Polymer-Based Fuel Cells that Operate from 80°C to 220°C

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Overall Objectives

- Develop ion-pair-coordinated polymer electrolytes to demonstrate a fuel cell that operates from 80°C to 220°C without humidification.
- Density functional theory (DFT) and small-molecule 31 P nuclear magnetic resonance (NMR) study of the interaction energy between different quaternary ammonium-biphosphate ion-coordinated pairs as a function of phosphoric acid doping level and water content.
- Develop new ion-pair-coordinated electrolyte systems with improved water tolerance.
- Demonstrate membrane electrode assembly (MEA) fabrication and high-performance high-temperature polymer electrolyte membrane fuel cell (HT-PEMFC) performance with newly developed phosphonated ionomer system.

Fiscal Year (FY) 2018 Objectives

- Obtain area specific resistance ≤0.1 Ω cm^2 at 160°C.
- Demonstrate MEA performance with peak power density (H_2/O_2) >1,000 mW cm^{-2}.
- Obtain water tolerance P_{H2O} >38.5 kPa.
- Achieve cell durability V_{loss} <10% at 160°C.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan [1]:

(A) Durability

(B) Cost

(C) Electrode performance.

Technical Targets

This project aims to develop ion-pair-coordinated polymer electrolytes for HT-PEMFCs operating in the temperature range of 80°–220°C without humidification for practical use in both stationary and automobile applications. Insights gained from this project will be applied towards the next stage HT-PEMFC systems. The technical targets for the developed polymer electrolytes in HT-PEMFCs in the Multi-Year Research, Development, and Demonstration Plan [1] are listed below.

- Q4. 2017: Water tolerance P_{H2O} >38.5 kPa.
- Q1, 2018: Area specific resistance (at 160°C) ≤0.1 Ω cm^2.
- Q2, 2018: Peak power density (H_2/O_2) >1,000 mW cm^{-2}.
- Q4, 2018: Durability during 80°–180°C AST, <10% V loss at 160°C.

FY 2018 Accomplishments

- Completed DFT modeling and small-molecule study through 31 P NMR, demonstrating that guanidinium-phosphate is the best candidate, having strongest interaction between base and phosphoric acid.
- Achieved water tolerance at 80°C, 80% relative humidity (RH) (P_{H2O} = 38.5 kPa), meeting the go/no-go criteria.
- Demonstrated a peak power density (H_2/O_2) of 1,134 mW cm^{-2} and area specific resistance of 0.09 Ohm cm^2 at 160°C utilizing a down-selected trimethyl ammonium-functionalized Diels-Alder poly(phenylene)s membrane and phosphonated ionomer.

INTRODUCTION

In FY 2016, we developed a new HT-PEMFC system [2] in which the ion-pair coordination between a quaternary ammonium polymer (QAP) and biphosphate increased the water tolerance of both the membrane and ionomer to widen the operating temperature of HT-PEMFCs to 80°–180°C, a major improvement from commercial phosphoric-acid-doped polybenzimidazole (PBI), which operates from 140°C to 180°C. In FY 2017, a systematic investigation of the ionic interaction strength of various acid-base and ion-pair-coordinated systems were conducted using both computational and 31 P NMR studies using small molecules. On the basis of these results, a down-selected trimethyl ammonium-functionalized Diels-Alder poly(phenylene) [2] was used as the QAP membrane and newly applied phosphonated polymer [3, 4] as ionomer supplied from University of Stuttgart. Implementation of these ion-coordinated membranes and phosphonated ionomers gave remarkably improved HT-PEMFC performance and durability.

APPROACH

Our general approach to developing a polymer-based fuel cell that operates at a temperature range of 80°–220°C was to implement a highly conductive, non-leachable solid phosphonated ionomer into the electrodes of HT-PEMFCs with our down-selected phosphoric-acid-doped, ion-pair-coordinated quaternary ammonium polymer membrane. The rationale behind this approach was that the ion-pair-coordinated phosphoric-acid-doped QAP membrane would exhibit high water tolerance and phosphonated ionomer would provide sufficient anhydrous proton conduction at both low and high temperatures without the need for phosphoric acid doping, leading to improvements in both HT-PEMFC performance and durability. For this, we first investigated the interaction energy between different acid-base and quaternary ammonium base–biphosphate system through DFT calculations and 31 P NMR. Through these analytical tools, we were able to discern which organic cations have the greatest interaction energies with phosphoric acid, thus giving us a strategy in designing new polymer structures for improved water tolerance and phosphoric acid retention in the membrane. Second, for electrode optimization, a fully solid phosphonated ionomer was utilized as a conductive binder. Through the elimination of leachable liquid phosphoric acid in these electrodes, remarkable improvements in both HT-PEMFC performance and cell durability were able to be attained in tandem with our ion-pair-coordinated membrane.

RESULTS

31 P NMR and DFT Study of Acid-Base and Ion-Pair-Coordinated Systems

Figure 1a shows the 31 P NMR spectra for various acid-base and ion-pair-coordinated systems with the chemical structures of the investigated organic bases shown in Figure 1b.

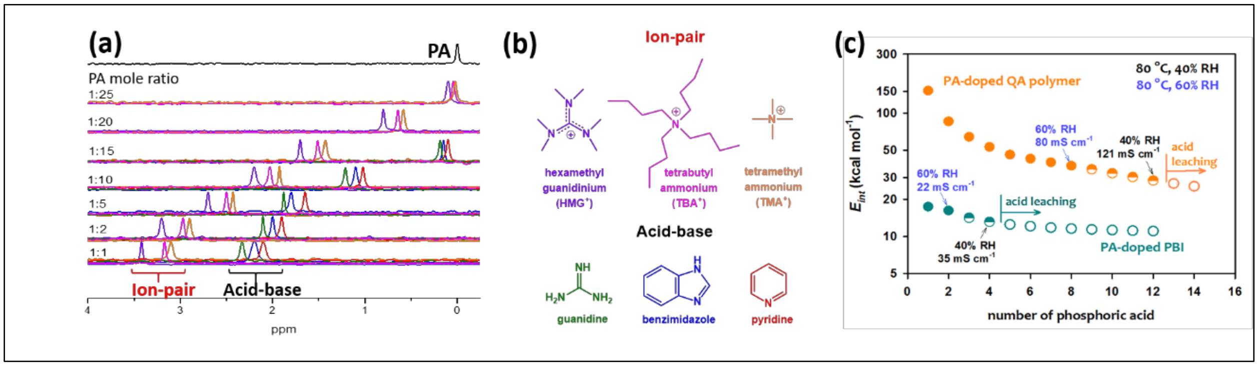
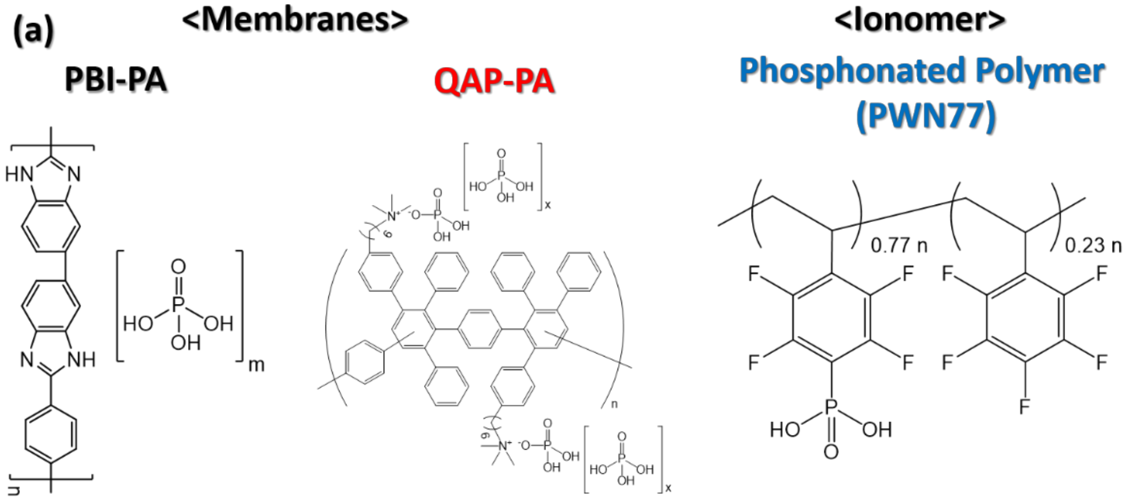


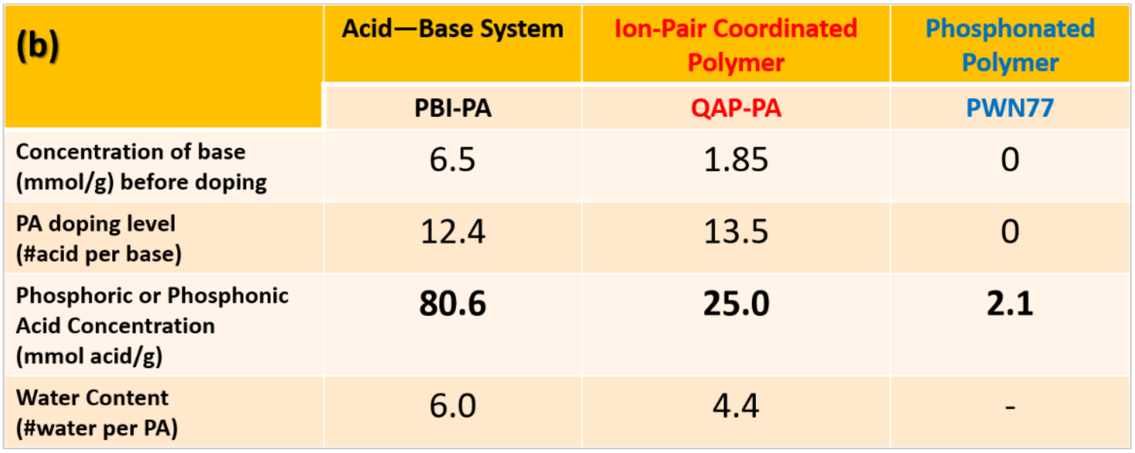
Figure 1. (a) 31 P NMR spectra for various ion-pair and acid-base compositions, (b) chemical structures of different bases studied, (c) DFT-derived interaction energies as a function of phosphoric acid doping level

If we consider the 31 P NMR chemical shift as an indicator of relative ionic interaction strength relative to pristine phosphoric acid (PA) reference standard at concentration of 5 M, we can observe that the ion-pair-coordinated systems all exhibit a higher interaction strength compared to the acid-base interactions with these interaction strengths in the following order: hexamethylguanidinium > tetrabutylammonium > tetraalkylammonium > guanidine > benzimidazole > pyridine. Computational works with these small molecules revealed that the water tolerance of the ion-pair-coordinated systems could be greatly increased, as with a greater interaction, the PA-doped QA polymer loses only 2 PA molecules at 80°C, 40% RH, in which the proton conductivity is 121 mS cm^{-1}. In contrast, the PA-doped PBI loses 8 PA molecules at the same condition in which the proton conductivity is 35 mS cm^{-1}.

Rational Design of Ion-Pair-Coordinated Membranes and Phosphonated Ionomers

Figure 2a shows the chemical structures of the various high-temperature polymer electrolytes. A commercial phosphoric-acid-doped PBI membrane as well as QAP-doped PA (QAP-PA) with polyphenylene backbone. It is noteworthy to point out that the polyphenylene backbone was necessary to attain both robust chemical stability at high and low pH (the membrane should be stable in high pH condition for a pretreatment step in alkaline solution as well as low pH when doping in phosphoric acid) and high temperature, as well as excellent mechanical properties. Also, the phosphonated ionomer, phosphonated poly(pentafluorosytrene) (PWN77), with a phosphonation degree of 77%, was selected due to its excellent balance in high proton conductivity over lower phosphonated polymers and high chemical resistance [2]. The various physical properties of these materials are shown in Figure 2b.





(b)	Acid—Base System	Ion-Pair Coordinated Polymer	Phosphonated Polymer
	PBI-PA	QAP-PA	PWN77
Concentration of base (mmol/g) before doping	6.5	1.85	0
PA doping level (#acid per base)	12.4	13.5	0
Phosphoric or Phosphonic Acid Concentration (mmol acid/g)	**80.6**	**25.0**	**2.1**
Water Content (#water per PA)	6.0	4.4	-

Figure 2. (a) Chemical structures of developed polymer electrolyte membranes and ionomers, (b) summary of the physical properties of polymer electrolyte membranes and ionomers

As shown, the QAP-PA and phosphonated polymer exhibited drastically lower phosphoric or phosphonic acid concentrations compared to polybenzimidazole phosphoric acid (PBI-PA) acid-base system which may give three main benefits. First, the mechanical properties of ion-pair-coordinated PEMs are significantly better due to lower liquid content [1]. Second, the ion-coordinated PEMs exhibit higher water tolerance. Third, phosphate anion poisoning on the oxygen reduction reaction catalyst is less.

Proton Conductivity and Water Tolerance

The proton conductivities as a function of temperature and RH are shown in Figure 3. The conducting phosphonate groups of PWN77, which are covalently bonded to the polymer backbone, have a significantly lower ionic conductivity at lower temperatures, but at a critical temperature—140°C—the conductivity of PWN77 exceeds that of both commercial polybenzimidazole-doped phosphoric acid and even the ion-pair-coordinated QAP-PA membrane. The phosphonated polymer, PWN77, is inherently dry across all temperatures, thus its proton conductivity is completely anhydrous in nature, which accounts for its relatively low proton conductivity at temperatures less than 100°C as the measured proton conductivities for PWN77, QAP-PA, and PBI-PA at 80°C were 6.5 mS cm^{-1}, 80 mS cm^{-1}, and 86 mS cm^{-1}. Phosphoric acid, however, most commonly used as 85 wt% concentrated aqueous solution, is exceedingly hygroscopic through strong hydrogen-bonding interactions with water and cannot completely rid of itself of water at temperatures lower than 140°C. This propensity to hold water contributes to the relatively higher conductivity at lower temperatures, even for phosphoric-acid-doped PBI systems where the polymer-phosphate acid-base interactions are very weak. It is worth noting that under water-generating conditions of a fuel cell, the conductivity for the phosphonated ionomer also can be boosted by a water-mediated phase, as shown by the RH-dependent conductivity values. Above 140°C, we see that the anhydrous proton conductivity of the phosphonated polymer electrolyte dominates, as a continual increase in conductivity is observed as the temperature reaches 200°C. Specifically, the proton conductivities at 160°C were 168 mS cm^{-1}, 103 mS cm^{-1}, and 125 mS cm^{-1} for PWN77, QAP-PA, and PBI-PA, respectively. The water tolerance of the selected high-temperature PEMs was examined as a function of RH at 80°C. As shown in Figure 3b, the conductivity of PBI-phosphoric acid showed an immediate and continual decrease in proton conductivity as the RH increased, which we attributed to the instantaneous leaching of phosphoric acid. For the ion-pair-coordinated quaternary ammonium polymer-phosphoric acid system, we found that the proton conductivity increased until reaching 40% RH, as the higher humidity helped promote water-mediated conduction, followed by a similar loss of conductivity through phosphoric acid leaching. The conductivity of the phosphonated polymer, however, steadily increased as the RH increased. As a result, although the absolute proton conductivity was lower at lower RH values, the conductivity increase as a function of RH was attributed to the water-mediated proton conduction process.

HT-PEMFC MEA Performance

MEAs using the ion-pair-coordinated QAP membrane and phosphonated ionomer and reference PWN77 ionomer/PBI-PA membrane cell were prepared with carbon-supported Pt-based catalysts. Catalyst loadings were A/C 0.5/0.6 mg_{pt}/cm^2 with both anode and cathode flow and backpressure held at 500 sccm and 10 psi, respectively. Figure 4 shows the H_2/O_2 fuel cell performance of the MEAs at 80°C, 120°C, 160°C, and 200°C. As shown, the PWN77 ionomer MEA showed much better peak-power densities of 1,130 mW/cm^2 and 1,480 mW/cm^2 at 160°C and 200°C, and across all temperature ranges. This significant increase in performance of the PWN77 ionomer/ion-pair-coordinated membrane system compared to PBI-PA membrane—despite the 40-fold decrease of phosphonic/PA concentration shown in Figure 2b—was attributed to a combination of lower phosphoric acid poisoning, exceptional water tolerance, and higher anhydrous proton conductivity at elevated temperatures.

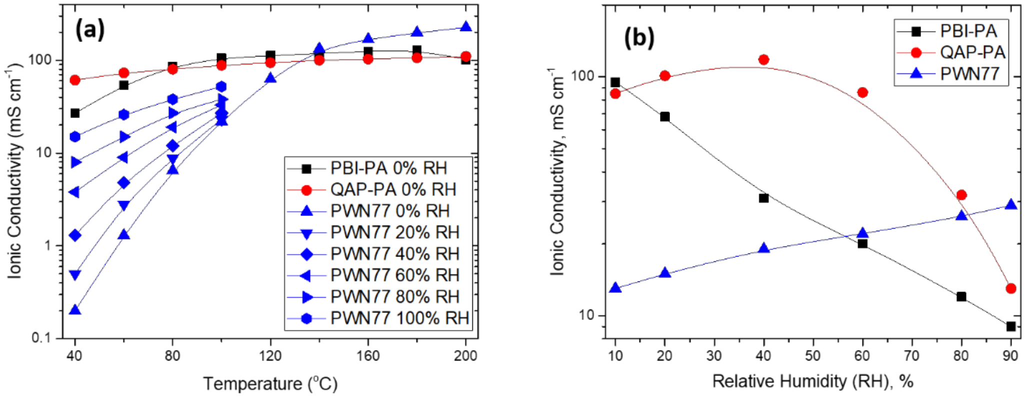


Figure 3. (a) Temperature-dependent and (b) RH-dependent ionic conductivities for various polymer electrolyte systems

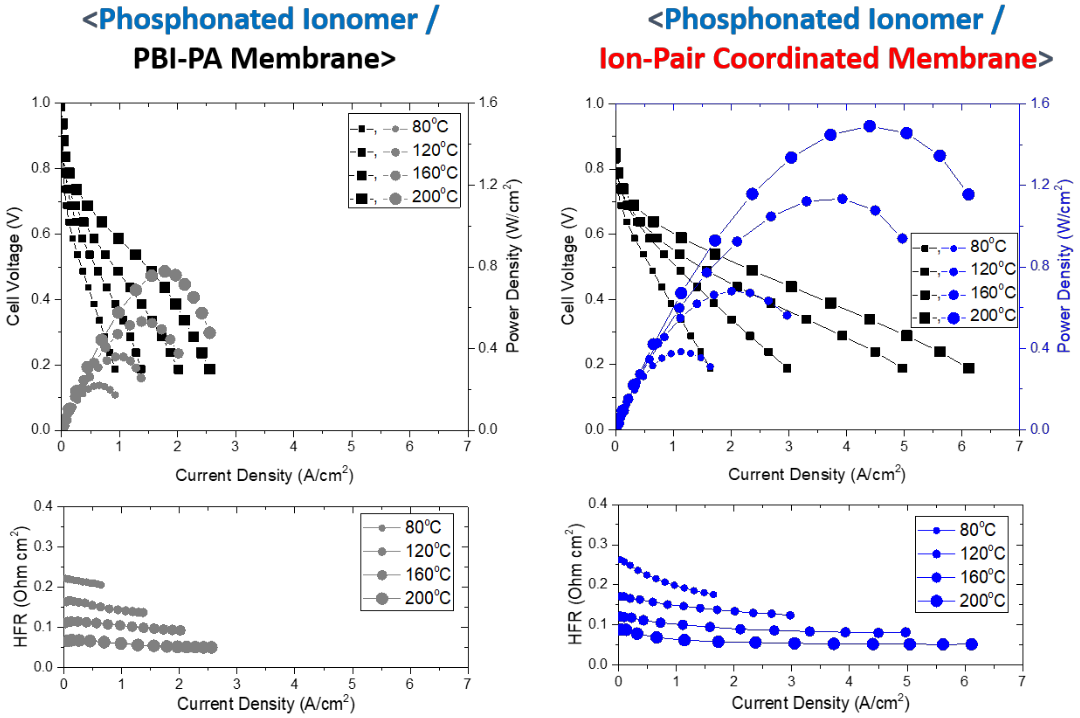


Figure 4. HT-PEMFC MEA performances for (a) phosphonated ionomer/PBI-PA membrane system, and (b) phosphonated ionomer/ion-pair-coordinated membrane at various temperatures

CONCLUSIONS AND UPCOMING ACTIVITIES

- DFT modeling and 31 P NMR studies of various organic base: phosphoric acid compositions revealed that the ion-coordinated system exhibited a stronger ionic interaction at all phosphoric doping levels, with guanidinium and tetramethylammonium quaternary ammonium bases exhibiting the highest interaction energies.

- Conductivity and water-tolerance measurements revealed that the newly developed ion-pair-coordinated polymer electrolytes exhibited high RH tolerance (up to 40% RH) at 80°C, and the phosphonated ionomer giving stable conductivity for over 200 h at 80°C, 80% RH conditions.

- HT-PEMFC MEA performance using the developed ion-pair-coordinated membrane and phosphonated ionomer was 1,134 mW cm^{-2} of peak power density (H_2/O_2) and area specific resistance of 0.09 Ohm cm^2 at 160°C.
- Durability AST experiments are ongoing and are to be completed before the end of the project term.

SPECIAL RECOGNITIONS AND AWARDS/PATENTS ISSUED

1. Yu Seung Kim and Albert Lee, "Polymer Electrolytes for Fuel Cells," US Patent Application Publication, Feb. 9, 2018.

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3. Y.S. Kim, K.S. Lee, G. Purdy, Y.-K. Choe, C. Fujimoto, J. Han, and C. Bae, "A New Class of Fuel Cells Based on Ion Pair-Coordinated Proton Exchange Membranes," Abstract Number 1470 232nd ECS Meeting, Oct. 1–5, 2017, National Harbor, Maryland.
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2. Kwan-Soo Lee, Jacob S. Spendelow, Yoong-Kee Choe, Cy Fujimoto, and Yu Seung Kim, "An Operationally Flexible Fuel Cell Based on Quaternary Ammonium-Biphosphate Ion Pairs," *Nature Energy* 1 (2016): 1.
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4. Vladimir Atanasov, Dietrich Gudat, Bastian Ruffman, and Jochen Kerres, *Eur. Polym. J.* 49 (2013): 3977.