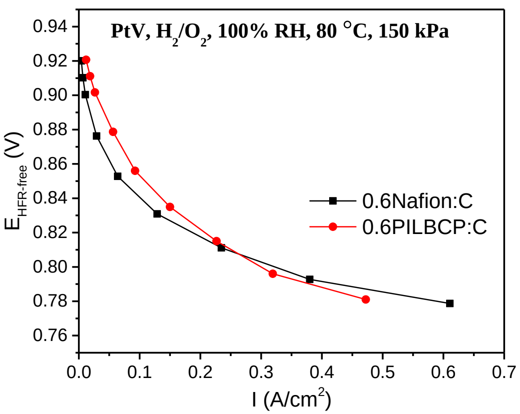
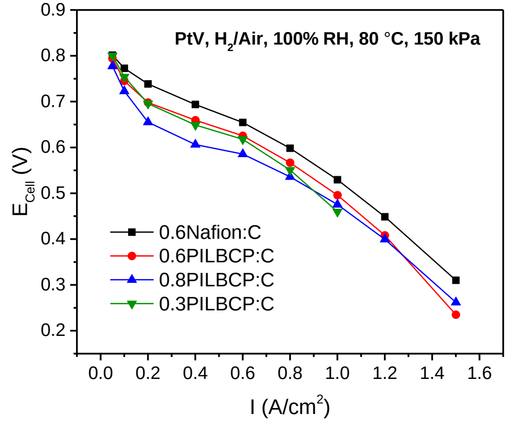
Accomplishments and Progress: PILBCP MEA Performance

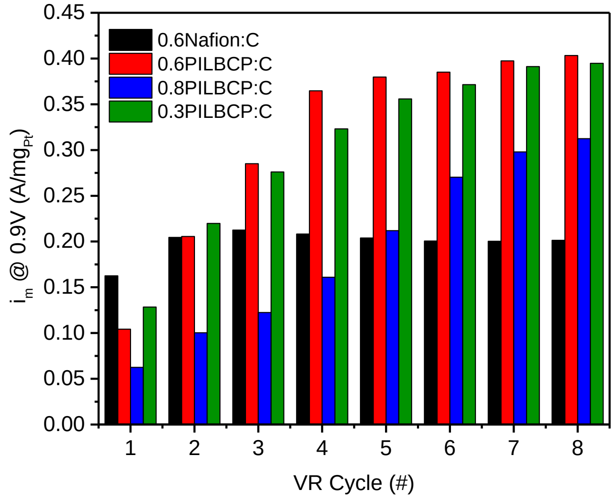
H_2/O_2



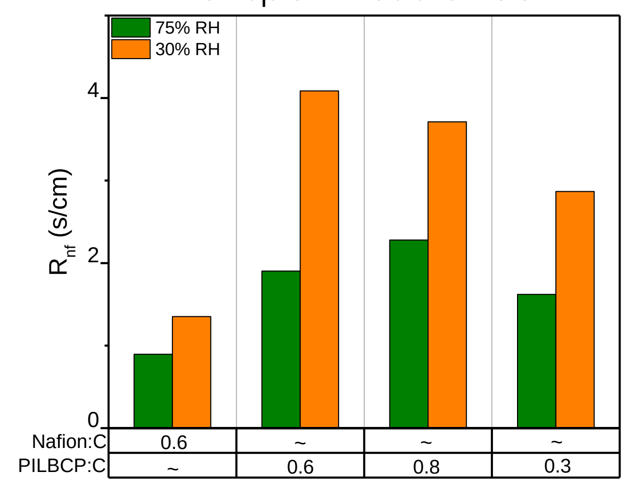
H_2/Air



Mass Activity

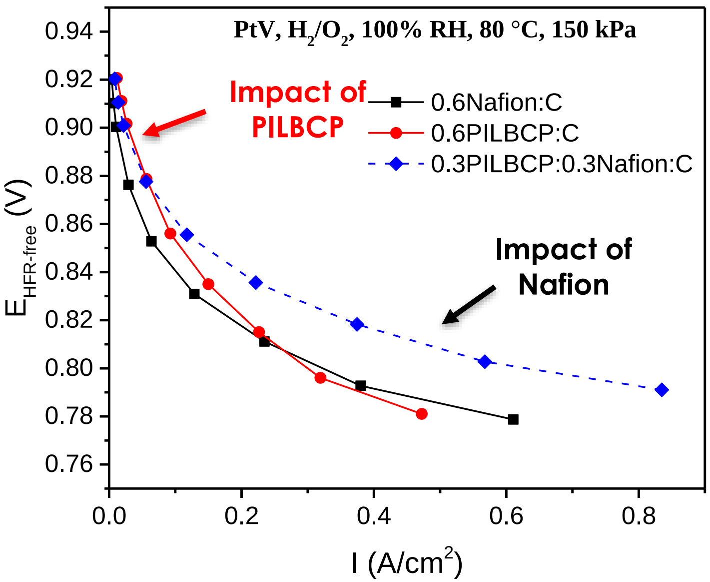


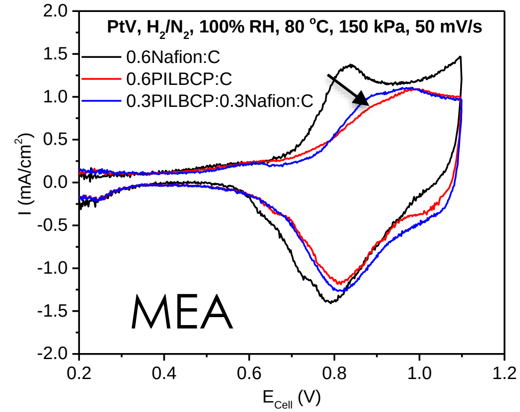
Non-Fickian O_2 Transport Resistance

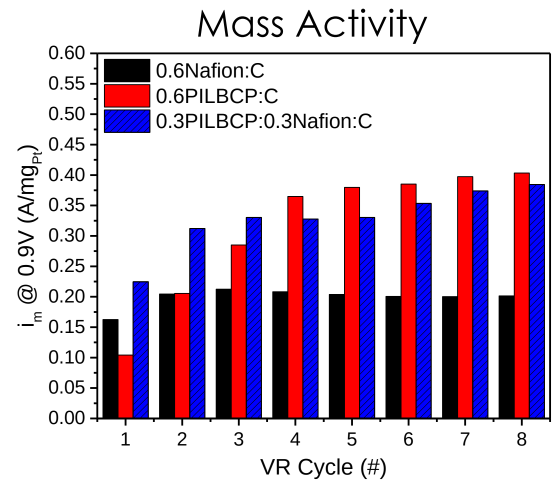


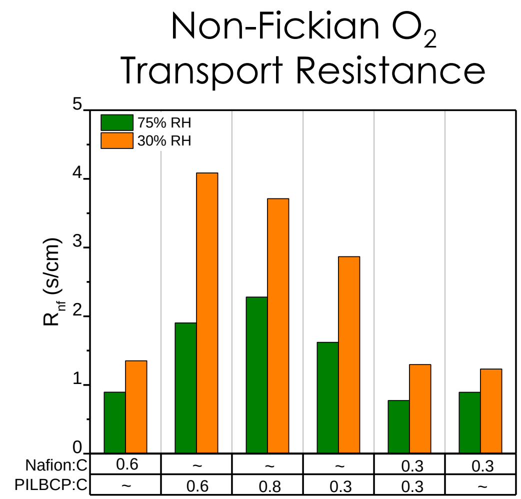
- ❑ PILBCP ionomer yields significant improvements in specific and mass activity at low current densities.
- ❑ Improvement in the kinetic region of the polarization curve is in line with what would be expected based on RDE testing with free ILs
- ❑ Loss in performance in comparison to Nafion ionomer in the cathode catalyst layer at HCD and when switching to air from O_2.
- ❑ Poor performance of PILBCP ionomer is likely due to incomplete dispersion, resulting in insufficient contact with catalyst and a low ECSA

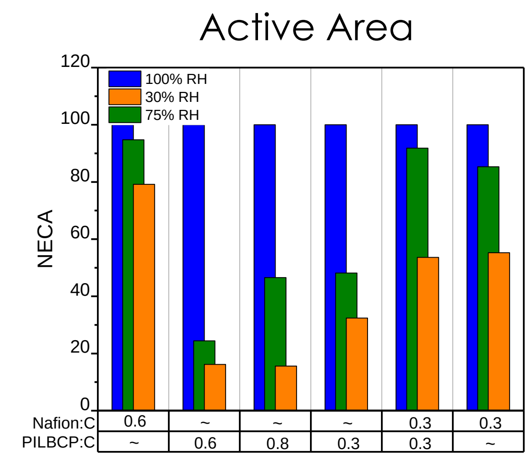
Accomplishments and Progress: PILBCP/Nafion mixed ionomer







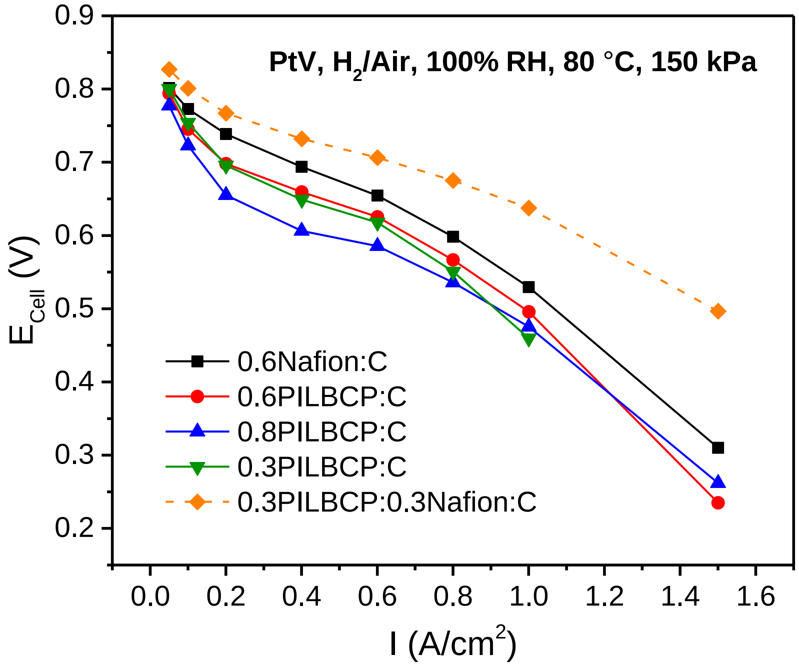




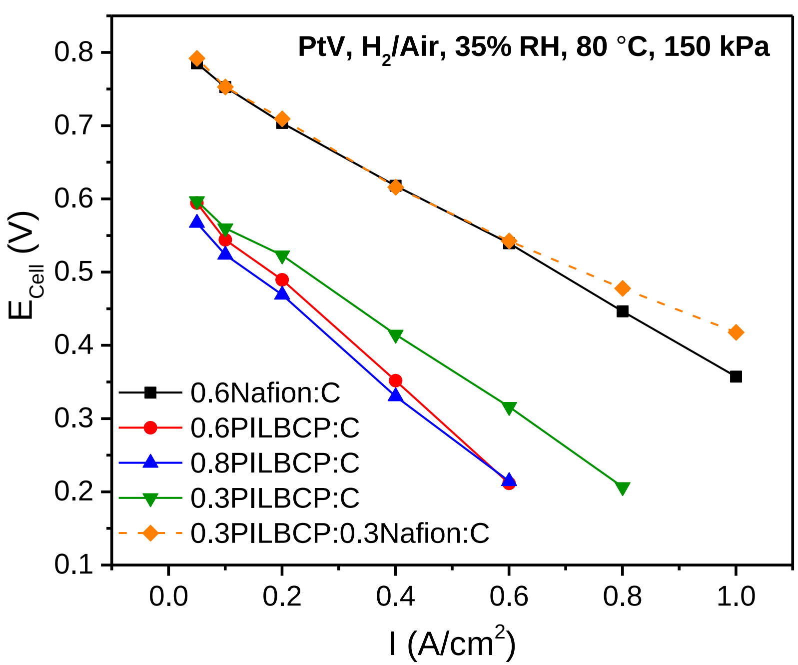
- Using a mixed Nafion/PILBCP ionomer, the kinetic performance enhancement of the PILBCP is retained but not with a significant increase in HCD performance
- Mixing Nafion with the PILCP results in a decrease in O_2 transport resistance and an increase in measured ECSA
- The Nafion acts to fill in the gaps between the less than optimal dispersion of the PILBCP ionomer

Accomplishments and Progress: PILBCP/Nafion mixed ionomer

H_2/air: 100% RH



H_2/air: 30% RH



- ❑ Mixing Nafion with the PILBCP yields greatly improved performance in H2/air at 100% RH.
- ❑ At low RH, 30%, the mixed ionomer matches that of Nafion, even surpassing it at HCD, with 50% of the Nafion mass in the catalyst layer.
- ❑ This demonstrates the promise of the PILBCP ionomer. Future work will push to completely remove reliance on Nafion.

Future Work

- Synthesis and ex-situ/half-cell screening of PILBCP and IL
- Development of new PILBCP chemistries
- 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
- 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 2:
MEA Performance and Durability

Materials Development

Subtask 2.1 → M2.2, M2.1

- Catalyst ink formulation and rheology
- Capacitive IL deposition

Ex-situ Characterization

Subtask 2.2

- Transport through PILBCP/IL composites

In-situ Characterization

Subtask 2.3 → M2.2, M2.3, M2.4

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

Project end goal: Demonstrate >1.2 W/cm^2 at 250 kPa in 50 cm^2 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

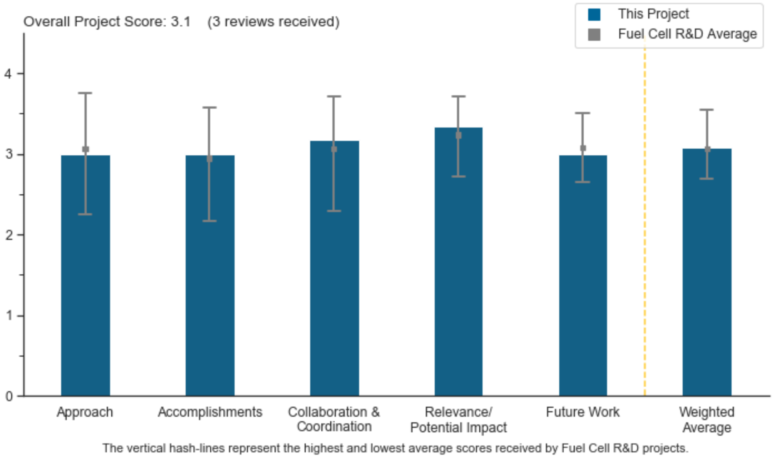
Responses to previous year AMR comments

- ILs will leach from the catalyst layer

Leaching of free IL during fuel cell operation is of concern. We can address this by (1) removing free IL and only using the PILBCP ionomer, (2) changing the chemistry of the IL to be one composed of more hydrophobic ions, and (3) optimize the coating protocols to minimize IL loading and proportionally decrease leaching.

- ILs are too expensive and approach is not likely to be cost effective

By addressing the HCD at low Pt loadings with a new ionomer that mitigates ion specific adsorption, has a high O_2 permeability, and enhances the ORR activity, we can significantly reduce the production and operational costs associated with current PEMFCs. At this early stage, the reviewer's comment has merit in terms of material costs. ILs and their precursors are expensive and the synthesis protocol for the PILBCP is currently time consuming. However, the total quantity per mass of IL and ionomer within the catalyst layer of a PEMFC stack represents a very small fraction of the stack cost. GM estimates that the quantity of IL needed in the catalyst layers represents less than 1% of the stack cost. Additionally, in contrast to Pt-based catalysts, the cost of IL and PILBCP ionomer is amenable to the economics of scale and it is likely that cost reductions can be achieved through manufacturing scale-up.



- Oppositely charged ionic groups in a single polymer could neutralize each other

Once the PILBCP is solidified into the phase-separated block configuration, it is highly unlikely that the charged species in the two groups would come into contact with each other in any significant fraction. This would be a sterically and entropically prohibitive process. However, it is possible that while dispersed in the catalyst ink, the oppositely charged groups of the block co-polymer could neutralize each other. Our preliminary work suggests that this is not the case but we will do SAXS/WAXS and TEM on re-cast polymer films to demonstrate the re-formation of the phase separated charged blocks after casting from a polymer/solvent solution.

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

❑ Technical Targets

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 $mV_{iR\text{-}free}$	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	←

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