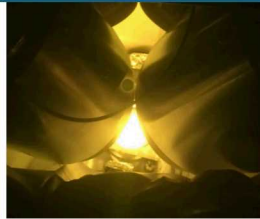
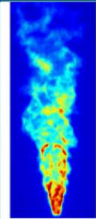


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SAND2020-4172PE

Project ID: fc320

Electrode Ionomers for High Temperature Fuel Cells



PRESENTED BY

Michael Hibbs, PI, Sandia National Laboratories

2020 DOE Hydrogen and Fuel Cells Program Annual Merit Review and Peer Evaluation Meeting, 2020



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Timeline

- Project start date: 10/1/2018
- Project end date: 9/30/2020
- Percent complete: 65%

Budget

- Total project budget: \$1000K
 - DOE share: 100%
- Funding received in FY18: \$275K
- Funding received in FY19: \$344K
- Funding planned for FY20: \$281K
- Total DOE Funds Spent*: \$548K

*As of 3/24/20

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
Sandipkumar Maurya



Barriers

- Cost
- Electrode performance
- Durability

Relevance/Impact

Project Objective

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

FY20 Objective

Fabrication and performance testing of single cells.

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.

Targets

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

Approach

Overall technical approach

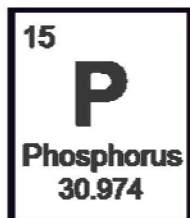
- Synthesis and testing of ionomers with pendant phosphonic acid groups.

FY20 developments

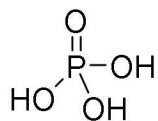
- Focus on fluorophenyl phosphonic acid groups for better durability.
- Testing of poly(terphenylene) from LANL.
- Testing of poly(phenylene) from SNL.

Date	Milestone/Deliverable	Complete
12/18	Prepare 10-20g batches of BrDAPP and BrC6PP	100%
3/19	Prepare batches of PC6PP with 2 IECs between 1.5 and 3.0	100%
6/19	Prepare batches of PDAPP with 2 IECs between 1.5 and 3.0	100%
9/19	Measure membrane ASR using the high temperature MEA construction. ASR will be $<0.05 \Omega \text{ cm}^2$ at 200 °C. (Go/No Go)	100%
12/19	Investigate HOR and ORR activity of catalyst in contact with the ionomers	80%
3/20	Optimize electrode structure of HT-PEMFCs using down-selected catalysts	50%
6/20	Measure fuel cell durability of low PGM HT-PEMFCs at 200°C	30%
9/20	Measure fuel cell performance and durability	10%

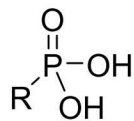
Accomplishments and Progress: Phosphonated polymers without anhydride formation



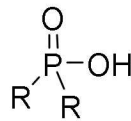
Number of C–P bonds



Phosphoric acid

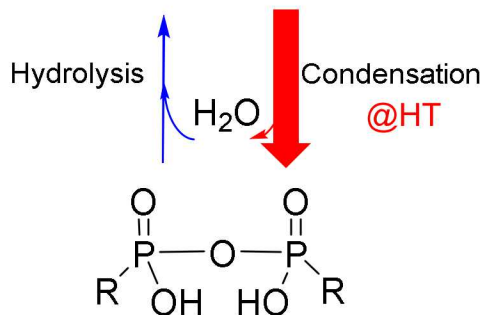


Phosphonic acid



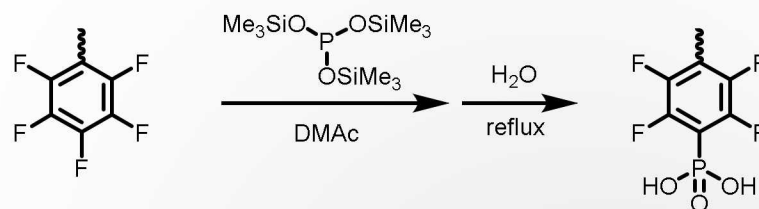
Phosphinic acid

H⁺ conductive groups



Phosphonic acid (PA) functionalization

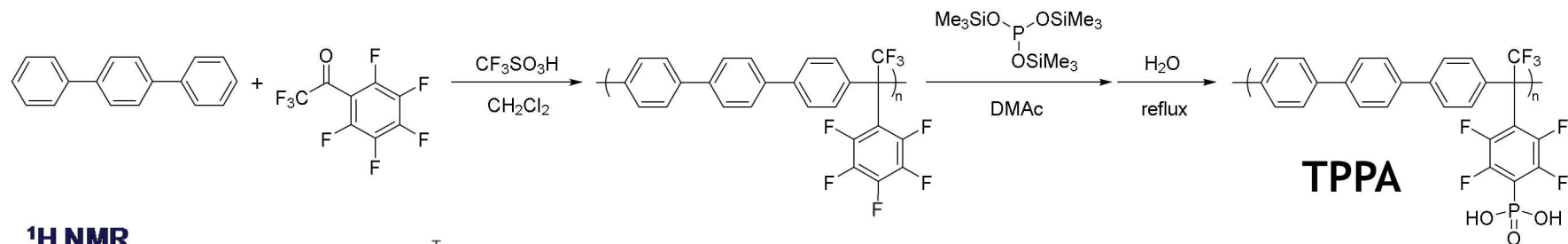
$\text{S}_{\text{N}}^{\text{Ar}}$ Michaelis-Arbuzov reaction



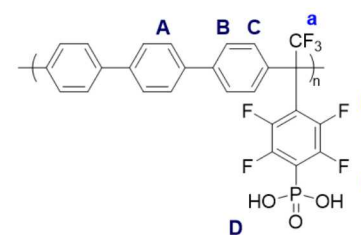
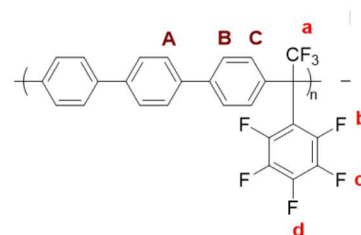
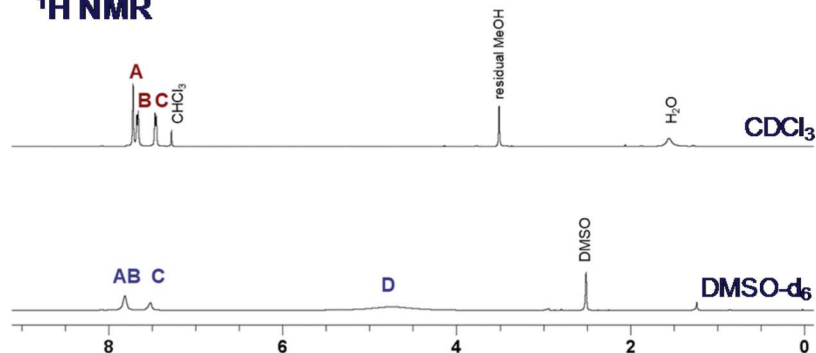
- High acidity PA due to the electron-withdrawing effect of fluorine does not allow anhydride formation.
- Efficient functionalization of PA
- Facile hydrolysis

- Testing of ionomers in FY19 showed degradation due to phosphonic anhydride formation.
- The fluorophenyl group stabilizes the phosphonic acid and increases acidity.

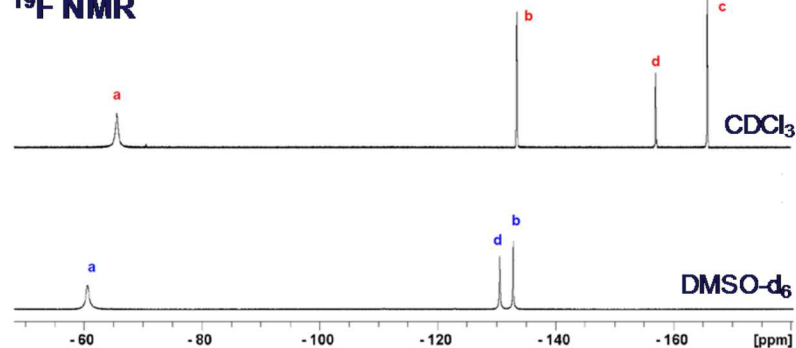
Accomplishments and Progress: Synthesis of Phosphonated poly(terphenylene) (LANL)



^1H NMR



^{19}F NMR

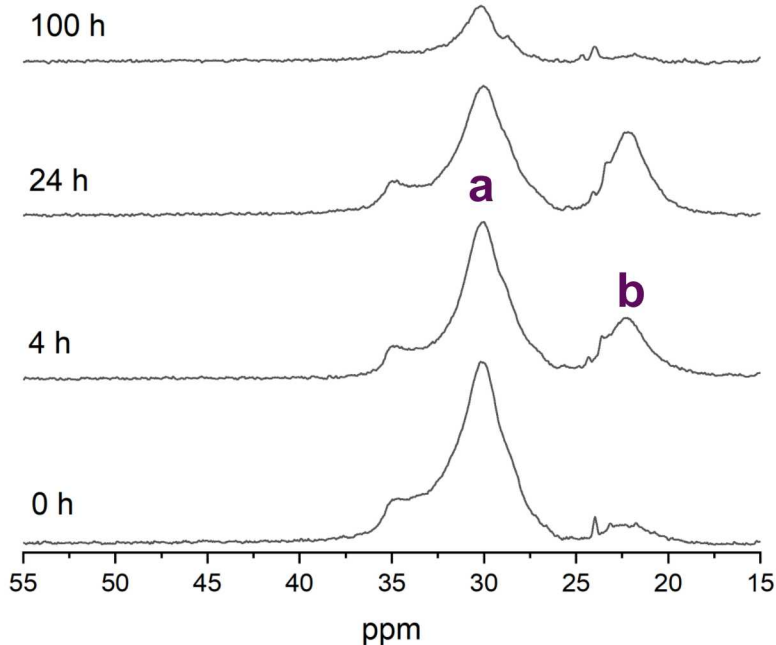


- Synthesized phosphonated ionomers (TPPAs) via acid catalyzed polycondensation followed by $\text{S}_{\text{N}}\text{AR}$ Michaelis-Arbuzov reaction.
- Confirmed chemical structure of TPPAs by ^1H NMR and ^{19}F NMR
- IEC = 1.9 meq/g

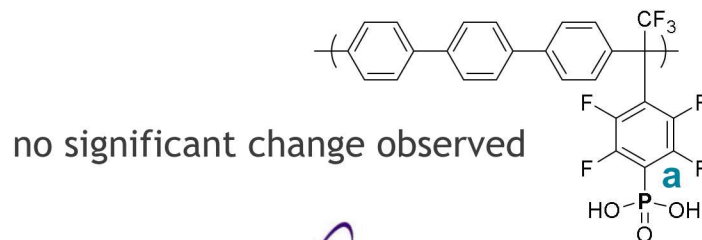
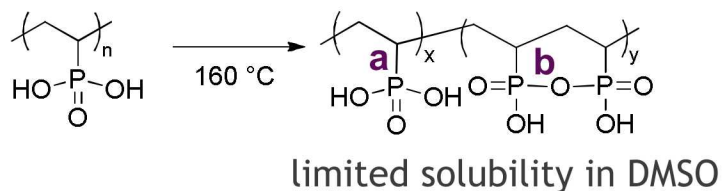
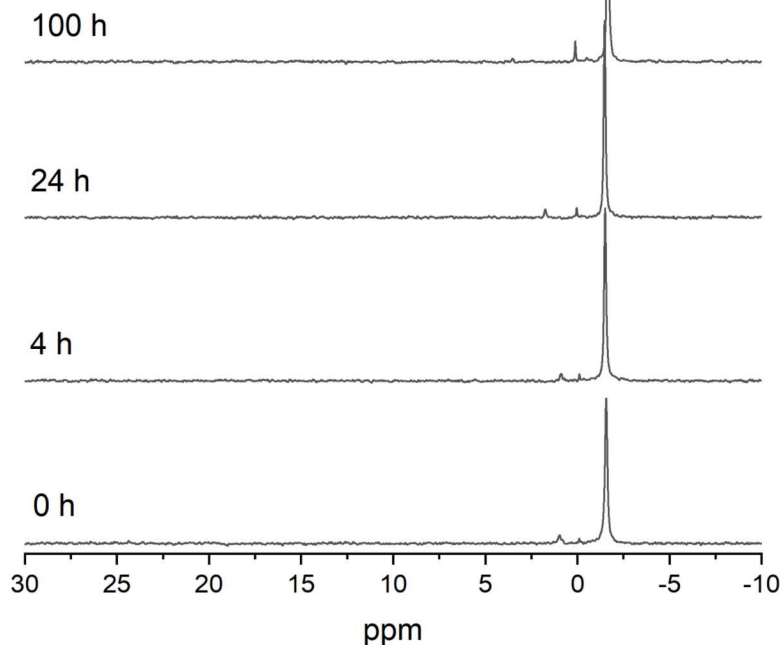
Accomplishments and Progress: Phosphonic acid stability at high temperature

- Poly(vinylphosphonic acid) and TPPA were dissolved in DMSO- d_6 (2.5 wt%)
- ^{31}P NMR spectra were taken after thermal treatment at 160 °C

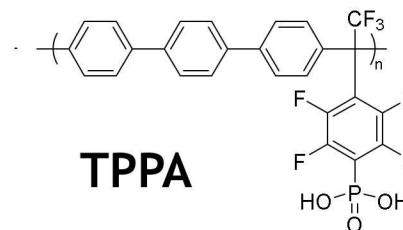
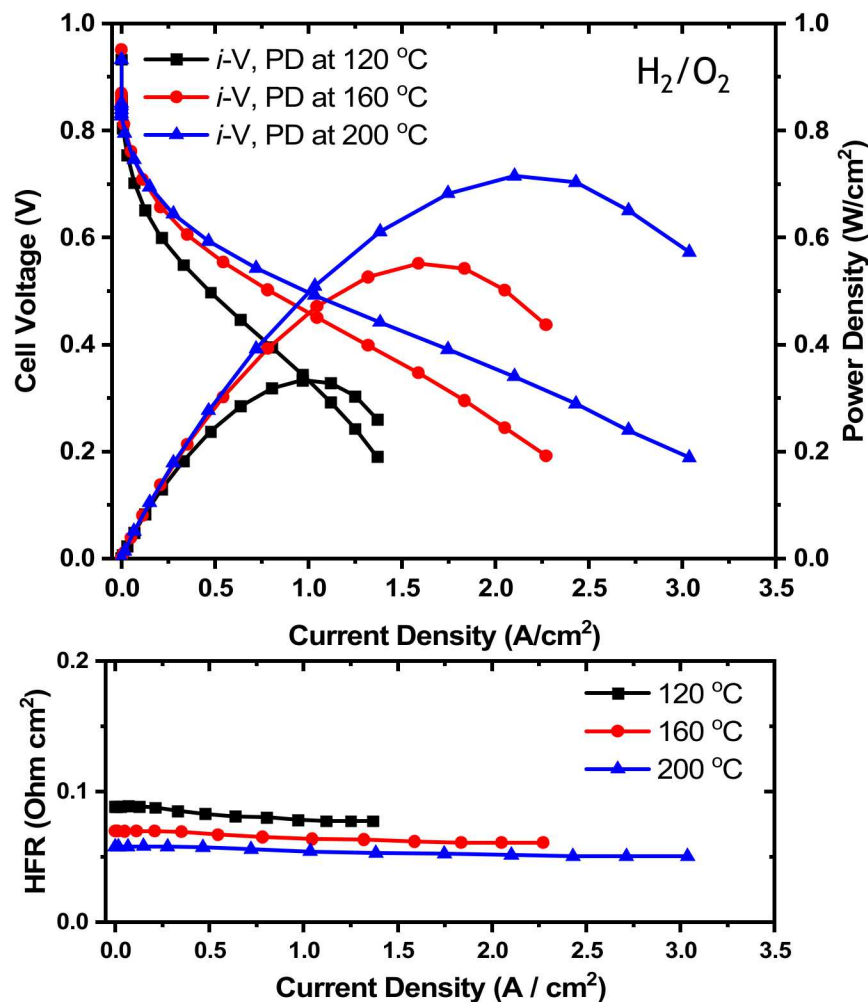
PVPA



TPPA



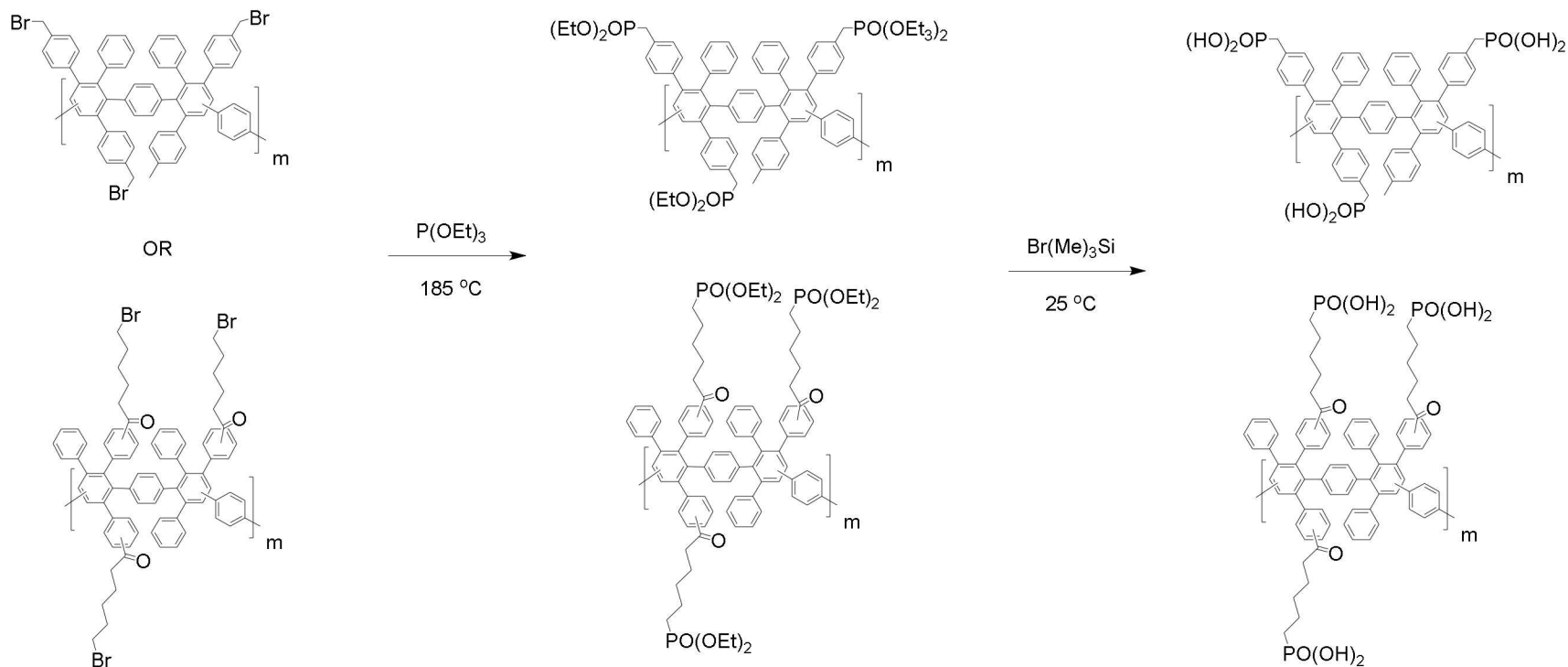
Accomplishments and Progress: HT-PEMFC performance of MEA using TPPA ionomer



- Membrane: PA-doped QAPOH (ion-pair PEM)
- Ionomer: phosphonated polymer (TPPA)
- Flow anhydrous gases, H₂/O₂ flow = 500 sccm.
- A/C backpressure = 10 psi.
- A/C Pt loadings were 0.75/0.6 mg_{pt}/cm² using commercial 75 wt% PtRu / 60 wt% Pt/C catalysts.
- MEA fabrication → GDE air brushing on carbon cloth GDL.

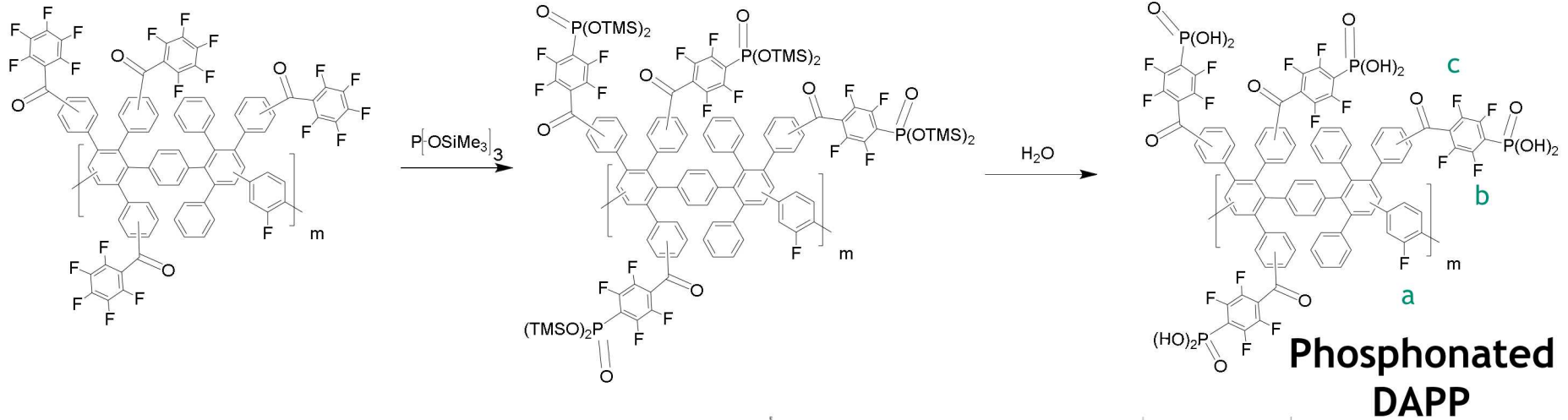
- Peak power density of 300-700 mW cm⁻² at 120-200°C.
- Cell HFR was < 0.1 Ohm cm².
- **Demonstrated use of phosphonated polymer as an ionomer for the first time.**

Accomplishments and Progress: Synthesis of phosphonated poly(phenylene)s (SNL)

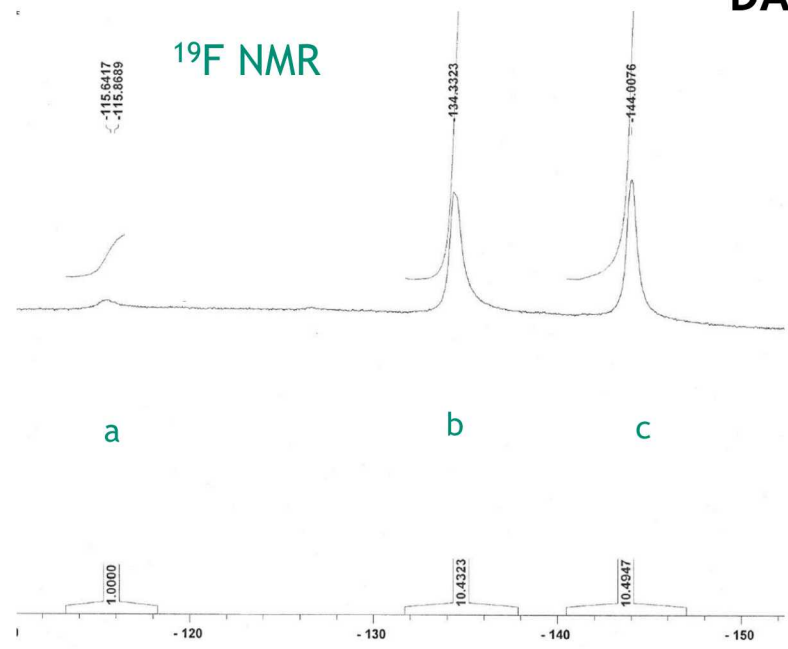


- Synthesized poly(phenylene)s with pendant phosphonic acid groups on 1- and 6-carbon tethers.
- Confirmed chemical structure by ^{19}F NMR and ^{31}P NMR (not shown).
- Low conductivities and crosslinking due to anhydride formation.

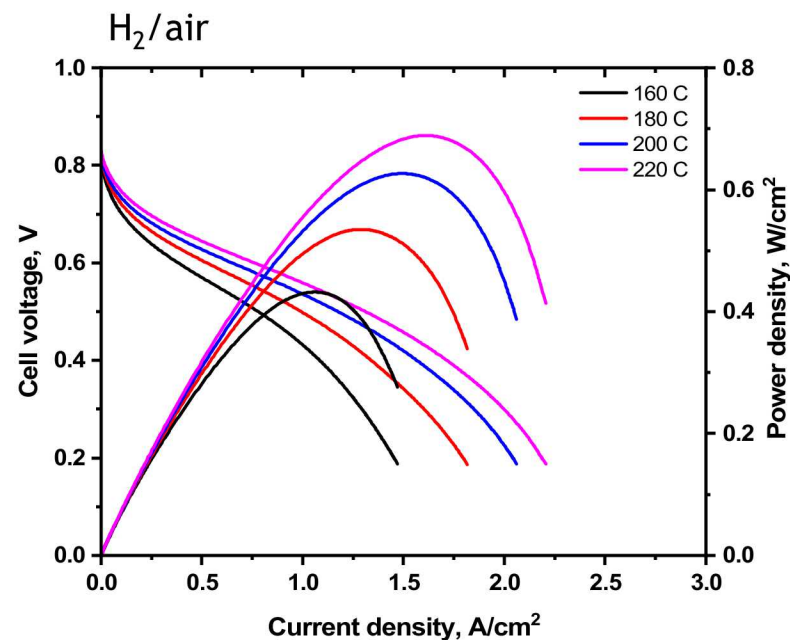
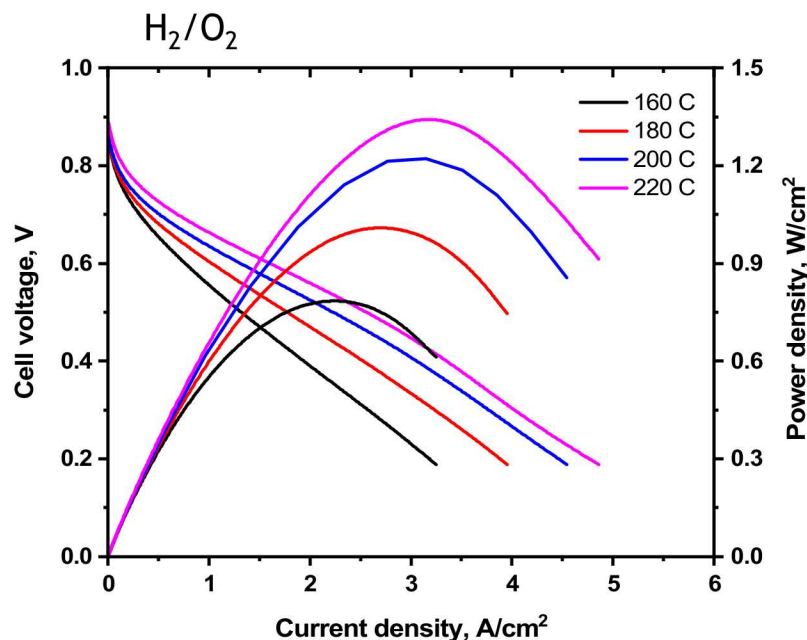
Accomplishments and Progress: Synthesis of Phosphonated poly(phenylene) (SNL)



- Synthesized phosphonated DAPP by fluorophenyl acylation reaction followed by SnAR Michaelis-Arbuzov reaction.
- Confirmed chemical structure by ¹⁹F NMR and ³¹P NMR (not shown).
- IEC ≈ 3 meq/g (calculated from ¹⁹F NMR).
- Water uptake = 30%.



Accomplishments and Progress: HT-PEMFC performance of MEA using phosphonated DAPP ionomer



- Membrane: PA-doped QAPOH (ion-pair PEM)
- Ionomer: phosphonated DAPP
- Flow anhydrous gases, H₂/O₂ or air flow = 500 sccm.
- A/C backpressure = 10 psi.
- A/C Pt loadings were 0.75/0.6 mg_{Pt}/cm² using commercial 75 wt% PtRu / 60 wt% Pt/C catalysts.
- MEA fabrication → GDE air brushing on carbon cloth GDL.
- Electrode composition: LANL proprietary

- Project target for FY20: power density >500 mW/cm² (H₂/Air) with <0.125 mgPGM/cm².
- We have achieved the fuel cell performance portion of the target: 700 mW/cm².
- Remaining time will be used to achieve PGM loading and durability targets (slide 3).

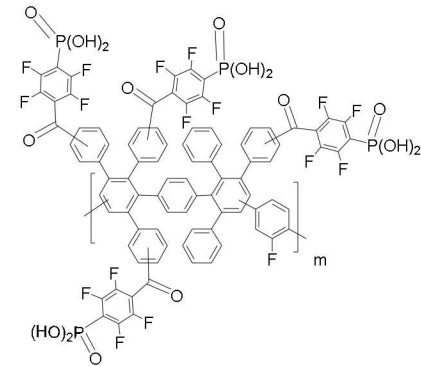
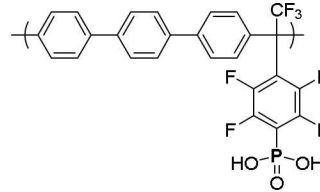
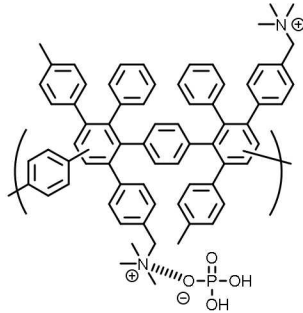
Accomplishments and Progress: HT-PEMFC performance improvement

FY18

FY19

FY20

Ionomer structure



Maximum power density at 200 °C, H_2/O_2 , ion-pair membrane

0.5 W/cm²0.7 W/cm²1.35W/cm²

Significant improvement in cell performance by changing the design of the ionomer.

Responses to Previous Year Reviewers' Comments

“The performance level is low. The gap with conventional HT-PEM fuel cells should be considered and discussed, major causes should be identified, and solutions should be proposed.”

- Performance data in last year's slides were based on materials available before this project started. The first technical back-up slide shows a comparison with a commercial PA-PBI membrane HT-PEM fuel cell. At 160 °F, peak power density for the PA-PBI system is only about 15% higher. At higher temperatures, the PA-PBI performance decreases due to loss of phosphoric acid whereas the phosphonated ionomer performance increases at higher temperatures.

“The team should discuss and explain the justification for the performance difference with previously developed PA-ADAPP and PPFS when the temperature is increased from 160 °C to 200 °C”

- That data was acquired before the start of this project. In the system with PA-ADAPP ionomer, the performance declined at temperatures above 160 °C due to evaporation of the phosphoric acid. This wasn't a problem for the system with PPFS, thus demonstrating the value of phosphonated polymers as ionomers.

“Selecting one route and improving the initial performance with conventional PGM-loading on electrodes should be prioritized.”

- Agreed. In FY20, the focus has been entirely on the two ionomers with fluorophenyl phosphonic acid groups and testing to date has been with conventional PGM loadings.

Collaboration and Coordination

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 Sandipkumar Maurya	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
Advent Technologies Inc. Emory de Castro	No-cost collaboration Material supply Tech validation

Remaining Challenges and Barriers

- Optimizing handling and processing conditions for batches of phosphonated DAPP
- Better understanding of conductivity measurements on phosphonated DAPP
- Reducing Pt loading in MEAs
- Increasing OCV by better design of MEA gaskets

Proposed Future Work

Remainder of FY 2020

- (SNL)
- Fuel cell performance optimization (LANL)

FY 2021

- Fuel cell durability testing (LANL)

Any proposed future work is subject to change based on funding levels.

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.

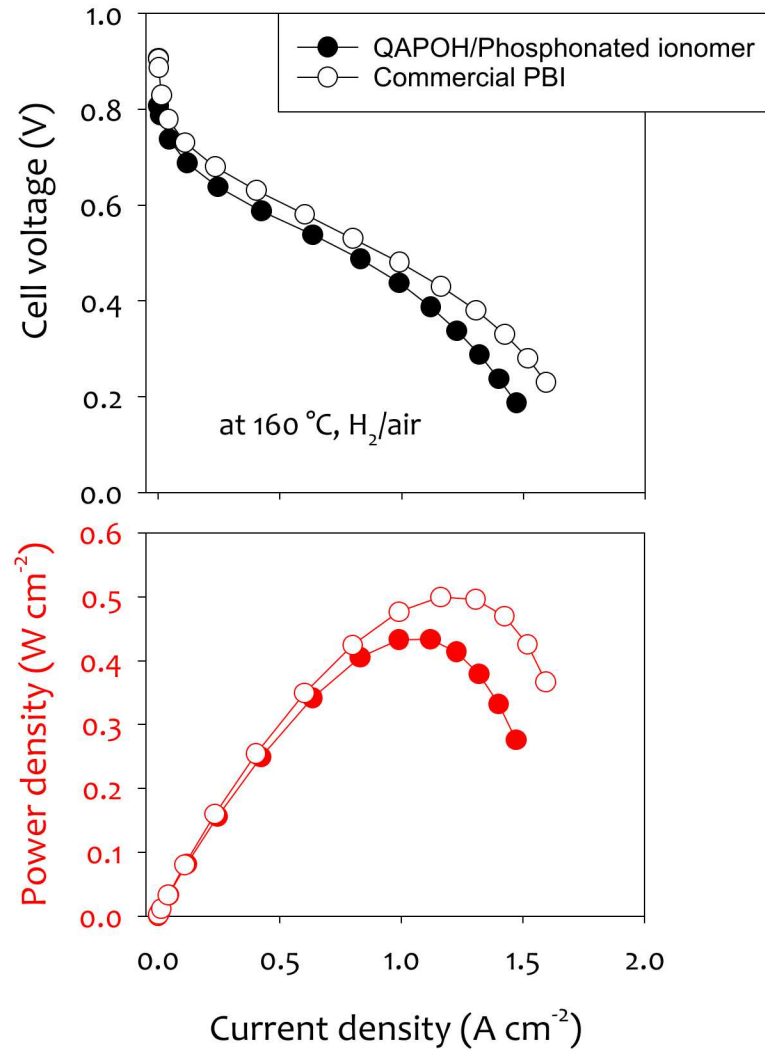
Approach: Synthesis of ionomers based on poly(phenylene) backbones with covalently attached phosphonic acid groups. FY20 research focused on fluorophenyl phosphonic acid groups

Accomplishments: Synthesis of poly(terphenylene) and poly(phenylene), both with fluorophenyl phosphonic acid groups. Fuel cell testing of both ionomers and a power density of 1.35W/cm² at 200 °C in H₂/O₂.

Collaborations: Phosphonated DAPP ionomers have been sent to LANL for fuel cell testing. Performance data from LANL drives plans for structural variations at SNL.

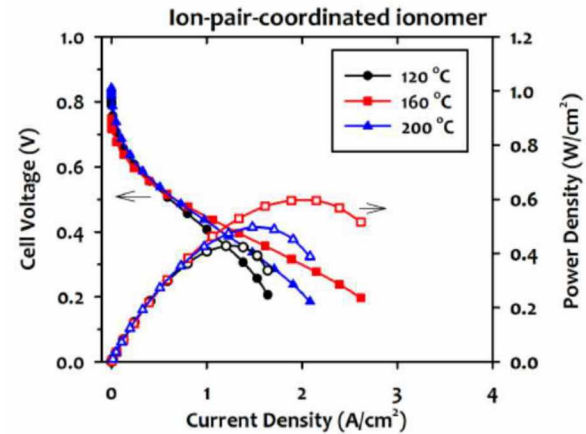
Technical Back-up Slides

Fuel cell performance with commercial PBI

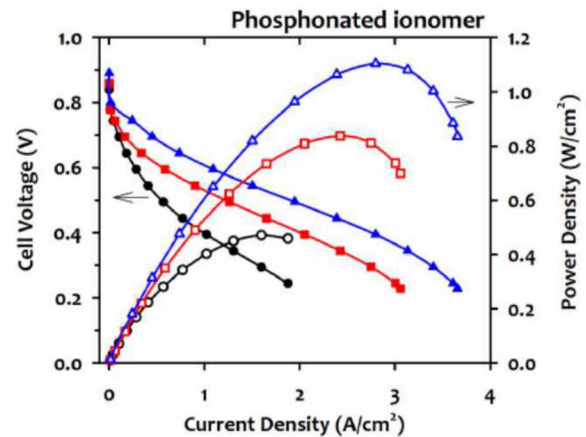


Fuel cell performance with ion-pair vs. phosphonated ionomer

Membrane: PA-ADAPP
Ionomer: PA-ADAPP



Membrane: PA-ADAPP
Ionomer: 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