Project ID: FC175

Polymer-based fuel cells that operate from 80–220 °C

PI: Yu Seung Kim

Los Alamos National Laboratory

June 15, 2018

Overview

Timeline

- Project start date: 5/1/2017
- Project end date: 10/30/2018
- Percent complete: 70%

Budget

- Total project funding: $300K
  - DOE share: 100%
- Funding received in FY18: $270K
- Total DOE Funds Spent*: $200K

*As of 4/17/2018

Barriers

- B. Cost
- C. Electrode performance
- A. Durability

Project lead

- Los Alamos National Laboratory
  - Yu Seung Kim (PI), EunJoo Park, Albert Lee, Dongguo Li, Gerie Purdy

Collaborators (No cost)

- Sandia National Laboratory
  - Cy Fujimoto
- Rensselaer Polytechnic Institute
  - Chul Sung Bae, Junyoung Han
- National Institute of Advanced Industrial Science and Technology
  - Yoong-Kee Choe
- University of Stuttgart
  - Vladimir Atanasov
- Nanosonic, Inc.
  - William Harrison
- Toyota Motor North America, Inc.
  - Hongfei Jia

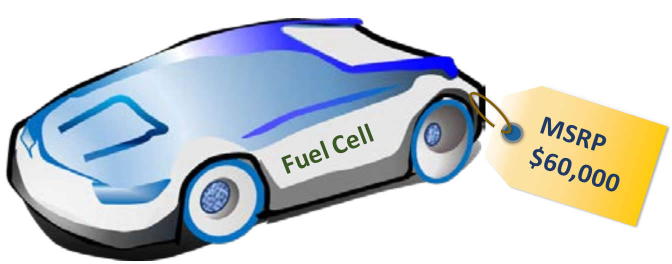
Relevance

Objective

- Development of a feasible ion-pair coordinated polymers to demonstrate a fuel cell that is operational from 80–220°C without humidification.

Cost Reduction of a Fuel Cell Car

- Current fuel cell car retail price: $60,000.
- Projected fuel cell system cost: $45/kW for 500,000 vehicles
- Target cost: $40/kW (2020)
  $30/kW (ultimate)
- Further cost reduction strategy is necessary



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

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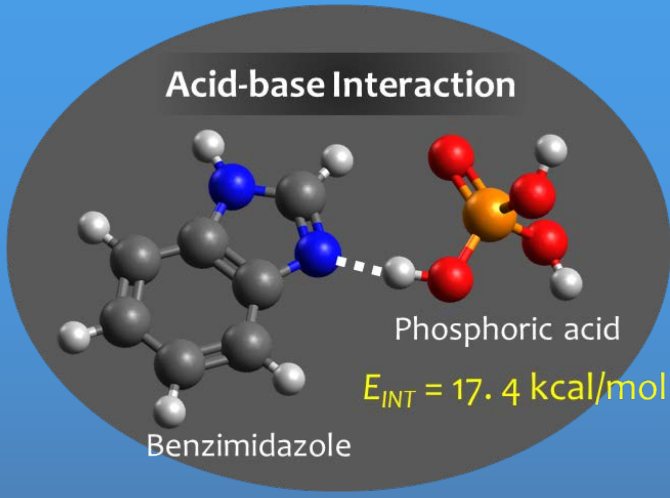
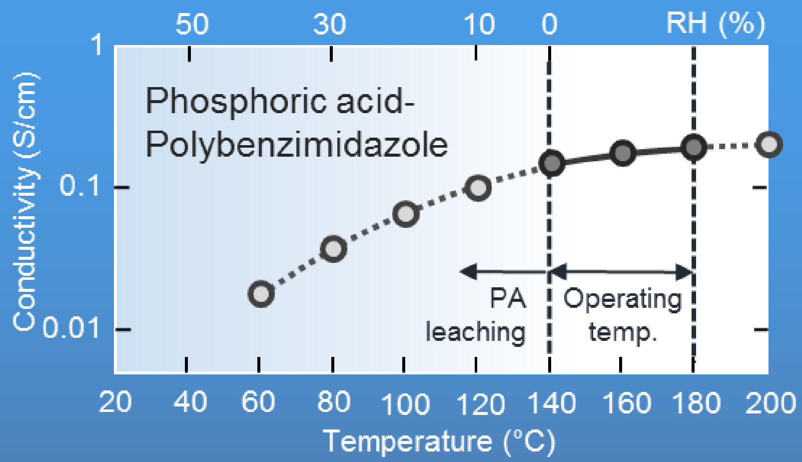
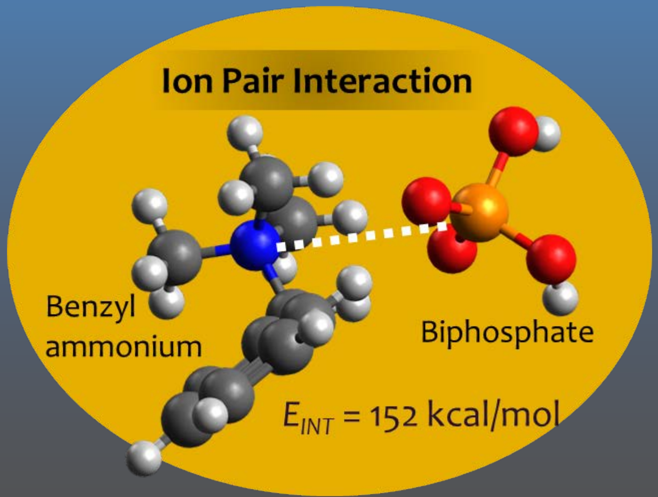
Approach: Ion-Pair Coordinated Fuel Cells

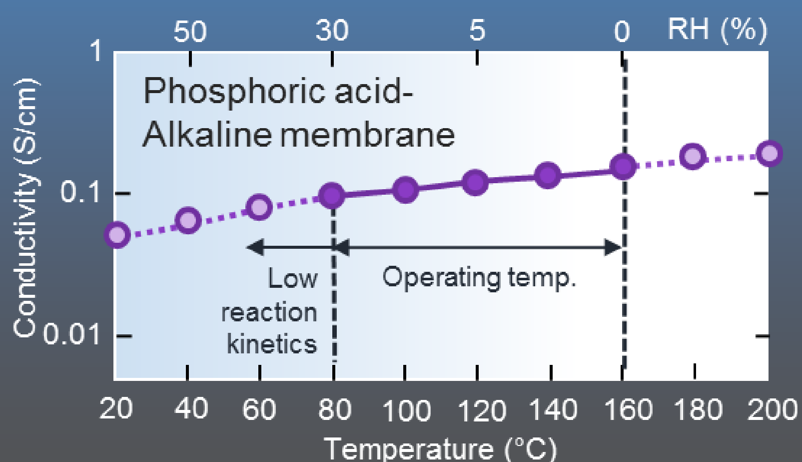
Previous High-Temperature Membrane Fuel Cell





LANL Technical Concept High-Temperature Membrane Fuel Cell





* *Nature Energy*, **1**, 16120 (2016)

Approach: Project Phases and Milestones

DFT Calculation — ✓ Determine the interaction energy between quaternary ammonium and phosphate — **100 %**

Small Molecule Study — ✓ Determine the best quaternary ammonium and phosphate phase — **100 %**

MEA verification — ✓ Demonstrate the membrane *in-situ* and *ex-situ* performance (conductivity, water tolerance) — **60 %** See below

Milestone (4/30/18)	Units	Baseline* (2016)	Target	Current Status (as of April 15 2018)
ASR (160 °C)	Ω cm^2	0.24	< 0.10	0.09
Peak Power Density (H_2/O_2)	mW cm^{-2}	800	1000	1134
Water Tolerance (Go-No-Go, April 30, 2018)	kPa	**21.3**	**38.5**	**42.6**
Durability during 80-180 °C AST	V loss at 160 °C	30%	<10%	Not evaluated yet

* *Nature Energy*, **1**, 16120 (2016)

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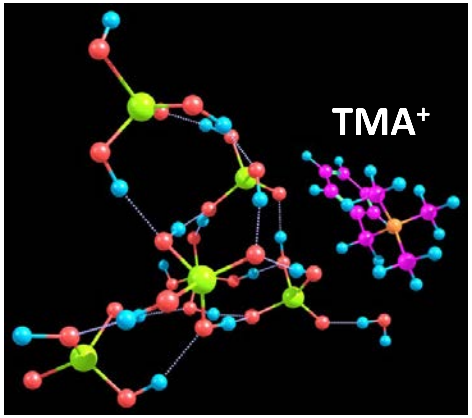
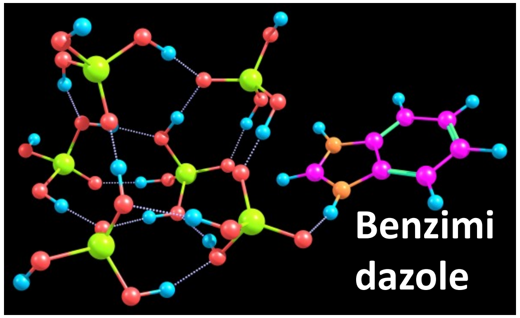
Accomplishment: DFT Calculation

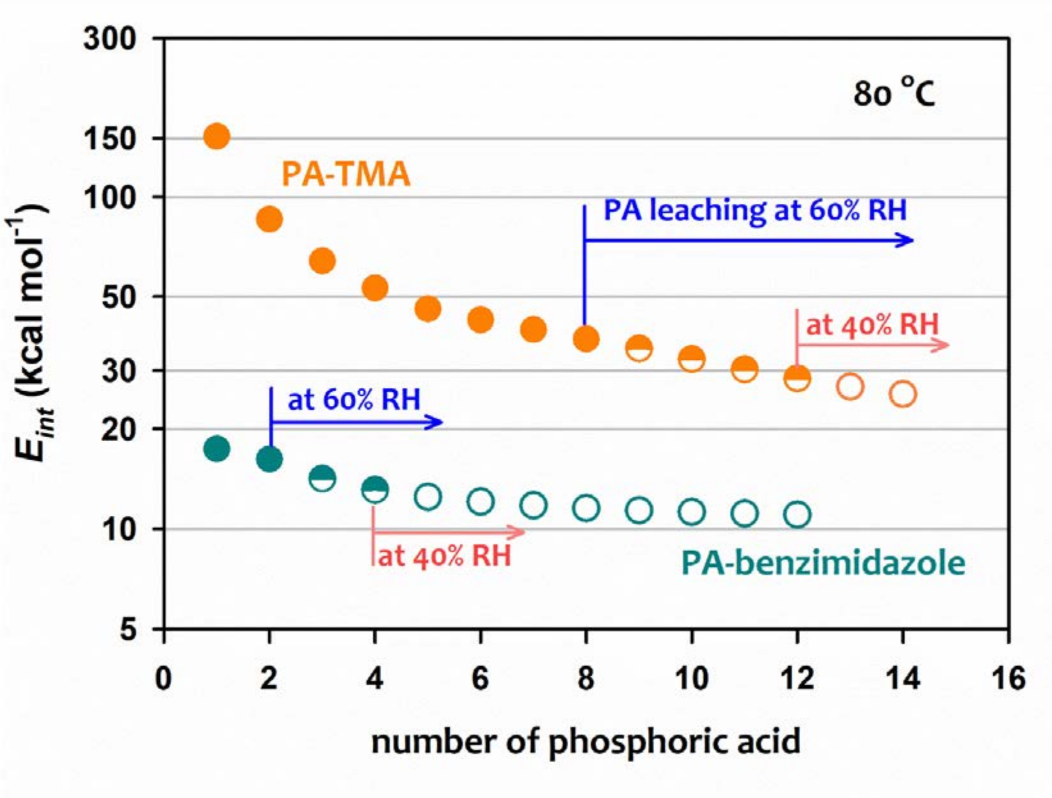
$(PA)_n^-$--- TMA^+ (ion-pair)



$(PA)_n$--- Benzimidazole (acid-base)

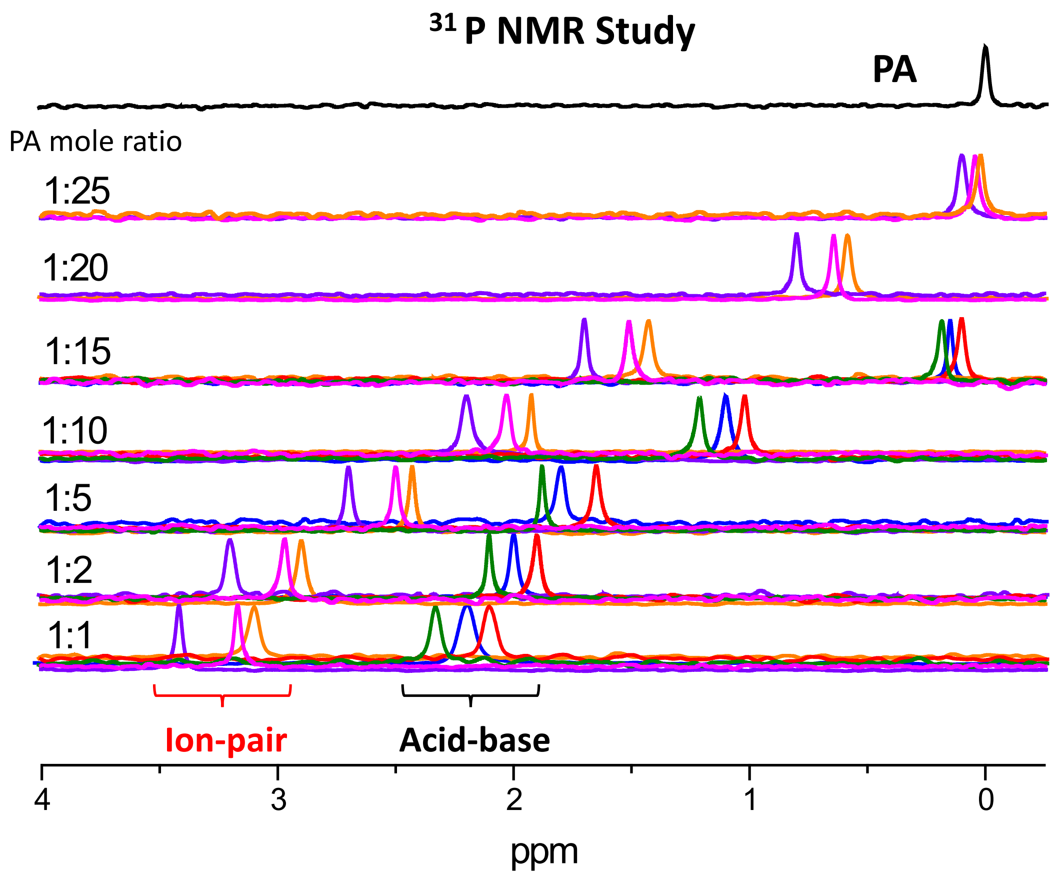


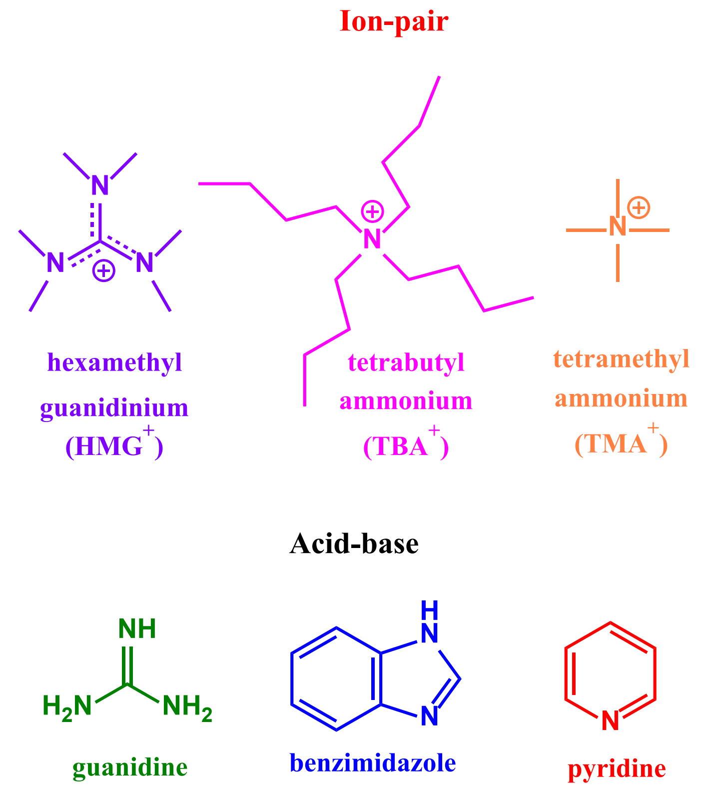
Interaction energy (E_{int}) of PA-TMA and PA-benzimidazole as a function of number of PA



- Ion pair coordinated system has higher interaction energy with PA than acid-base coordinated system at a given number of PA.
- Better water retention can be achieved with stronger interaction energy.

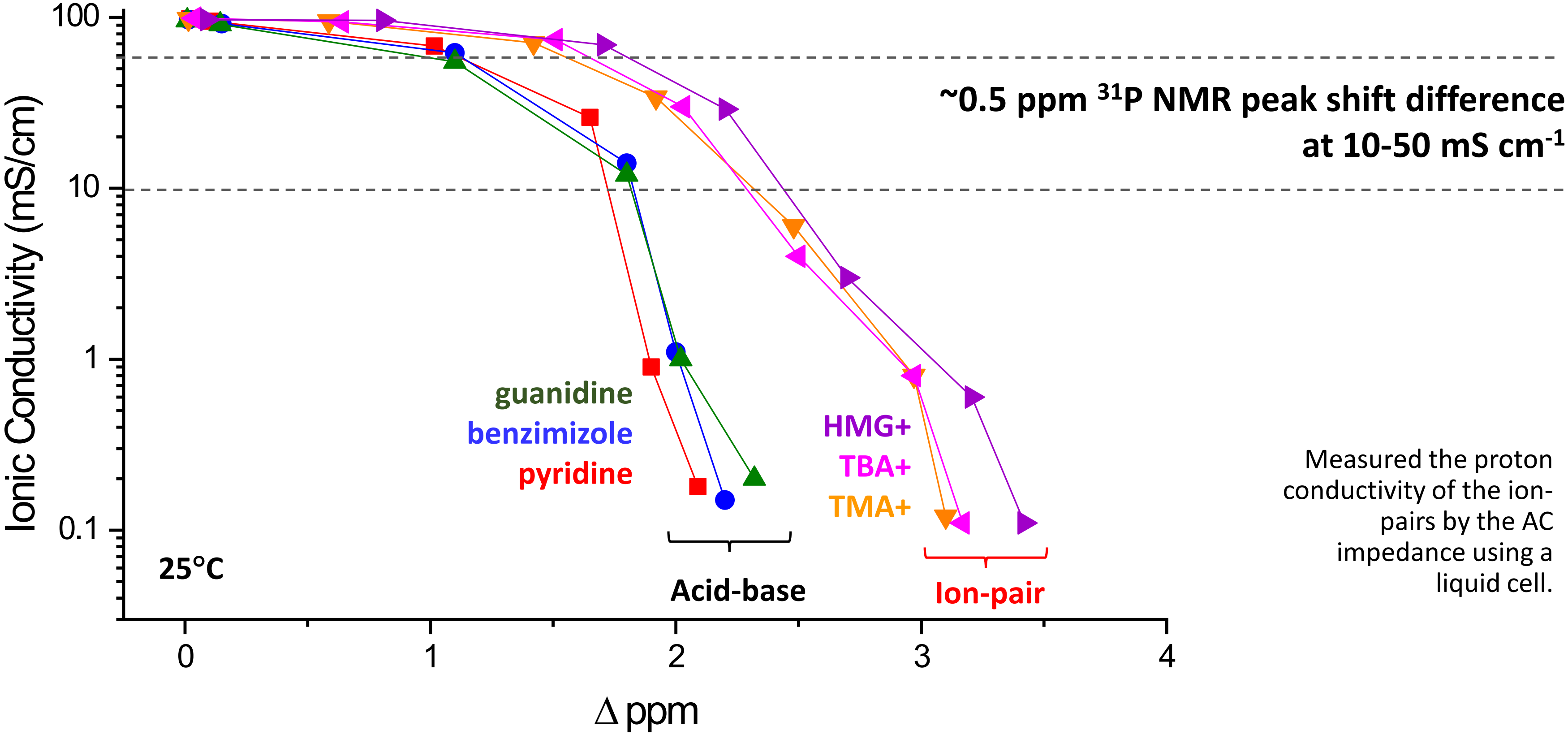
Accomplishment: Interaction Measurement (^{31}P NMR)





- ^{31}P NMR shows a single peak, indicating exchanging electrons in the phosphate phase.
- Ion pair coordinated system has higher interaction energy – consistent with DFT study.
- Interaction energy HMG > TBA > TMA >> guanidine > benzimidazole > pyridine

Accomplishment: Proton Conductivity



Measured the proton conductivity of the ion-pairs by the AC impedance using a liquid cell.

- Ion pair coordinated system has stronger interaction at a given conductivity.
- Hexamethyl guanidinium (HMG^+) exhibits the strongest interaction at a given conductivity.

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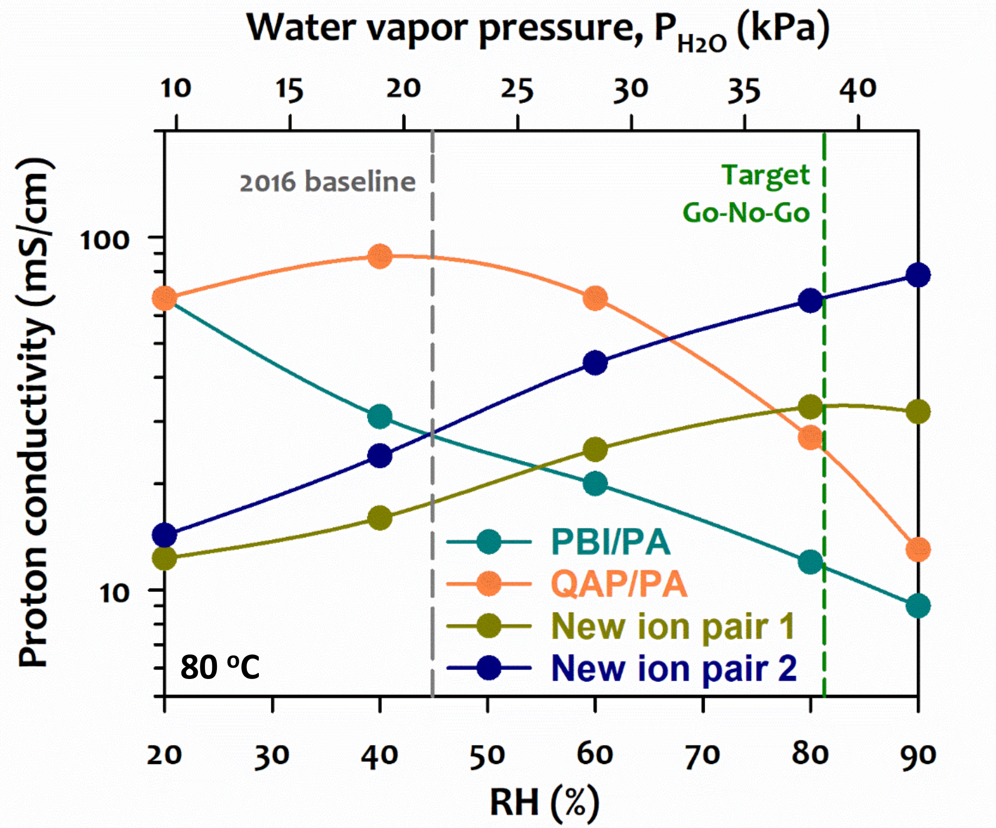
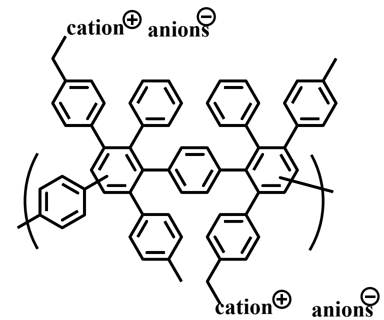
Accomplishment: Water Tolerance



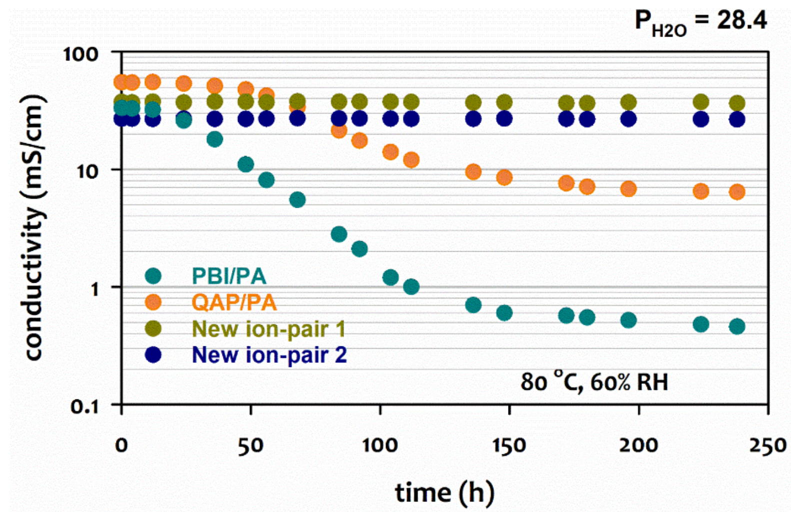
PA doping process: see Back-up Slide #1.

Chemical structure of ion-pair coordinated membrane



QAP
cation/anion: TMAOH/PA

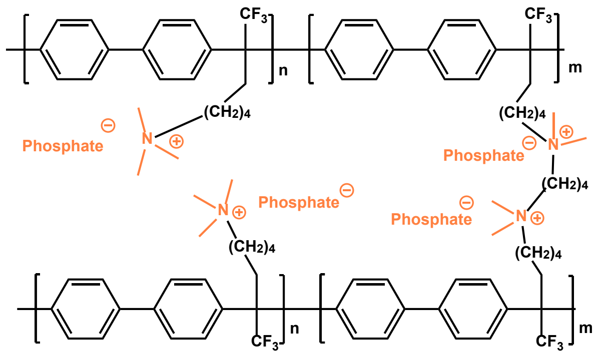
New ion pair 1, 2
cation/anion: proprietary info.



Highlight: Met the water tolerance go-no-go decision criteria (max. conductivity at P_{H2O} > 38.5 kPa) with two newly designed ion-pair coordinated systems.

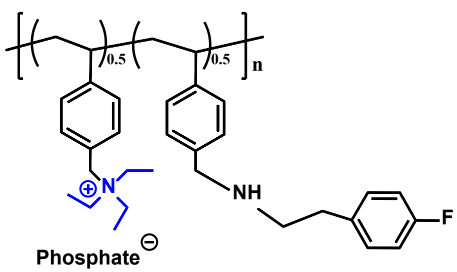
Membrane Synthesis

Membrane: Ammonium-phosphate ion-pair coordinated cross-linked poly(biphenylene) (PA-XL-BPN, Technical Back-up Slide #2)*



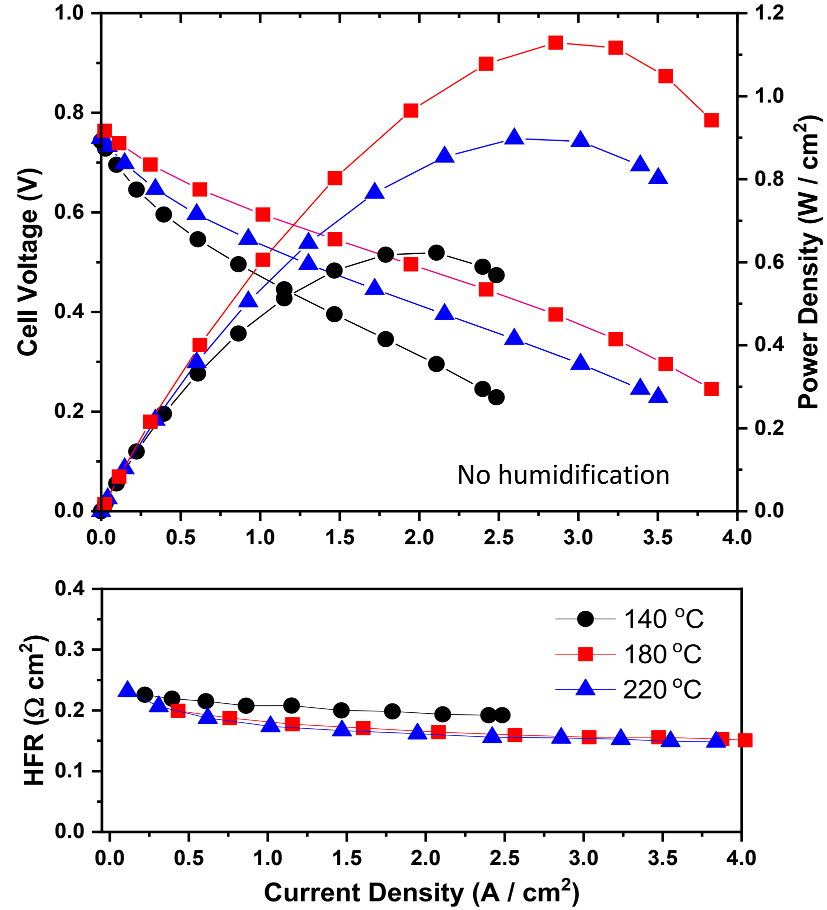
IEC = 2.6 meq/g
M_n = 70,000 Daltons
PDI = 1.8

Ionomer: Ion-pair coordinated polystyrene (PA-QAPS, Technical Back-up Slide #3)



High IEC ion-pair coordinated crosslinked poly(biphenylene) is developed.

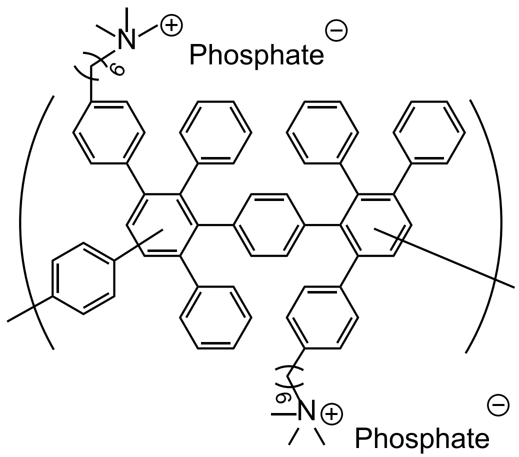
Highlight: Fuel cell peak power density (> 1 W cm^{-2}) milestones.



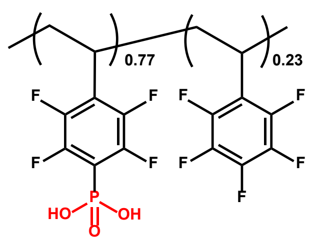
H_2/O_2, 285 kPa abs backpressure; membrane: PA-XL-BPN; ionomer: PA-QAPS, Pt 0.6 mg/cm^2 for both electrodes

Accomplishment: Ionomer development

Membrane: Ion-pair coordinated poly(phenylene) (PA-DAPP)

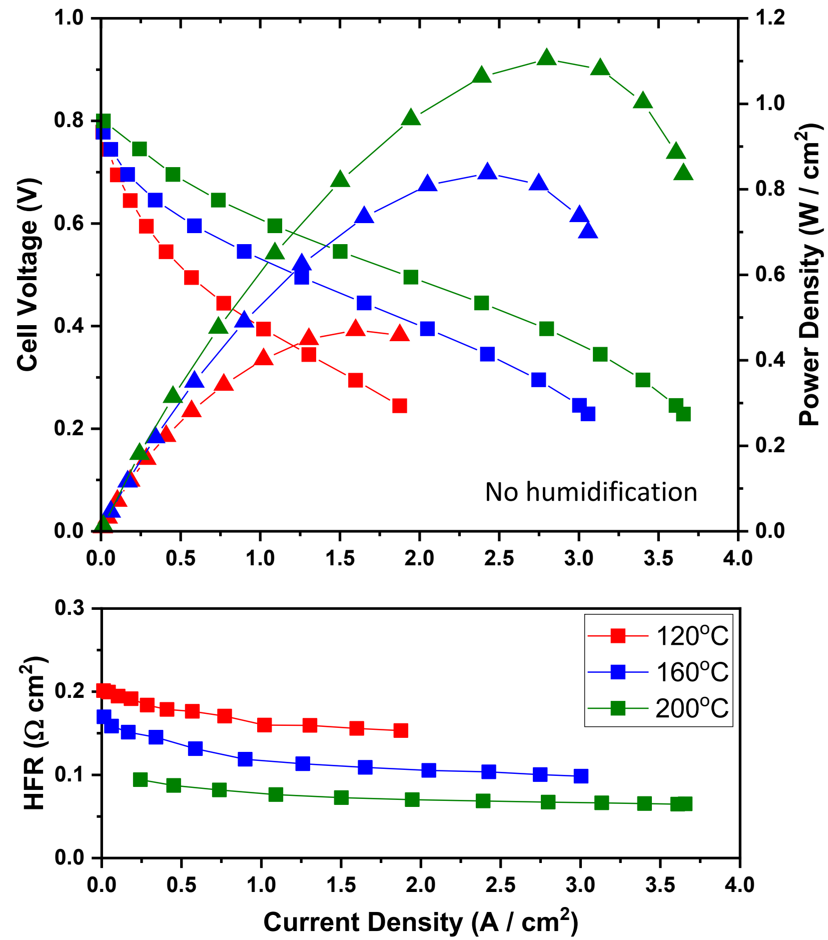


Ionomer: Phosphonated poly(pentafluorostyrene) (PPFS, Technical Slide 4)*



Developed phosphonated ionomer (non-acid leachable) for ion-par system.

Highlight: Obtained ASR of 0.09 Ω cm^2 at 160°C Exceed the ASR (< 0.1 Ω cm^2) milestone



Measured in H_2/O_2, 147 kPa abs backpressure; membrane: PA-DAPP; Pt-Ru 0.5 mg_{Pt}/cm^2 for anode and Pt 0.6 mg/cm^2 for cathode

Responses to Previous Year Reviewers' Comments

This project was not reviewed last year.

Project Coordination

Los Alamos National Lab
- Yu Seung Kim
- Albert Lee
- Eun Joo Park
- Dongguo Li
- Gerie Purdy

Material Design
- Cationic group
- Phosphate group
- Structure-property relationship

Material Preparation
- Down selection

Material Preparation
- Conductivity
- Water tolerance

Fuel Cell Test
- Initial performance
- Durability

Polymer Synthesis
- Poly(biphenylene)s

RPI
Chulsung Bae
Junyoung Han

Polymer Precursor
- Diels-Alder PPs

Sandia National Laboratories
Cy Fujimoto

Ionomer Preparation
- Phosphonated polymers

U of Stuttgart
Vladimir Atanasov

Scaled-up Synthesis
- Poly(arylene ether)s

Nanosonic Inc.
William Harrison

AIST (Japan)
- Yoong-Kee Choe

DFT Modelling
- Ion-pair interaction

Tech Validation

Toyota Motors
Hongfei Jia

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Collaboration

- **Material Exchange:** Critical component to achieve the project objective

Sandia National Laboratory (Cy Fujimoto) **– Federal Lab., within DOE program**

- Hexamethyl ammonium functionalized poly(phenylene)s 6 pieces (5” × 5”)
- Benzyl ammonium functionalized poly(phenylene)s 3 pieces (5” × 5”)

Rensselaer Polytechnic Institute (Chulsung Bae) **– University, within DOE program**

- Crosslinked biphenylene membranes: 6 pieces (4 ” × 4 ”)
- Crosslinked terphenylene membranes: 6 pieces (4” × 4 ”)

University of Stuttgart (Vladimir Atanassov) **– University (foreign), outside DOE program**

- Phosphonated polystyrenes with different IECs: 10 pieces (2” × 2”)

Nanosonic Inc. (William Harrison) **– Industry, inside DOE program (SBIR)**

- Quaterary ammonium functionalized poly(arylene)s: 9 pieces (4” × 4”)

Toyota Motor North America, Inc. (Hongfei Jia) **– Industry, outside DOE program**

- Ion liquid electrolyte: few grams

- **DFT Modeling:** Useful information provided to design materials

National Institute of Advanced Industrial Science and Technology (Yoong-Kee Choe, LANL visit) **– National Lab (Foreign), outside DOE program**

- Ion-pair interaction calculation

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Remaining Challenges and Barriers

- **Within the project (ending October 30/2018)**

  No substantial technical challenges remained.

- **After the project**
  - Electrode development
    - Ionomer design
    - Understanding catalyst-ionomer interfacial reaction
    - Low Pt loading and non-PGM catalysts
  - Membrane development
    - Increasing molecular weight & IEC
    - Mechanically stable thin film construction
    - Incorporating super-base cations into polymeric materials
    - Understanding proton conduction in the ion pair networks
  - Tech validation
    - Correlation of fuel cell AST and field test performance
    - Fuel cell start-up stability
    - Techno-economic analysis

Current and Proposed Future Work - Technical

With this project

Membrane development

- Complete synthesis of guanidinium poly(phenylene)s (Technical Backup Slide #5).

Ionomer development

- Synthesis of phosphonated ionomers.

Fuel cell testing

- Initial performance with Pt-based catalysts under H_2/O_2 and H_2/air conditions.
- *In-situ* water tolerance test (humidity-temperature cycling 80 – 160 °C).

❖ Currently no alternative development pathways is planned; however we may add some additional work based on AMR comments.

Beyond this project

Investigation of interface between catalyst and ion-paired ionomer

- Hydrogen oxidation reaction
- Oxygen reduction reaction
- Funding (LANL-Toyota CRADA)

Current and Proposed Future Work - Technology Transfer Activities

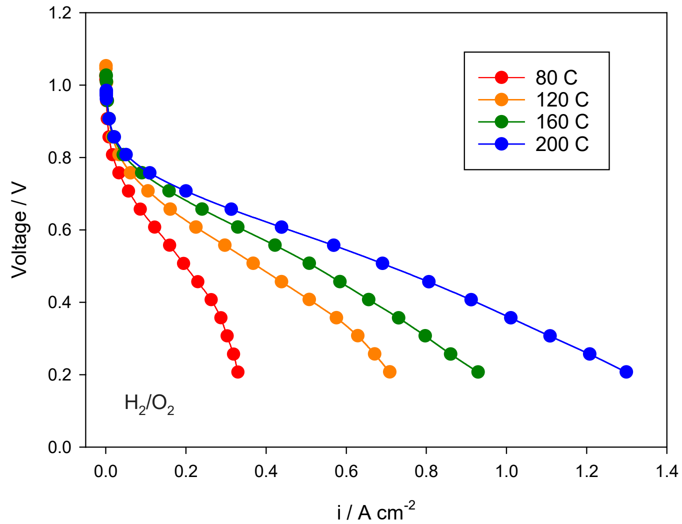
SBIR Phase II

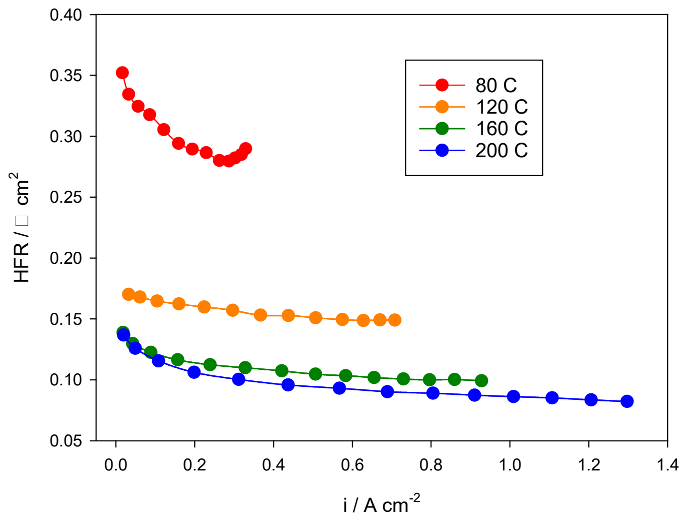
- Technology transfer effort to Nanosonic Inc. (SBIR Phase II) to produce scale-up synthesis of ion-pair coordinated membranes.

Patent application

- Kwan-Soo Lee and Yu Seung Kim, "Proton exchange membrane fuel cells" US Patent Application No. 62/377,163.
- Sarah Park, Sandip Maurya, Yu Seung Kim, "Polymer electrolytes for alkaline membrane fuel cells" S133606 (March, 2, 2018)
- Albert Lee and Yu Seung Kim, "Polymer electrolytes for fuel cells" (Feb. 9, 2018).

The performance of Nanosonic membrane tested by LANL





Summary

Objective: Development of feasible ion-pair coordinated polymers to demonstrate a fuel cell that operates at 80–220°C without humidification.

Relevance: Aiming to make ion-pair coordinated membranes having comparable proton conductivity and durability without humidification. Successful development of such ion-pair coordinated membranes enable to operate fuel cells at the wide-range of temperature without humidification.

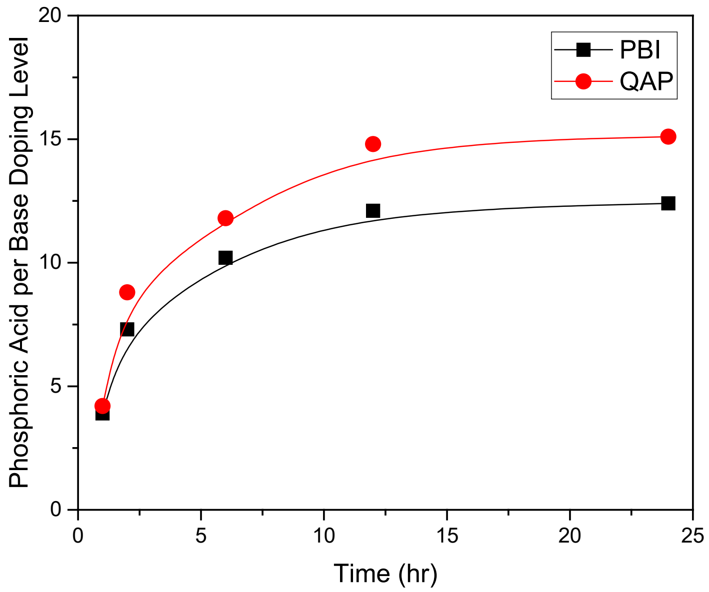
Approach: DFT modeling and small molecule study (^{31}P NMR) determine the best candidate materials that have strong ionic interactions. The selected ion pairs are incorporated in membranes and demonstrate good water tolerance and low cell resistance in membrane electrode assemblies.

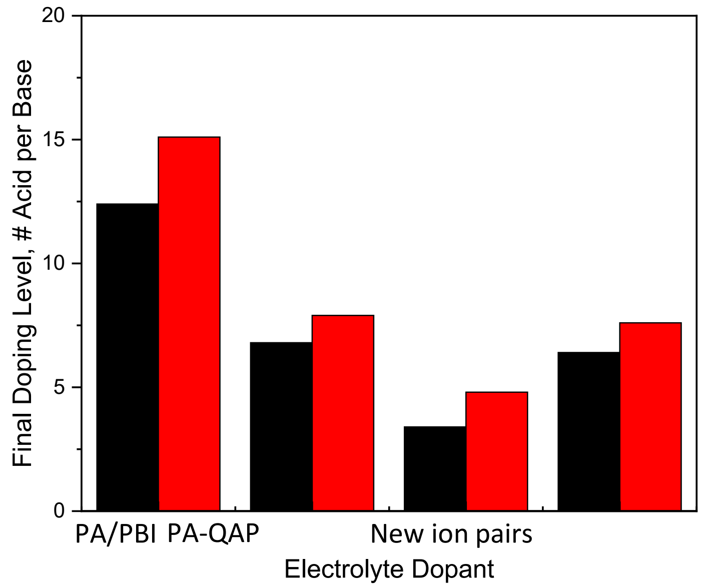
Accomplish-ments (FY 18) Completed the DFT modeling and small molecule study, demonstrating guanidinium-phosphate is the best candidate having strongest interaction. **Achieved water tolerance at 80 °C, 80% RH (P_{H2O} = 38.5 kPa),** met the go-no go decision criteria. Demonstrated **> 1 W/cm^2 peak power density** of ion-pair coordinated HT-PEMFC.

Collaborations: Collaboration in the area of chemical synthesis, MEA integration, electrochemistry and fuel cell testing. Extensive communications with several industrial partners, including RPI, University of Stuttgart (Germany), Sandia National Laboratories, AIST (Japan) Nanosonic, Inc and Toyota Motors North America.

Technical Back-Up Slides

Determination of Phosphoric Acid Doping Level





Typical doping process

→ Completely submerge membrane in 85 wt% phosphoric acid bath under ambient conditions.

→ Hang dry membrane until excess phosphoric acid drips off.

→ Dry at 80^{o}C under air for 2 hr.

→ 12 h was found to be appropriate to achieve non-excess doping levels.

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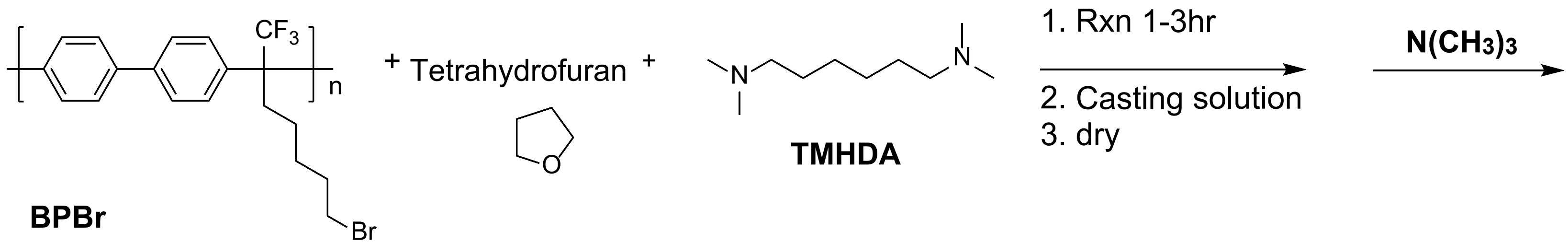
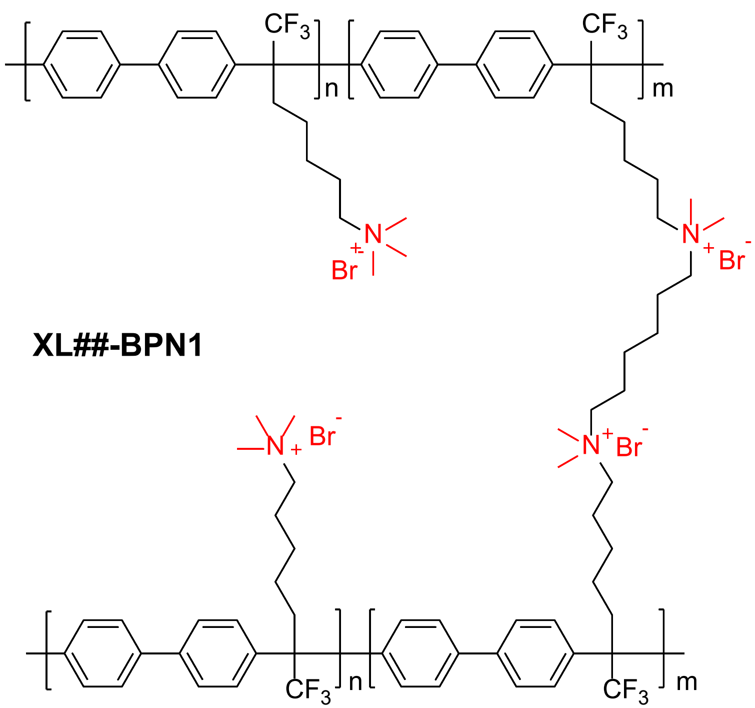
Synthesis and Properties of Cross-linked BPN

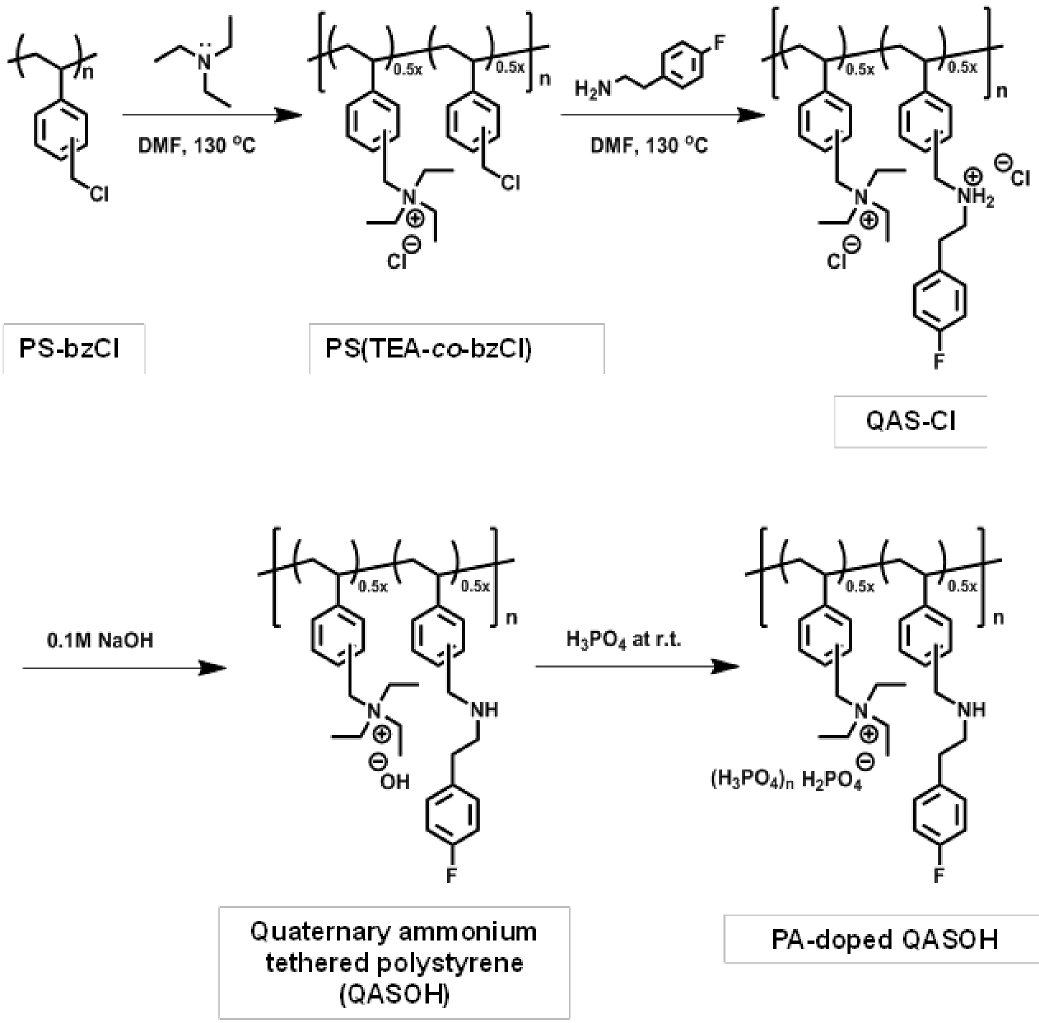




Theoretical IEC	IEC_t	OH^- counter ion form		
		WU(%) at 25°C	λ	Swelling (%)
2.61	2.52	109.6	24.1	31.1

Cl^- counter ion form			
tensile (MPa)	Elongation (%)	tensile (MPa)	Elongation (%)
50 °C / 50 %RH		25 °C / 50 %RH	
18.2	17.5	25.1	17.9
16.5	7.4	22.0	7.8
15.3	8.4	15.8	5.7

Synthesis and Properties of PA-QAPS*



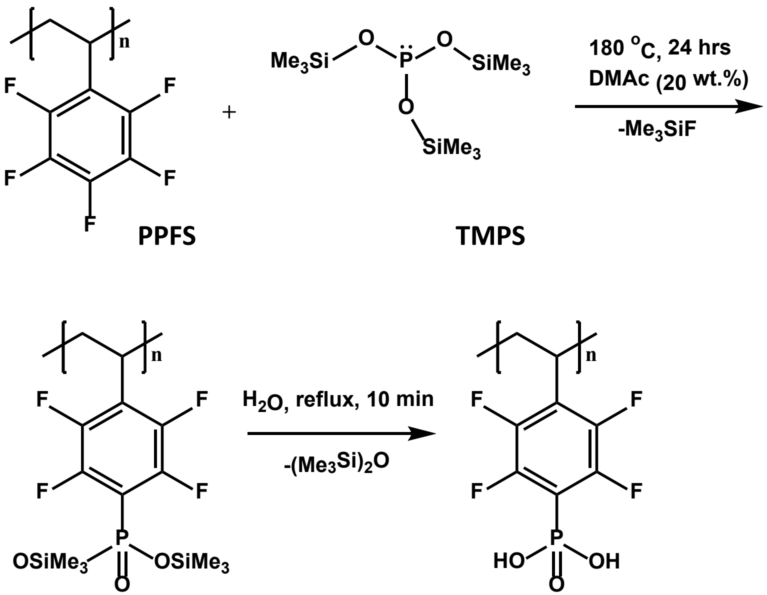
Concentration of base moiety (meq./g)	Number of PA per base moiety	Polymer content[a] (%)
2.0	2.7 ± 0.0	35

[a] for dry membrane.

Number of H_2O		
Per base moiety		Per PA (doped)
Un-doped	Doped	
23	14	5.2

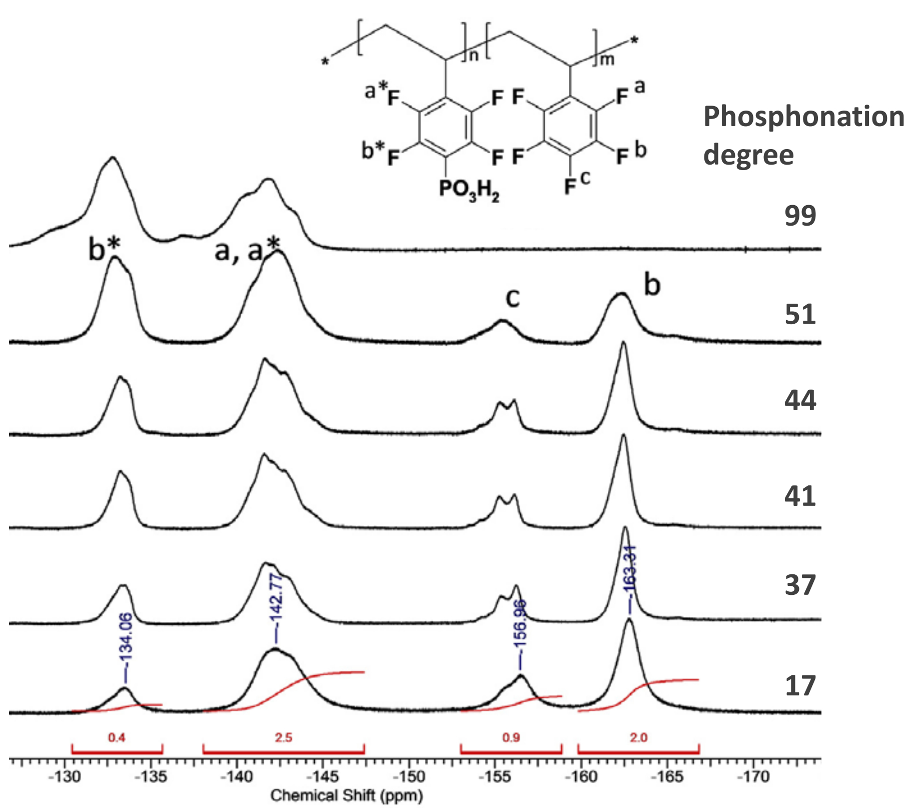
* *Nature Energy*, **1**, 16120 (2016)

Synthesis of Phosphonated Poly(pentafluoro styrene)*



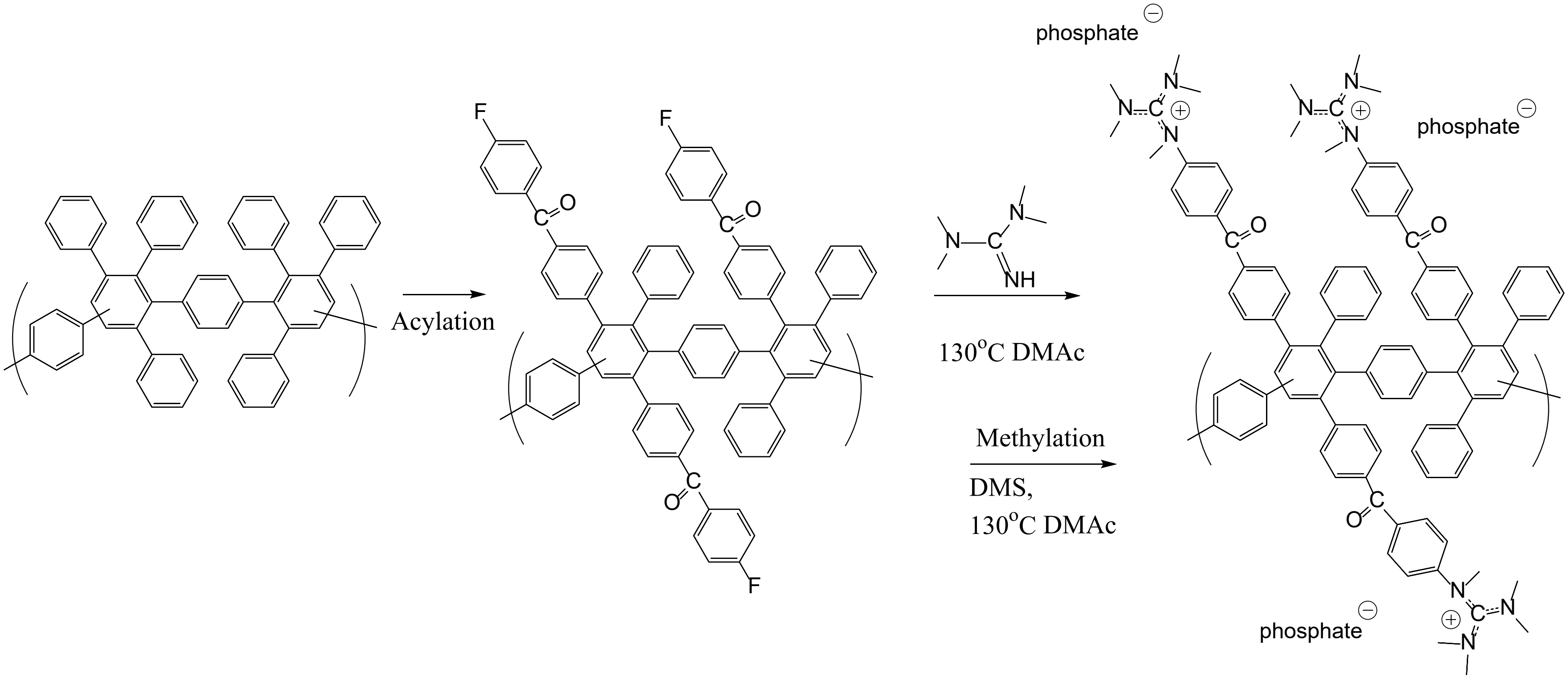
TMPS/PPFS (mol %)	Phosphonation ^{19}F NMR (%)	Phosphonation IEC (%)	IEC-direct/total (mequiv. g^{-1})
200	100	99	7.4/8.0
90	66	51	1.9/4.1
80	42	41	1.4/3.5
70	41	44	1.6/3.8
60	36	32	1.1/2.9
40	17	17	0.5/1.6

^{19}F NMR spectra of PPFS



J. Power Sources, **343**, 363-372 (2017)

Synthesis of Phenyl Guanidinium Funct. Poly(pheneylene)s



Poly(phenylene)-based anion exchange polymers and methods thereof" USP applications US 2017/0190831 A1, K.S. Lee, Y.S. Kim, C. Fujimoto (2017)

IEC = 1.9 – 2.5 meq/g