IV.B.12 High Temperature Polymer Electrolytes Based on Ionic Liquids

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Objectives

- Increase conductivity at high temperature (~120^{o}C) and low relative humidity (<50% RH)
- Improve fundamental understanding of conduction in 'free' proton containing ionic liquids; identify limits of conduction at low RH
- Probe the dependence of properties on ion capacity, water content and temperature
- Develop robust polymer systems

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- O. Stack Material and Manufacturing Cost
- P. Durability
- R. Thermal and Water Management

Approach

- Investigate ionic liquids based on imidazole cations and dihydrogen phosphate ($H_2PO_4^-$) or bisulfate (HSO_4^-) anions capable of proton conduction (hopping candidates)
- Investigate conduction limits of these materials
- Incorporate the most promising candidates into polymeric materials

Accomplishments

- Many (>10) imidazole-acid pairs have been synthesized and screened
- Conductivity of imidazole-acid pairs has been quantified as a function of temperature and water uptake
- First-generation norbornene-based polymers that have been synthesized and tested exhibit relatively high conductivity under dry conditions (40 mS/cm at 80^{o}C and 0% RH)

Future Directions

- Incorporate alternate imidazole functionality into the polymer; modify sidechain length and acidic/basic character to determine impact on conductivity
- Investigate copolymers (random and block) for control of water uptake properties and conduction limits (0-100% functionalized materials)
- Investigate tethered acidic moeities compared to free acids

Introduction

It is generally agreed that for transportation applications, fuel cells must be operated at 120°C or greater, with minimal backpressure and low relative humidity (less than 50% RH). For stationary applications, the operating conditions are even more demanding, requiring temperatures greater than 150°C at extremely low relative humidity, although tolerance to liquid water may not be an issue in these systems. While fluorinated proton-conducting membranes are the keystones of polymer electrolyte membrane fuel cells, there are several well-recognized limitations with the sulfonated fluorocarbon-based membranes currently in use. For example, they require high backpressures and high relative humidity to operate much above 80°C, and these conditions require too much parasitic power to be practical from a system standpoint. Additionally, mechanical stability limits performance under these harsh conditions even if parasitic power were not an issue. Adding selected hygroscopic inorganic compounds has modestly extended this upper temperature limit, but performance at 120°C is still inadequate. Thus, a critical need in fuel cell development is for a proton conducting membrane that can be operated at elevated temperatures and low relative humidity.

Approach

Our approach to exploring this problem is to investigate ‘free’ proton-containing ionic liquids. These ‘free’ proton ionic liquids are based on imidazole cations and dihydrogen phosphate ($H_2PO_4^-$) or bisulfate (HSO_4^-) anions capable of proton conduction (hopping candidates). While these substances have the ability to act as anhydrous proton conductors, they are extremely hygroscopic and may exhibit greatly increased conductivity even at relatively low RH. Candidate materials are evaluated in terms of conductivity, water uptake and thermal stability in the ionic liquid form. The most promising of these materials are tethered to a polymer architecture based on polynorbornene. Polynorbornene has been chosen due to its availability, ease of functionalization and polymerization, and its ability to be polymerized into well-defined block copolymers. Thermal stability and conductivity of these polymers can also be characterized in terms of chemistry, water content and temperature in order to increase fundamental understanding of these materials, with the ultimate goal being a robust high-temperature membrane with adequate chemical and physical properties.

Results

Several acid-imidazole pairs have been synthesized and characterized in terms of water uptake, conductivity, melting point and thermal stability. These materials were found to be thermally stable to >200°C and to have high water uptakes. The conductivity of two target acid-imidazole pairs can be found in Figure 1 as a function of water content and temperature. Conductivity ranged from 7-80 mS/cm depending on the water content and temperature of the sample, with samples at increased temperatures and with increased water contents demonstrating higher conductivity. Due to the high conductivity of some of these ionic pairs, imidazole functionality was incorporated into polynorbornenes by the chemistry shown in Figure 2. A major hurdle was the elimination of the exo-isomer of the monomer, which inhibited polymerization. The conductivity of the first-generation polymer in liquid water is shown in Figure 3. While the reported conductivity for this polymer is low for fuel cell applications, 5-12 mS/cm, considering the presence of only a weakly ionic imidazole group in these

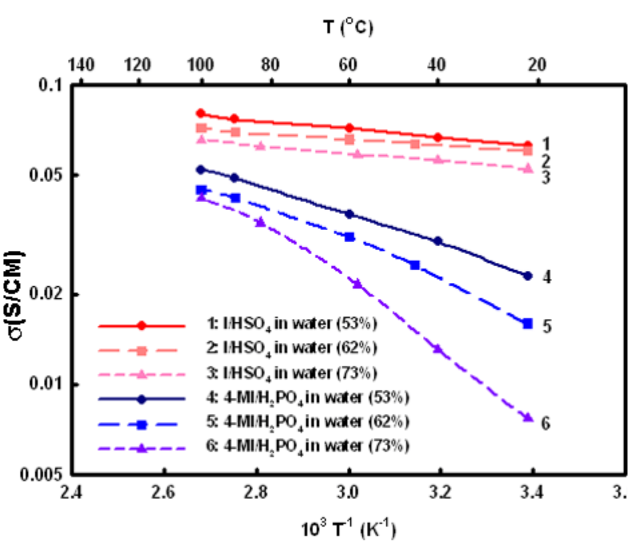

Figure 1. Dependence on Water Content and Temperature of ‘Free’ Proton-Conducting Acid-Imidazole Pairs

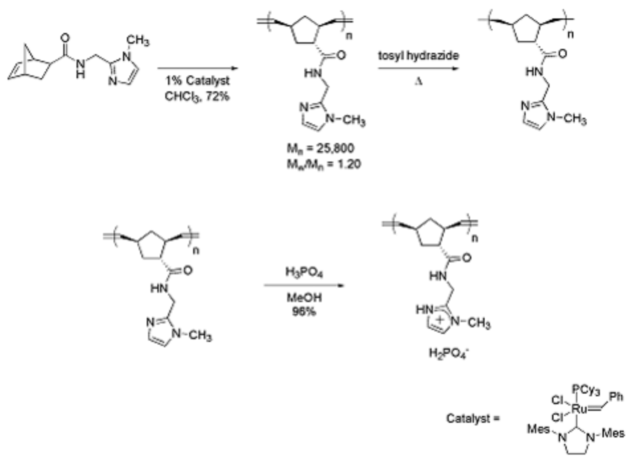

Figure 2. Synthetic Route from Norbornene Monomer to Ionic Liquid Analogs of Polynorbornene

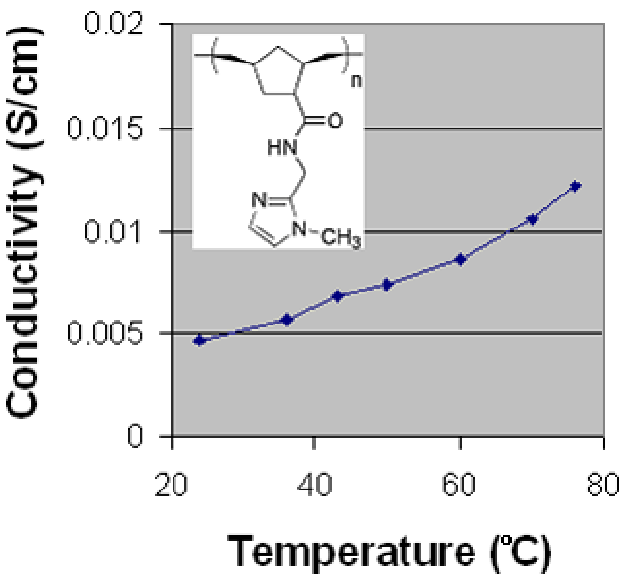

Figure 3. Conductivity of Imidazole-Functionalized Polynorbornene in Liquid Water as a Function of Temperature (see inset for chemical structure)

experiments, these results are compelling. The addition of an acidic group, dihydrogen phosphate, greatly increased the conductivity of the membrane even under dry conditions, as shown in Figure 4. While the reported conductivity is still a factor of 2 below that of Nafion under hydrated conditions, it is a significant improvement for a water-free system.

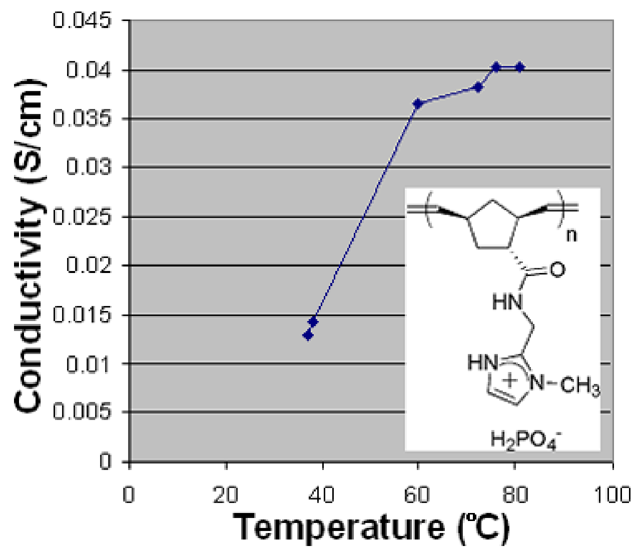

Figure 4. Conductivity of Imidazole-Functionalized Polynorbornene with Dihydrogen Phosphate in 1:1 Ratio to Imidazole as a Function of Temperature Under Dry Conditions (see inset for chemical structure)

Conclusions

Proton-conducting, ionic liquids are interesting candidates for high temperature membrane applications, particularly due to their ability to conduct by a hopping mechanism. The results presented here demonstrate reasonable conductivity in these systems even under dry conditions and good thermal stability. These systems presented here are related to current phosphoric acid-based systems. Future work in this area will involve tethering the role of the anion in conduction in these systems so that water tolerance can be increased and the role of the anion in conduction can be better understood. The systems presented here with the highest conductivity were water-soluble and would not be suitable for operation when in contact with high relative humidity or liquid water. Future work will also involve synthesis of block copolymers in which structural elements can be added to provide the mechanical properties necessary to keep the membranes robust, yet functional.

FY 2004 Publications/Presentations

1 Robert D. Gilbertson, Gregory S. Long, Yu Seung Kim, Bryan S. Pivovar, Wayne H. Smith, Michael E. Stoll, Debra A. Wrobleski, E. Bruce Orler, "Synthesis and Characterization of Imidazole Functionalized Polynorbornene Derivatives for High Temperature Fuel Cells," 2003 Spring Meeting of the American Chemical Society, March 28-April 2, 2004, Anaheim, CA.

2 Bryan Pivovar, Yu Seung Kim, Rob Gilbertson, Greg Long, E. Bruce Orler, Michael Stoll and Wayne Smith, "Preliminary Investigation into the Use of Bi-sulfate and Bi-phosphate Based Room Temperature Ionic Liquids as High Temperature Conducting Membrane Materials for Fuel Cell Applications," 2003 Fuel Cell Seminar, November 3-6, 2003, Miami Beach, FL.