Electrode Ionomers for High Temperature Fuel Cells
## Overview

### Timeline
- Project start date: 10/1/2018
- Project end date: 9/30/2020
- Percent complete: 20%

### Budget
- Total project funding: $1000K
- Funding received in FY19: $0K
- Total DOE Funds Spent*: $102
*As of 2/28/19

### Barriers
- Cost
- Electrode performance
- Durability

### Project lead
- Sandia National Laboratories
  - Michael Hibbs (PI)
  - Cy Fujimoto
  - Ehren Baca

### Collaborators
- Los Alamos National Laboratory
  - Yu Seung Kim
  - Albert S. Lee
  - EunJoo Park
Relevance/Impact

Objective
Synthesis of durable ionomers and demonstration of their use in fuel cells that can operate at temperatures between 200-300 °C.

Targets
• > 500 mW/cm² peak power density under hydrogen/air conditions.
• Total precious group metal (PGM) loading of < 0.125 mgPGM/cm².
• <5% performance decrease after 1000 h operation at 200 °C.

Advantages of this technology
• Higher catalytic activity at higher temperatures (less catalyst needed).
• Easier thermal management (smaller radiators).
• No water needed (elimination of humidifiers).
• All of these lead to lower fuel cell costs.

Further cost reduction of fuel cells
High temperature and low RH fuel cell operation could enable fixed cost savings of $7.5/kW_{net} by eliminating or reducing the size of BOP components such as humidifier and radiator.

N. Dale, Nissan Motors
Relevance

Previous high temperature fuel cell membrane

Acid-base interaction energy calculated for small molecule model = 17.4 kcal/mol

LANL/SNL-developed high temperature fuel cell membrane

Impact of strong ion-pair interaction:
• Better performance at low temperature/high RH because biphosphate doesn’t leach out
• Better performance at high temperatures because biphosphate doesn’t evaporate
Approach: Proof of Concept
High Temperature Fuel Cell Performance
From DOE FCTO AOP Lab call project (2016-2018)

Membrane: PA-ADAPP
Ionomer: PA-ADAPP

Membrane: PA-ADAPP
Ionomer: PPFS

Measured in H₂/O₂, 147 kPa abs backpressure; Pt-Ru/C 0.75 mgPt/cm² for anode and Pt/C 0.6 mg/cm² for cathode

Better cell performance at 200 °C because phosphate can’t evaporate or leach out of electrodes.
Approach: Ionomer Structures

Prepare ionomers with covalently bonded phosphonic acid groups

General structure of proposed ionomers

Target characteristics
- $H^+$ conductivity > 100 mS/cm from 200-300 °C
- IEC between 1.5-3 meq/g
- $M_w$ between 20-200K (low $M_w$ to improve solubility)
- Solubility: 2-5 wt% in DMAc or DMSO
- Stability: <5% performance loss over 1000 hours

Features
- Diels-Alder polymerization forms poly(phenylene) without a catalyst and parent polymers are soluble in low-polarity organic solvents.
- Aromatic backbone for good mechanical properties at high temperatures
- No heteroatoms for maximum chemical and thermal stability
- Acid groups can’t evaporate or leach out
- Low acid content relative to acid-doped and biphosphate-ammonium ion pair systems
- Good interfacial compatibility with polyaromatic based ion-pair coordinated membrane
- DOE-owned intellectual property
Approach: Potential Obstacles and Mitigating Strategies

The proposed phosphonation reactions might have low yields or unwanted side products.

Several phosphonation routes are known and several ionomer structures are proposed. Success does not depend on a single synthetic scheme.

Limited ionomer solubilities might make electrode preparation difficult.

- Use low $M_w$ parent polymers.
- Increase ion content (IEC).
- Use polymers with protected phosphonic acid groups to prepare electrodes, then deprotect in the solid state.

The phenyl groups of the ionomers may adsorb on the surface of HOR catalyst and reduce activity.

Introduce (1) methyl groups onto backbone phenyl units or (2) poly(fluorene) backbone to fuse aromatic rings. Both options hinder phenyl group adsorption.
- Batches of BrC6PP, BrDAPP, and pentafluorophenyl DAPP have been prepared (Q1 milestone).
- Addition of protected phosphonic acid groups to DAPP is in progress (Q2 milestone).
Accomplishments and Progress

- Synthesis of poly(biphenylene) with tetrafluorophenyl phosphonic acid groups confirmed by $^{19}$F NMR. (Q2 milestone additional option)
- IEC = 2.2 meq/g
- Low molecular weight was designed to help with solubility.
- Fuel cell testing is TBD.
<table>
<thead>
<tr>
<th>Milestone</th>
<th>Type</th>
<th>Description</th>
<th>Proposed completion date</th>
<th>Actual completion date</th>
<th>Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly(phenylene) parent polymers</td>
<td>Q1 Progress Measure</td>
<td>Prepare 10-20g batches of BrDAPP and BrC6PP</td>
<td>12/31/2018</td>
<td>12/21/2019</td>
<td>Material is being used in phosphonation experiments.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Synthesis of PDAPP</td>
<td>Q3 Progress Measure</td>
<td>Prepare batches of PC6PP with 2 IECs between 1.5 and 3.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Membrane ASR</td>
<td>Go/No Go Decision</td>
<td>Measure membrane ASR using the high temperature MEA construction. ASR will be &lt;0.05 Ω cm² at 200°C.</td>
<td>9/30/2019</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Responses to Previous Year Reviewers’ Comments

This project was not reviewed last year.
## Collaboration and Coordination

<table>
<thead>
<tr>
<th>Partner</th>
<th>Project Roles</th>
</tr>
</thead>
</table>
| Sandia National Laboratories  | Project lead  
| Michael Hibbs                | Management and coordination  
| Cy Fujimoto                  | Synthesis of phosphonated DAPP-based ionomers  
| Ehren Baca                   | Synthesis of base membranes for PA-ADAPP ion pair membranes  
|                               | Characterization of ionomers                                                 |
| Los Alamos National Laboratory| Subrecipient  
| Yu Seung Kim                 | Synthesis of phosphonated polybiphenylene ionomer  
| Albert Lee                   | Evaluation of catalytic activity with new ionomers  
| Eun Joo Park                 | Fabrication of MEAs with new ionomers and fuel cell performance assessment  
|                               | Fuel cell durability assessment                                               |
Proposed Future Work

Remainder of FY 2019
• Synthesis of PCXPP ionomer with at least one X value, April 2019
• Synthesis of PDAPP and/or partially fluorinated PDAPP, June 2019
• Measure membrane ASR in MEA with new ionomers, September 2019

FY 2020
• Measure catalytic activity with new ionomers, December 2019
• Continue synthesis of down-selected ionomers, throughout FY 2020
• Optimize electrode structure using down-selected catalysts and ionomers, March 2020
• Low PGM fuel cell durability testing at 200 °C, June 2020
• Complete fuel cell performance and durability measurements, September 2020

Any proposed future work is subject to change based on funding levels.
Objective: Synthesis of durable ionomers and demonstration of their use in fuel cells that can operate at temperatures between 200-300 °C.

Relevance: Aiming to reduce fuel cell costs by enabling operation at high temperatures without humidification and low PGM loading.

Approach: Synthesis of ionomers based on poly(phenylene) backbones with covalently attached phosphonic acid groups.

Accomplishments: Synthesis of halogenated DAPP parent polymers is complete. Synthesis of phosphonated poly(biphenylene) with IEC of 2.2 meq/g is complete.

Collaborations: Phosphonated DAPP ionomers will be sent to LANL for fuel cell testing. Poly(biphenylene)s will be prepared and tested at LANL.
Technical Back-up Slides
## FY19 and FY20 Milestones

<table>
<thead>
<tr>
<th>Milestone</th>
<th>Description</th>
<th>Proposed completion date</th>
<th>Actual completion date</th>
<th>Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly(phenylene) parent polymers</td>
<td>Prepare 10-20g batches of BrDAPP and BrC6PP</td>
<td>12/31/2018</td>
<td>12/21/2018</td>
<td>Material is being used in phosphonation experiments.</td>
</tr>
<tr>
<td>Synthesis of PC6PP</td>
<td>Prepare batches of PC6PP with 2 IECs between 1.5 and 3.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Synthesis of PDAPP</td>
<td>Prepare batches of PDAPP with 2 IECs between 1.5 and 3.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Membrane ASR</td>
<td>Measure membrane ASR using the high temperature MEA construction</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Interfacial electrochemistry</td>
<td>Investigate HOR and ORR activity of catalyst in contact with the ionomers</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fuel cell performance optimization</td>
<td>Optimize electrode structure of HT-PEMFCs using down-selected catalysts</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fuel cell durability</td>
<td>Measure fuel cell durability of low PGM HT-PEMFCs at 200°C</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>