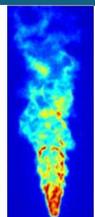


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Project ID: fc320

Electrode Ionomers for High Temperature Fuel Cells



PRESENTED BY

Michael Hibbs, PI, Sandia National Laboratories

2019 DOE Hydrogen and Fuel Cells Program Annual Merit Review and Peer Evaluation Meeting, April 29 - May 1, 2019



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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





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

Balance of Plant

- Humidifiers
- Large radiators
- Reactant quality control



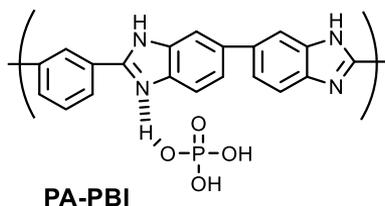
Simple Balance of Plant

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

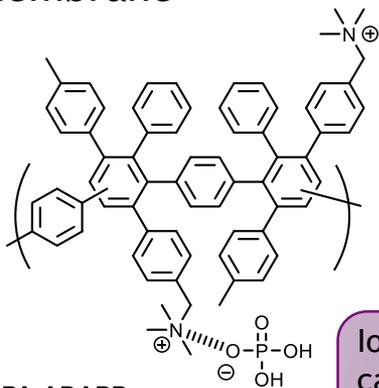


Previous high temperature fuel cell membrane

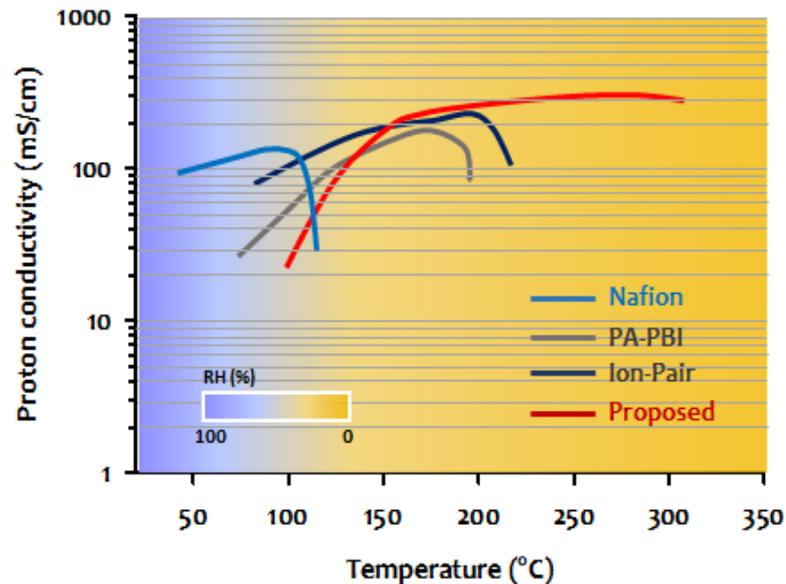


Acid-base interaction energy calculated for small molecule model = 17.4 kcal/mol

LANL/SNL-developed high temperature fuel cell membrane



Ion-pair interaction energy calculated for small molecule model = 152 kcal/mol



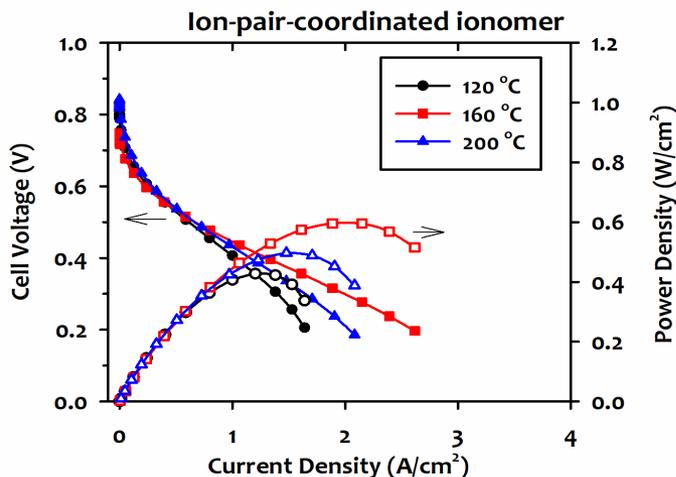
Impact of strong ion-pair interaction:

- Better performance at low temperature/high RH because biphosphate doesn't leach out
- Better performance at high temperatures because biphosphate doesn't evaporate

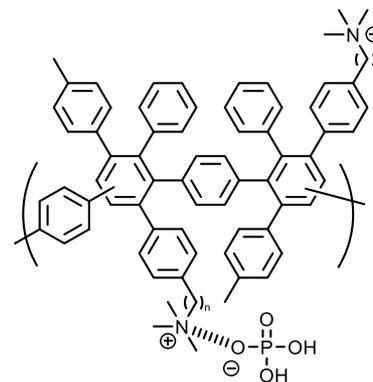
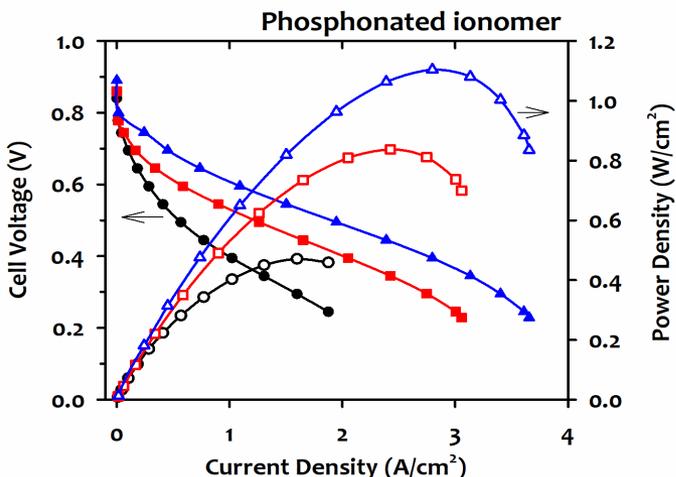
5 Approach: Proof of Concept

High Temperature Fuel Cell Performance
 From DOE FCTO AOP Lab call project (2016-2018)

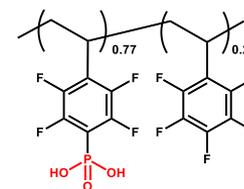
Membrane: PA-ADAPP
 Ionomer: PA-ADAPP



Membrane: PA-ADAPP
 Ionomer: PPFS



PA-ADAPP



PPFS

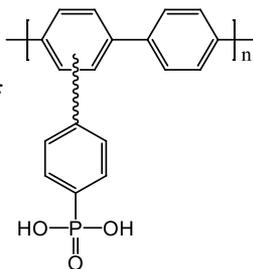
Measured in H₂/O₂, 147 kPa abs
 backpressure; Pt-Ru/C 0.75
 mg_{Pt}/cm² for anode and Pt/C 0.6
 mg/cm² for cathode

Better cell performance
 at 200 °C because
 phosphate can't
 evaporate or leach out
 of electrodes.



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



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

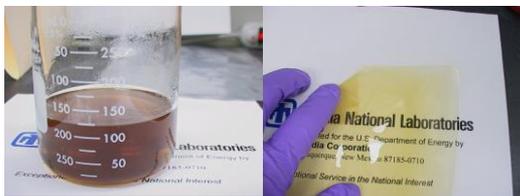
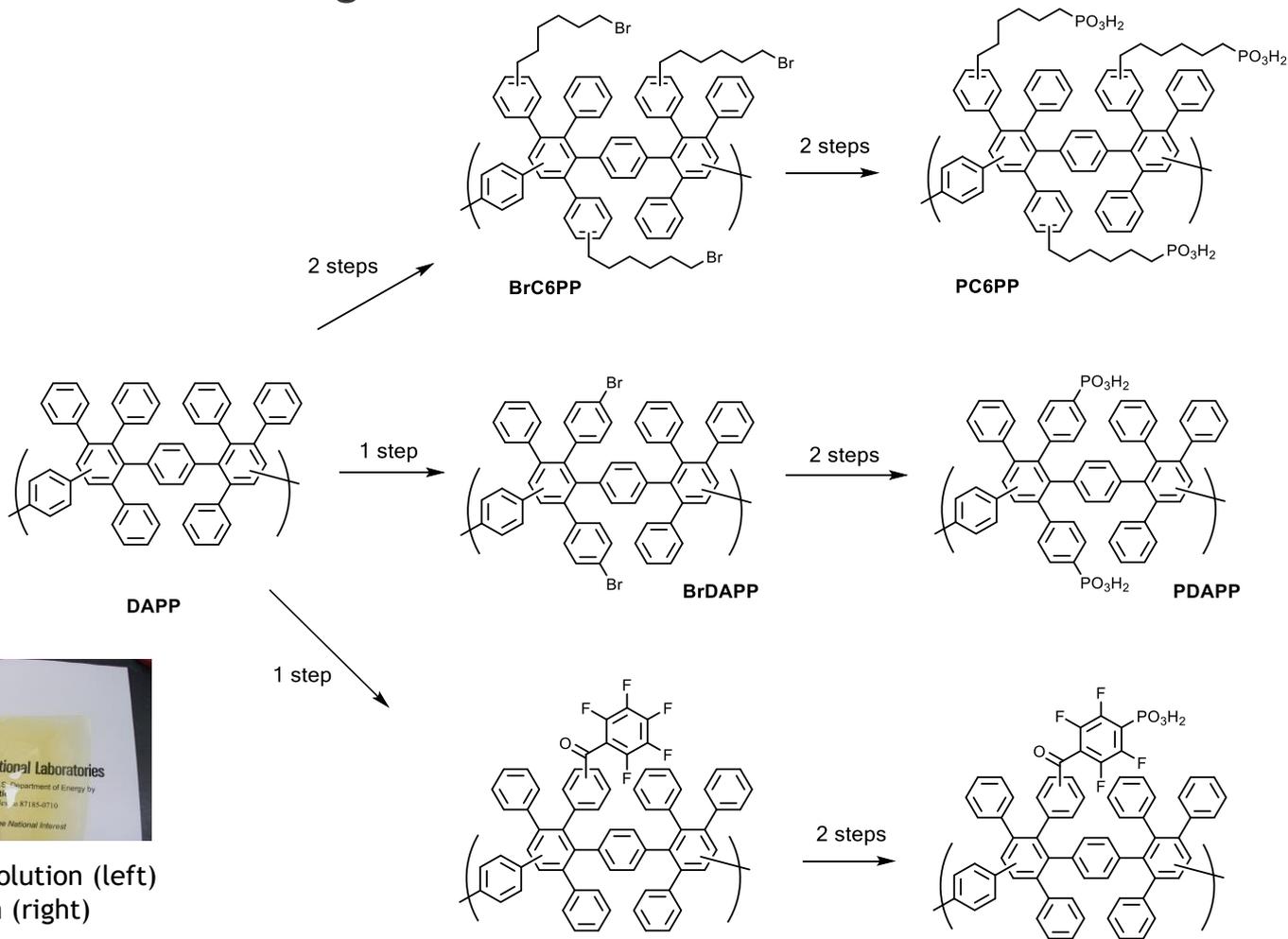
Several phosphonation routes are known and several ionomer structures are proposed. Success does not depend on a single synthetic scheme.

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.

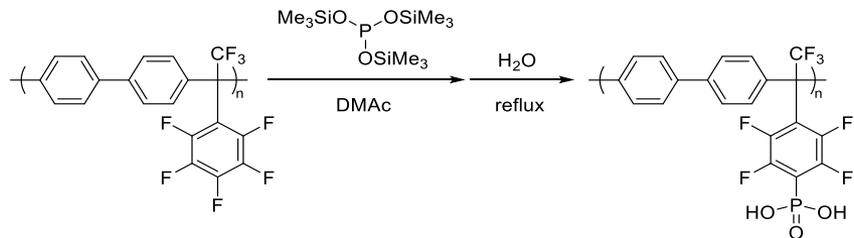
The phenyl groups of the ionomers may adsorb on the surface of HOR catalyst and reduce activity.

Introduce (1) methyl groups onto backbone phenyl units or (2) poly(fluorene) backbone to fuse aromatic rings. Both options hinder phenyl group adsorption.

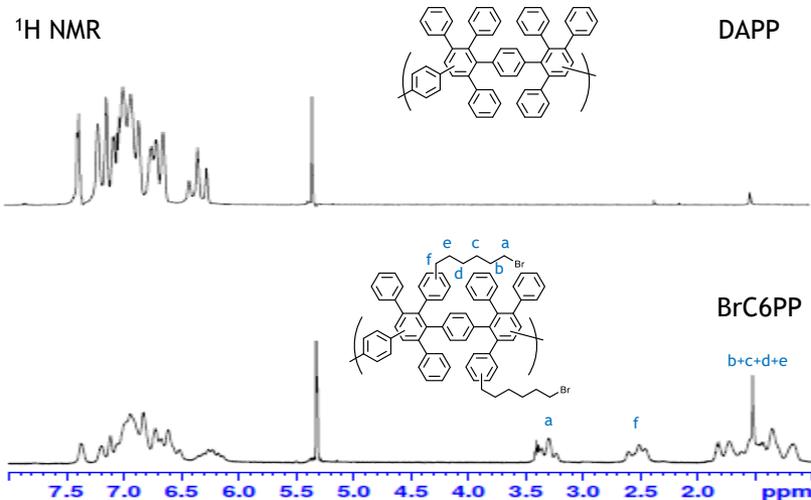
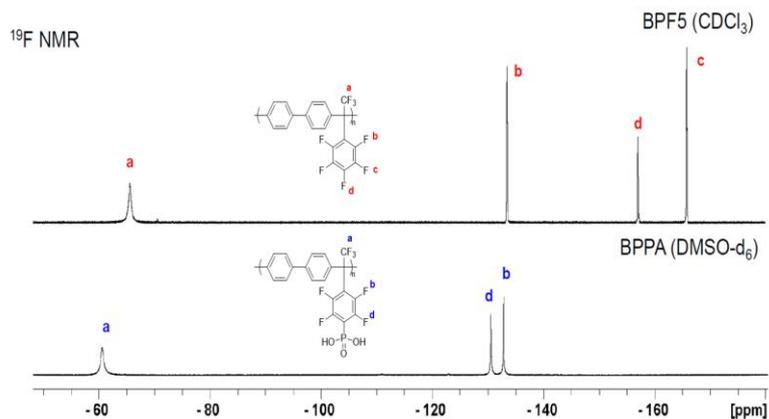


DAPP-based polymer in solution (left)
DAPP-based polymer film (right)

- 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).



- Synthesis of poly(biphenylene) with tetrafluorophenyl phosphonic acid groups confirmed by ¹⁹F NMR. (Q2 milestone additional option)
- IEC = 2.2 meq/g
- Low molecular weight was designed to help with solubility.
- Fuel cell testing is TBD.





Milestone	Type	Description	Proposed completion date	Actual completion date	Status
Poly(phenylene) parent polymers	Q1 Progress Measure	Prepare 10-20g batches of BrDAPP and BrC6PP	12/31/2018	12/21/2019	Material is being used in phosphonation experiments.
		Prepare batches of PC6PP with 2 IECs between 1.5 and 3.0			
Synthesis of PDAPP	Q3 Progress Measure	Prepare batches of PDAPP with 2 IECs between 1.5 and 3.0			



This project was not reviewed last year.



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



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



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