
Polymerized Ionic Liquid Block Copolymer/Ionic Liquid Composite Ionomers for High Current Density Performance

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- Drexel University, Philadelphia, PA
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- Texas A&M University, College Station, TX
- General Motors, Pontiac, MI

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Project End Date: December 31, 2020

Overall Objectives

- Develop polymerized ionic liquid block copolymer/ionic liquid (PILBCP/IL) composite ionomer to replace perfluorosulfonic acid (PFSA)-based ionomers.
- Improve low current density performance with kinetic enhancements through ionic liquid interlayer.
- Improve high current density (HCD) performance by mitigating ionic specific adsorption and increasing oxygen permeability of the ionomer thin film.
- Increase Pt utilization at low relative humidity for high-surface-area carbons (HSC) with protic ionic liquid interlayers.

Fiscal Year (FY) 2019 Objectives

- PILBCP synthesis.
- Ionic liquid synthesis and screening.
- Baseline testing of Nafion/IL composites.
- Ex situ and in situ screening of PILBCP/IL composite ionomers.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan¹:

- (A) Durability
- (B) Cost
- (C) Water management.

Technical Targets

The DOE technical targets and our current project status are listed in Table 1 for comparison.

FY 2019 Accomplishments

- Established baseline half-cell activity (oxygen reduction reaction [ORR]) metrics for Nafion/[MTBD][beti]² composite electrodes
- Synthesized first generation of PILBCP with proton conducting and IL-functionality blocks.
- Demonstrated greater than 100% improvement in ORR activity with both free ionic liquids and first generation PILBCP with half-cell rotating disk electrode (RDE).
- Developed new methodology for loading catalyst layers with IL thin films (<2 nm thick).
- Quantified the reduction in ionomer specific adsorption in the presence of an IL interlayer.

¹ <https://www.energy.gov/eere/fuelcells/downloads/fuel-cell-technologies-office-multi-year-research-development-and-22>

² [MTBD][beti] – [7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene][bis(perfluoroethylsulfonyl)imide]

- Demonstrated ~3X improvement in mass activity for PtCo/HSC with Nafion/PILBCP mixed ionomers in a 50-cm² membrane electrode assembly (MEA).
- Achieved greater than 1.0 W/cm² in a 50-cm² MEA with Nafion/PILBCP mixed ionomer.

Table 1. 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-free}	A/mg _{PGM}	0.6	0.6	>0.44	←
Loss in catalytic (mass) activity	% loss	30%	-	<40%	←
Performance at 0.8 V (150 kPa, 80 °C)	A/cm ²	0.30	0.31	>0.3	←
Power at rated power (150 kPa, 94 °C)	W/cm ²	0.80	-	>1.0	←
Power at rated power (250 kPa, 94 °C)	W/cm ²	1.01	1.05	-	>1.2
PGM utilization (150 kPa, 94 °C)	kW/g _{PGM}	6.4	-	>8	←
PGM utilization (250 kPa, 94 °C)	kW/g _{PGM}	8.1	10	-	>9.1
Catalyst cycling (0.6–0.95 V, 30,000 cycles)	mV loss at 0.8 A/cm ²	24	-	<30	←

PGM – platinum group metal

KB – Ketjen black

INTRODUCTION

It has been demonstrated that a means of further fuel cell cost reduction is through improvement in HCD performance [1]. For low-PGM electrodes, the interface between Pt and the PFSA-based ionomer electrolyte has been shown to be a major source of HCD performance limitation. The local O₂ transport resistance, $R_{O_2}^{Pt}$, at the Pt catalyst and PFSA ionomer interface is attributed to the presence of the ionomer thin film in carbon-ionomer agglomerates [1]. Although the presence of the ionomer is critical for proton transport to the catalysts, the metal/ionomer interface creates an inherent barrier to reactant transport through (1) specific adsorption of the sulfonic acid groups of the ionomer onto the Pt surface, and (2) migration of the polymer chains toward the catalyst surface as a consequence of that specific adsorption [1]. Both result in an impeded O₂ transport, exacerbating O₂ starvation at HCD.

In our previous DOE-funded project, “Highly Accessible Catalysts for Durable High-Power Performance,” we demonstrated that interface modification with ILs such as [MTBD][beti] can more than double the ORR activity of Pt/V as measured in a half-cell RDE. In the MEA, enhancement of ORR activity increases with current density, up to 1.5–3x at 2.5 A/cm². Analysis at General Motors has determined that IL cost can be <1% of the stack cost. Electrochemical stability of ILs has been sufficiently proven [2, 3]. Despite much promise, practical implementation of IL in the MEA is not developed. Reproducibility in adding IL to the electrode is currently not sufficient. Although untested, there is concern whether IL, being a free liquid, will remain in the electrode without being washed out in the long term. In this project, we propose that combining the IL with novel ionomers will improve and stabilize the catalyst/ionomer interface to minimize interfacial O₂ transport resistances that become limiting at HCD. The goal of this project is to develop a PILBCP/IL composite ionomer to replace traditional PFSA-based ionomers and address their associated limitations (Figure 1). 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.

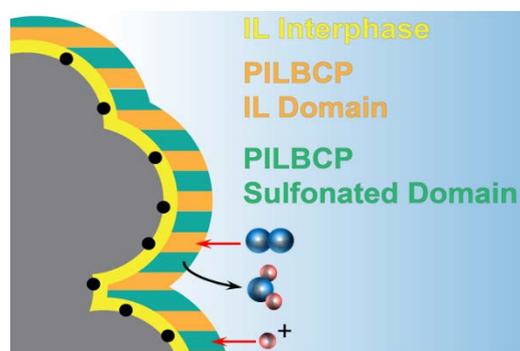


Figure 1. Schematic of the interface between catalyst, IL interphase, and PILBCP ionomer. The PILBCP is composed of an IL domain that optimizes the interaction with the IL interphase and a sulfonated domain that provides fast proton transport and water management.

APPROACH

Free Ionic Liquid Interlayer

ILs have demonstrated an improvement in both the ORR activity and durability for carbon-supported Pt-based electrocatalysts. They also have the potential to mitigate many of the detrimental impacts of the ionomer catalyst interface, including (1) specific adsorption of ionic components, (2) low oxygen permeability, and (3) poor humidity tolerance. The anhydrous protonic conductivity of ILs also has the potential to facilitate high Pt utilization for porous carbons at low humidity conditions. These combined attributes will facilitate improvements to HCD performance over a broad relative humidity range. Full integration of the IL into the catalyst layer necessitates a conformal coating where thin IL films cover the catalyst, on the order of nanometers, to limit the impact on reactant transport at both the meso- and macro-pore scale. We use a capacitively driven deposition process where the ionic precursors of the IL are sequentially attracted to the electrode through applied potential. A potential above the pzc of the electrode, but below the onset of passage of any faradaic charge, in an electrolyte containing the requisite organic anion draws the anion to the electrode surface. The potential is maintained while excess ion is washed and then switched to lower potential as the anion is introduced. Ion-exchange reactions at the metal/electrolyte interface then induce condensation of the hydrophobic IL thin film. In this way, we can deposit IL thin films on either free catalysts or preformed MEA electrodes, integrated with current ionomer distribution methodologies. The broad range of IL chemistries available for both the cation and anion yields the ability to tune the interphase layer chemistry for the optimization of desired properties. Targeted properties of the IL include its O₂ solubility/diffusivity, electrochemical stability, water solubility, and hydrophobicity.

Sulfonated PILBCP Ionomers

To address the challenges of replacing PSFA-based ionomers while combining proton conductivity and IL functionality for an ideal interface between the ionomer and IL, the synthesis of a new polymer materials platform for ionomers in PEM fuel cells is proposed: sulfonated PILBCPs. This new ionomer will comprehensively possess multiple desired properties including high proton conductivity, IL-philicity, and high electrochemical stability with discrete nanostructured channels. PILBCPs in general are a distinct set of block copolymers that combine the properties of both ILs and block copolymers, where the resulting material can possess orthogonal properties (in this case, high proton conductivity [from the sulfonated polymer] and IL-philicity [from the polymerized ionic liquid]) through the self-assembly of two distinct polymers into well-defined nanostructures of long-range order (e.g., body-centered-cubic spheres, hexagonal cylinders, bicontinuous gyroid, lamellae) with tunable morphology and domain size. Advantages of PILBCP ionomers include a combination of properties that cannot be obtained by other PFSA ionomers, namely (1) high proton conductivity, (2) lower degree of swelling, (3) more favorable O₂ diffusivity and solubility, (4) enhanced humidity tolerance, (5) optimal interface with ILs, and (6) a broad library of chemistries for the IL block. This provides flexibility to optimize the properties of the sulfonated PILBCP and its interaction with the IL thin

film on the surface of the catalyst. Sulfonated PILBCPs will help to optimize the interface between IL and ionomer, minimizing interfacial resistances and improving IL interphase retention.

RESULTS

The first year of this project was focused on the synthesis and development of the PILBCP ionomer, establishing baselines for Nafion and free IL effects in terms of ionic specific adsorption and ORR performance, and initial MEA testing of the free IL and PILBCP ionomer in the cathode catalyst layer. In pursuit of these aims we have successfully synthesized the first PILBCP chemistry (Poly(SS-H-b-VBMIm-TFSI)) in gram-scale quantities, established the methodology for quantifying the specific adsorption of charged groups in ionomers onto catalyst surfaces, established a new technique for loading IL into a catalyst layer, and began integration of the PILBCP ionomer into the fuel cell MEA.

Integration of free ILs into an MEA catalyst layer is not a trivial task. Care must be taken in ensuring sufficient catalyst coverage without blocking the secondary pores within the catalyst layer so as to minimize reactant gas transport losses. To this end, we have developed a sequential capacitive deposition procedure that allows us to electrochemically deposit thin films (<2 nm) of ILs conformally onto three-dimensional catalyst layers. We have demonstrated this procedure for both RDE catalyst films and extended single crystal surfaces (Figure 2). Following sequential deposition of the IL, we observe an increase in both catalyst activity and durability. This procedure can be readily extended to premade three-dimensional MEA catalyst layers.

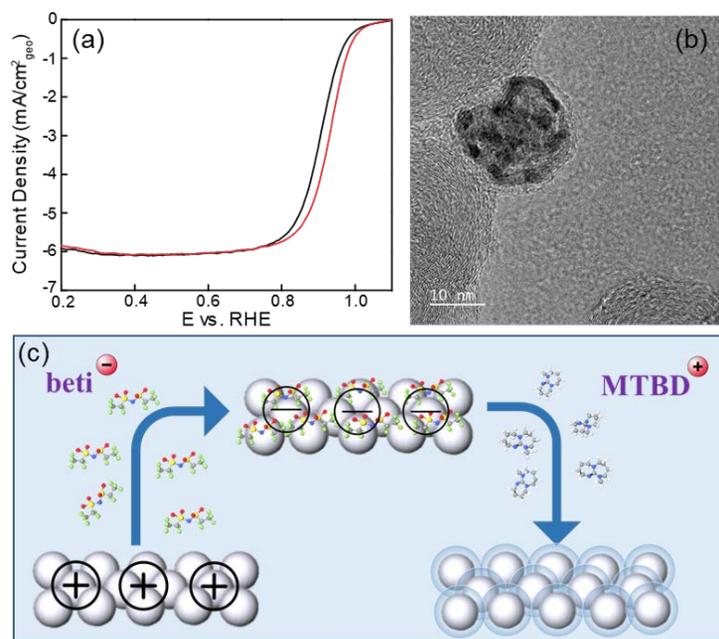


Figure 2. (a) ORR polarization curves for Pt/V (black line) and Pt/V + [MTBD][beti] (red line) following sequential capacitive deposition of the IL. Polarization curves measured in O₂ saturated 0.1 M HClO₄ at room temperature with a sweep rate of 20 mV/s and a rotation rate of 1,600 rpm. (b) Transmission electron microscopy of IL thin film deposited through sequential capacitive on Pt nanoparticle. (c) Schematic of the sequential capacitive deposition procedure.

Assessing the impact of free IL and the PILBCP ionomer on the specific adsorption of charged groups on the ionomer is required to quantify the impact of the ionomer on active site blocking, which is known to affect HCD performance. We have developed an experimental protocol to quantify ionomer specific adsorption, using CO displacement, and determine both the coverage and charge of the ion that is specifically adsorbing. By spin coating the ionomer as a thin film onto a Pt(111) single crystal, we can accurately assess the degree of specific adsorption of the ionomer as well as the impact of an IL interlayer on ionomer adsorption. In Figure 3, we plot the specific ion coverage as a function of potential as determined through CO displacement. At 0.35 and 0.4 V vs. reversible hydrogen electrode, where we would expect the sulfonate ion of Nafion to specifically

adsorb, we see a larger negative coverage on the Nafion-coated Pt(111) as compared to the bare Pt(111). This is indicative of a larger anionic coverage in the presence of Nafion, which is due to the specific adsorption of the sulfonate groups. When a free IL interphase is between the Nafion and Pt(111) surface, we see a decrease in the anionic coverage, back to where it is for the bare Pt(111). This demonstrates the ability of the IL to mitigate the specific adsorption of ionomer charged groups, which will have significant consequence for fuel cell HCD performance. This protocol will be used to assess the specific adsorption of the newly developed PILBCP ionomers.

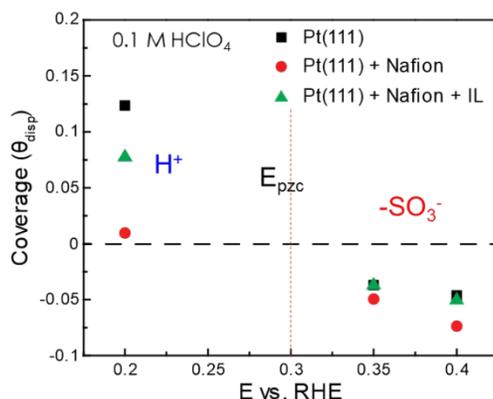


Figure 3. Coverage of specifically adsorbed ionic species on Pt(111) as a function of potential for bare Pt(111) (black square), Pt(111) + Nafion (red circles), and Pt(111) + Nafion + [MTBD][beti] (green triangles) as measured by CO displacement in 0.1 M HClO₄.

Following synthesis of the first iteration of the PILBCP ionomer, we have compared its impact on ORR activity in the half-cell with that of the free IL (Figure 4). Encouragingly, we find that the PILBCP yields similar kinetic improvements in the ORR when compared to the combination of the free IL and Nafion. This result indicates that we are getting IL functionality from the PILBCP. This is promising as the PILBCP will not be susceptible to washing from the MEA catalyst layer during operation, in contrast to the free IL, and will help to mitigate one of the major limitations associated with IL incorporation into the catalyst layer.

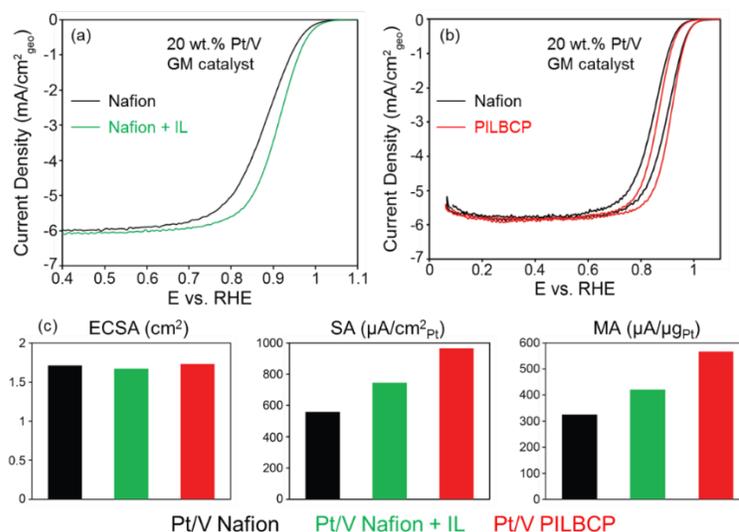


Figure 4. (a) ORR polarization curves for Pt/V with 5 wt % Nafion (black line) and Pt/V with 5 wt % Nafion + [MTBD][beti] (green line). (b) ORR polarization curves for Pt/V with 5 wt % Nafion (black line) and Pt/V with 5 wt % PILBCP (red line). All polarization curves recorded in O₂ saturated 0.1 M HClO₄ at room temperature with a sweep rate of 20 mV/s and a rotation rate of 1,600 rpm. (c) Electrochemically active surface area, specific activity, and mass activity measured in the RDE half-cell for Pt/V + Nafion (black), Pt/V + Nafion + [MTBD][beti] (green), and Pt/V + PILBCP (red).

In FY 2019, we have also begun MEA testing of both the free IL and the PILBCP ionomer incorporated into the cathode catalyst layer. Impedance testing has demonstrated that the protonic conductivity of the first generation PILBCP is on the order of that of Nafion at 60°C. Development of the proper ink composition is in progress. Our initial efforts are focused on gradual incorporation of the PILBCP into the cathode catalyst layer with PtCo/HSC. In Figure 5, we show that the addition of PILBCP into the cathode catalyst layer with a 0.4 PILBCP : 0.5 Nafion : HSC ratio results in a significant enhancement in performance at low and moderate current densities in a 50-cm² MEA. We measure a mass activity of 0.85 A/mg_{Pt}, which is nearly double the 0.44 A/mg_{Pt} DOE target.

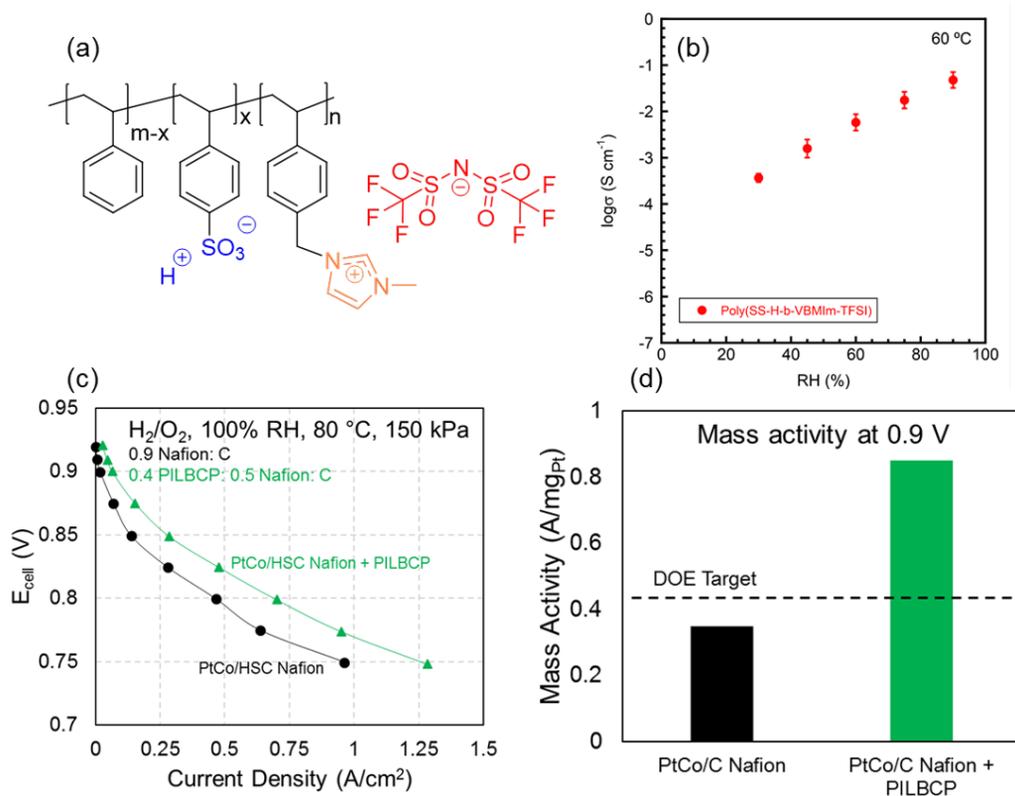


Figure 5. (a) Chemical structure of the first generation PILBCP. (b) Impedance measured ionic conductivity for the first generation PILBCP at 60°C as a function of relative humidity. (c) 50-cm² MEA polarization curves for PtCo/HSC + Nafion (black line/circles) and PtCo/HSC + Nafion + PILBCP (green line/triangles). (d) Mass activity for PtCo/HSC + Nafion (black) and PtCo/HSC + Nafion + PILBCP (green) extracted from the polarization curves in (c).

CONCLUSIONS AND UPCOMING ACTIVITIES

Progress toward milestones:

- Developed methodology for IL thin film deposition in three-dimensional catalyst layers
- Developed protocol for measuring ionomer specific adsorption
- Demonstrated impact of IL on ionomer specific adsorption
- Demonstrated greater than 20% improvement in ORR activity with ILs in half-cell RDE
- Synthesized gram-scale quantity of PILBCP
- Demonstrated an improvement in ORR activity with PILBCP
- Incorporated PILBCP into MEA cathode catalyst layer and demonstrated improvement in performance at low and moderate current densities.

Future work:

- Catalyst ink formulation and rheology
- Capacitive deposition for MEAs
- Development and testing of new PILBCP and IL chemistries
- Oxygen permeability measurements of PILBCP/IL composites both ex situ and in situ
- Full replacement of Nafion and other PFSA ionomers in the cathode catalyst layer
- Validation of National Renewable Energy Laboratory MEA testing by General Motors.

FY 2019 PUBLICATIONS/PRESENTATIONS

1. Y. Li, R. Gawas, and J. Snyder, “Ionic Liquid Interlayer for Enhanced Oxygen Reduction Reaction Electrocatalyst Activity and Durability,” Fall ECS Meeting, Atlanta, GA, October 13, 2019.
2. Y. Li, R. Gawas, and J. Snyder, “Ionic Liquid Interlayer for Enhanced Oxygen Reduction Reaction Electrocatalyst Activity and Durability,” Fall AIChE Meeting, Orlando, FL, November 13, 2019.

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3. M. Armand, F. Enders, D. MacFarlane, H. Ohno, and B. Scrosati, “Ionic-Liquid Materials for the Electrochemical Challenges of the Future,” *Nat. Mater.* 8 (2009): 621–629.