

Project ID: fc320

# Electro Ionomers for High Temperature Fuel Cells



*PRESENTED BY*

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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: \$500K
- Total DOE Funds  
Spent: \$82

## Barriers

- Synthesis of polymers
- 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.

## 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



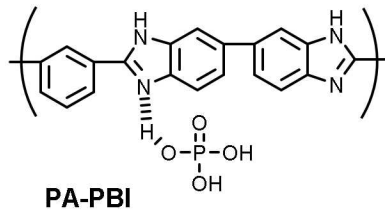
### Simple Balance of Plant

High temperature and low RH fuel cell operation could enable fixed cost savings of \$7.5/kW<sub>net</sub> by eliminating or reducing the size of BOP components such as humidifier and radiator.

N. Dale, Nissan Motors

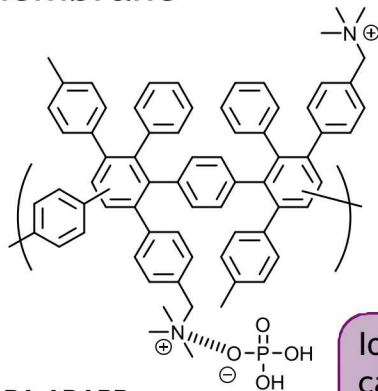
# Background

## Previous high temperature fuel cell membrane

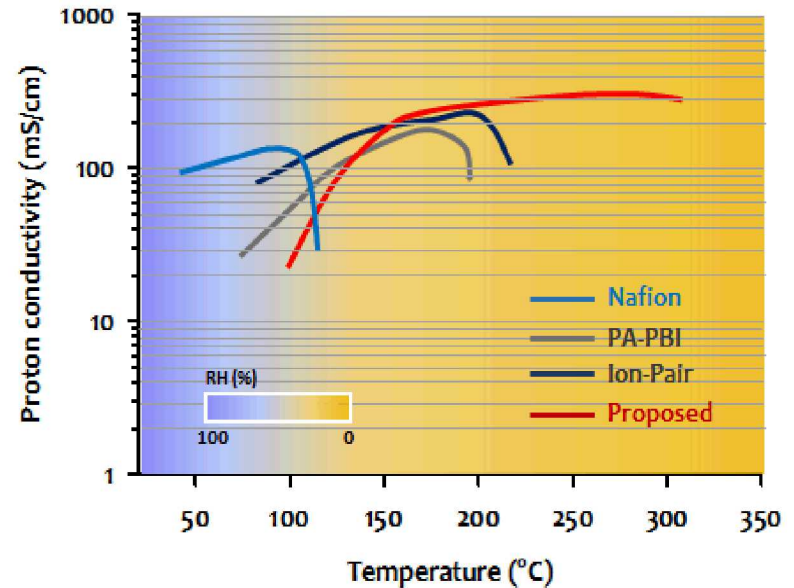


Acid-base interaction energy calculated for small molecule model = 17.4 kcal/mol

## LANL/SNL-developed high temperature fuel cell membrane



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



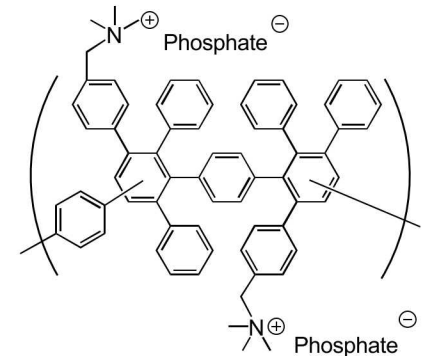
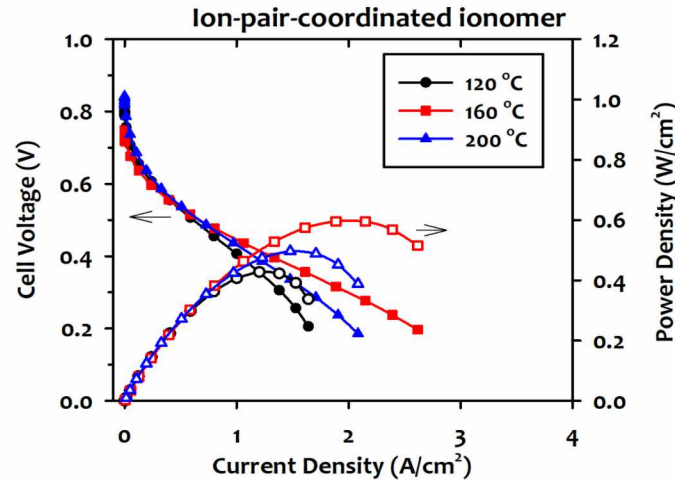
## Impact of strong ion-pair interaction:

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

# Proof of Concept

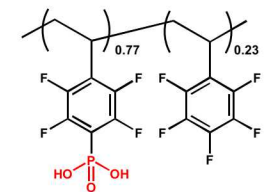
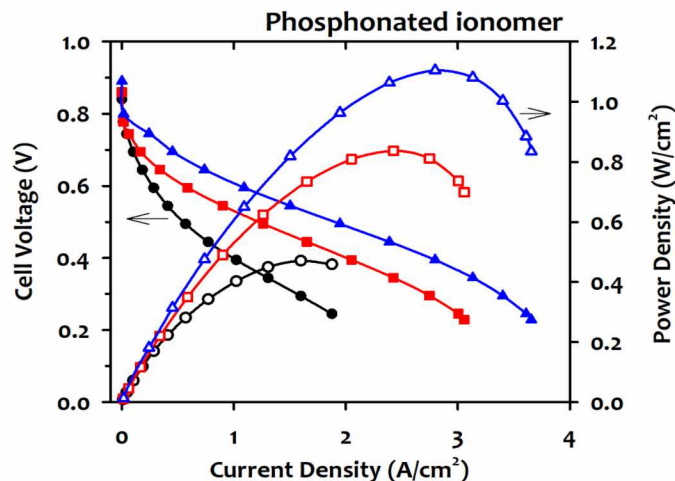
High Temperature Fuel Cell Performance  
From DOE FCTO AOP Lab call project (2016-2018)

Membrane: PA-DAPP  
Ionomer: PA-DAPP



PA-DAPP

Membrane: PA-DAPP  
Ionomer: PPFS

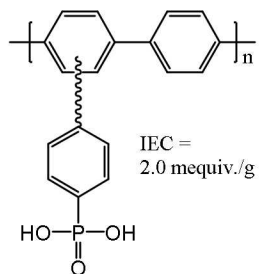


PPFS

Measured in H<sub>2</sub>/O<sub>2</sub>, 147 kPa abs  
backpressure; Pt-Ru/C 0.75  
mg<sub>Pt</sub>/cm<sup>2</sup> for anode and Pt/C 0.6  
mg/cm<sup>2</sup> 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

## Features

- 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

## Potential Obstacles and Mitigating Strategies

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

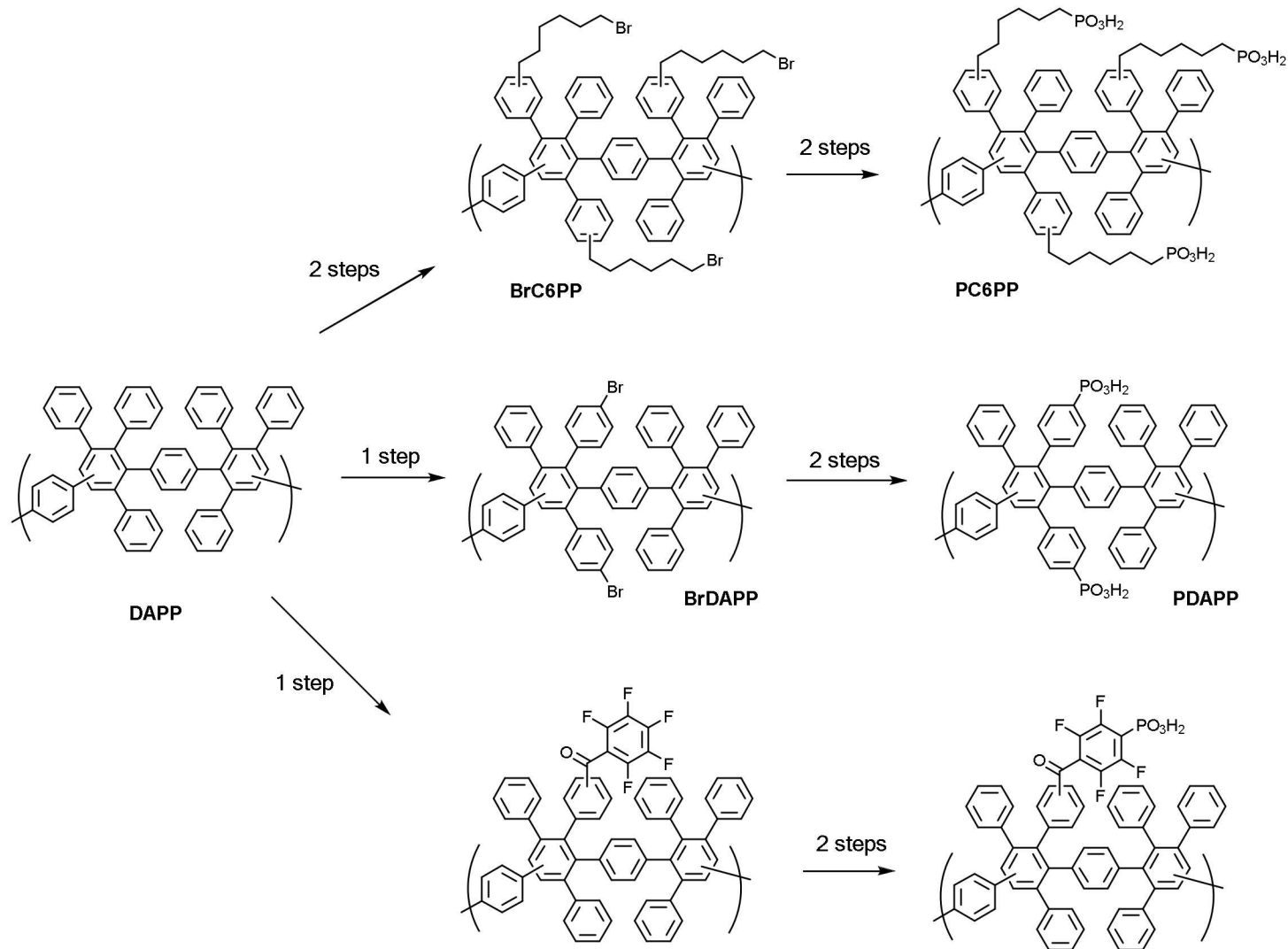
Several phosphonation routes are known and several ionomer structures are proposed. Success does not depend on a single synthetic scheme.

Limited ionomer solubilities might make electrode preparation difficult.

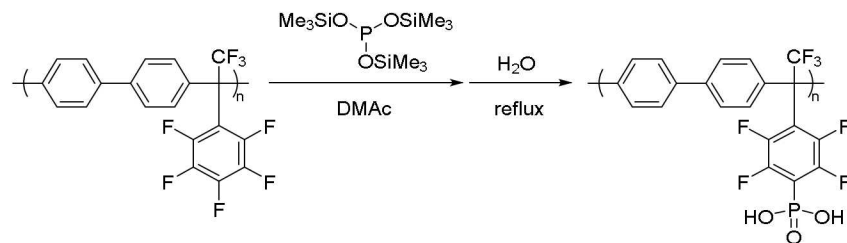
- Use low  $M_w$  parent polymers.
- Increase ion content (IEC).
- Use polymers with protected phosphonic acid groups to prepare electrodes, then deprotect in the solid state.

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.
- Addition of protected phosphonic acid groups is in progress.



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

# FY19 Milestones

Milestone	Description	Proposed completion date	Actual completion date	Status
Poly(phenylene) parent polymers	Prepare 10-20g batches of BrDAPP and BrC6PP	12/31/2018	12/21/2019	Material is being used in phosphonation experiments.
Synthesis of PC6PP	Prepare batches of PC6PP with 2 IECs between 1.5 and 3.0	3/31/2019		
Synthesis of PDAPP	Prepare batches of PDAPP with 2 IECs between 1.5 and 3.0	6/30/2019		
Membrane ASR	Measure membrane ASR using the high temperature MEA construction	9/30/2019		

# Summary

- 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.