ILBCP-IL Composite Ionomers for High Current Density Performance

FC309

PI: Joshua Snyder

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

April 29, 2019

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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)
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.

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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/cm² 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 W/cm² 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)

<table>
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<td><strong>Program Timeline</strong></td>
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<td>Quarterly Report and Milestones</td>
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<td>Yearly Go/No-Go Decision</td>
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<td>Annual Program Review</td>
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<td>Final Report</td>
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<td>Phases (Budget Periods)</td>
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<td>Phase 1: PILBCP/Ionic Liquid Composite Ionomer Development</td>
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<td>Phase 2: High Current Density Performance and Stability with PILBCP/IL Compositie Ionomers</td>
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<th>Task</th>
<th>2019</th>
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<td><strong>Task 0 - Program Management and Planning</strong></td>
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<tr>
<td>0.1 Project Kick-off Meeting</td>
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<td>0.2 Project Management, Planning, Review, and Reporting</td>
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<td>0.3 Final Report and Review Meeting</td>
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<td>1.1.1 PILBCP Ionomer Synthesis</td>
<td>TAMU</td>
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<td>1.1.2 IL Screening and Synthesis</td>
<td>Drexel</td>
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<tr>
<td>1.2.1 Establish Baseline with Nafion/[MTBD][beti] and Pt</td>
<td>Drexel/GM/NREL</td>
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<td>1.2.2 Ex-situ Screening of PILBCP/IL Composite Thin Films</td>
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<td>2.3.2 Pt Utilization: Vulcan vs. High Surface Area Carbon</td>
<td>NREL/GM</td>
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<td>2.3.3 Composite Ionomer and Catalyst Durability at OCV and AST</td>
<td>GM</td>
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<td>2.3.4 Limiting Current for Proton and Oxygen Transport</td>
<td>NREL</td>
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Collaboration

GM

Drexel University

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

NREL

PILBCP synthesis
Ex-situ Ionomer characterization

ATM

MEA diagnostics
MEA performance testing

Ink development
MEA diagnostics
Concept

**IL Interphase**

**PILBCP**

**IL Domain**

**PILBCP**

**Sulfonated Domain**

- **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 $\text{H}_3\text{O}^+$ transport block
  4. Domain organization in the absence of PFSA
Accomplishments and Progress: Previous EERE Results – FC144

H₂/air I-V curve

- H₂/air, 150kPa(abs), 100%RH, high stoich
- Differential 5 cm²

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

- 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: 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

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

![Diagram showing the process of capacitive deposition of IL on Pt electrodes.]

The chemical structure of [MTBD][beti] and the current density vs. potential (E vs. RHE) graph indicating the behavior of Pt(111) and Pt(111) + IL.
Accomplishments and Progress: Capacitive Deposition of IL

- 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 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][betti]
- 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

- PILBCP ionomer synthesis
- IL synthesis and screening

Subtask 1.2

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

Characterization

M1.1
M1.3
M1.4

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

GNG1: Demonstrate >1.0 W/cm² at 250 kPa in 25 cm² MEA with two PILBCP/IL chemistries
Future Work

Task 2: MEA Performance and Durability

Materials Development
- Subtask 2.1
  - 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
  - PILBCP/IL loading
  - Pt utilization
  - Composite ionomer/catalyst durability

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

Chain Architecture

Chemical Structure

Morphology & Properties

• High Proton Conductivity
• High IL-philic
• High Electrochemical Stability

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

\[ \text{Future Work: PILBCP Synthesis} \]

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\[ \begin{align*}
\text{(I)} & \quad \text{(II)} & \quad \text{(III)} & \quad \text{(IV)} \\
& \quad \text{(V)} & \quad \text{aromatic protons} & \\
\end{align*} \]

\[ \text{(I) (II) (III) (IV) (V) (VI)} \]

\[ \begin{align*}
\text{1H NMR (500 MHz, 23 °C) Chemical Shift (ppm)}
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Summary

- PILBCP Composite Ionomers
  1. Improved ORR
  2. Low humidity proton conduction
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  4. IL domain improves interaction with IL interphase, decreasing interfacial resistances
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- Technical Targets

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