

# V.B.10 High Temperature/Low Humidity Polymer Electrolytes Derived from Ionic Liquids

James M. Boncella (Primary Contact),  
Bryan Pivovar, Robert Gilbertson,  
Yu Seung Kim

Los Alamos National Laboratory  
Materials Physics and Applications Division  
P.O. Box 1663, MS J514  
Los Alamos, NM 87545  
Phone: (505) 665-0795; Fax: (505) 667-9905  
E-mail: boncella@lanl.gov

DOE Technology Development Manager:  
Nancy Garland  
Phone: (202) 586-5673; Fax: (202) 586-9811  
E-mail: Nancy.Garland@ee.doe.gov

Start Date: April 2003  
Projected End Date: September 2006

## Objectives

- Improve fundamental understanding of conduction in 'free' proton containing ionic liquids.
- Investigate how phase separation behavior affects conductivity in well-defined phase-separated ionomers.
- Probe the dependence of properties on ion capacity, water content and temperature.
- Increase conductivity at high temperature (~120°C) and low relative humidity (<50% RH).

## Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section (3.4.4.2) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (D) Thermal, Air and Water Management
- (B) Cost

## Technical Targets

This project is directed towards identifying candidates for proton-conducting membranes that have proton conductivities that meet the DOE technical targets for conduction at low relative humidity (<50% RH) and high temperature (~120°C).

## Approach

Our approach has been first to investigate the inherent proton conductivity of ionic liquids as a function of water content and then develop the synthetic methodology necessary to tether the ionic liquid constituents to a polymer backbone. Literature reports indicate that control of phase separation of proton-conducting membranes into structural and functional (proton-conducting) domains results in better conductivity at low RH than membranes with a random distribution of functionalities. Our approach has been to design well-defined phase-separated polymer membranes to investigate and understand how phase separation improves low RH conductivity, with the long-term goal being the synthesis of a material that meets the DOE technical goals.

## Accomplishments

Initial work on the synthesis of homopolymers in which norbornene is functionalized with an imidazolium side chain display good conductivity at 90°C and low RH as shown in Figure 1. While these polymers show good conductivity when dry, they are unstable at high RH and slowly dissolve in water. In order to overcome these shortcomings, the synthesis of co-polymers that contain an imidazole functionalized block as well as a pure norbornene block was pursued. The synthesis of the first member of a new class of norbornene functionalized co-polymers is shown in Figure 2.

While the phase separation is only beginning to develop when the mole fraction of monomers is 1:1, the conductivity is still high (0.06 S/cm, 10% RH) at 60°C despite the fact that the concentration of imidazolium groups is lower than in the homopolymer.

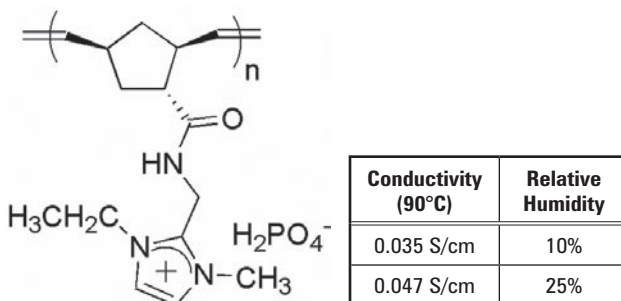
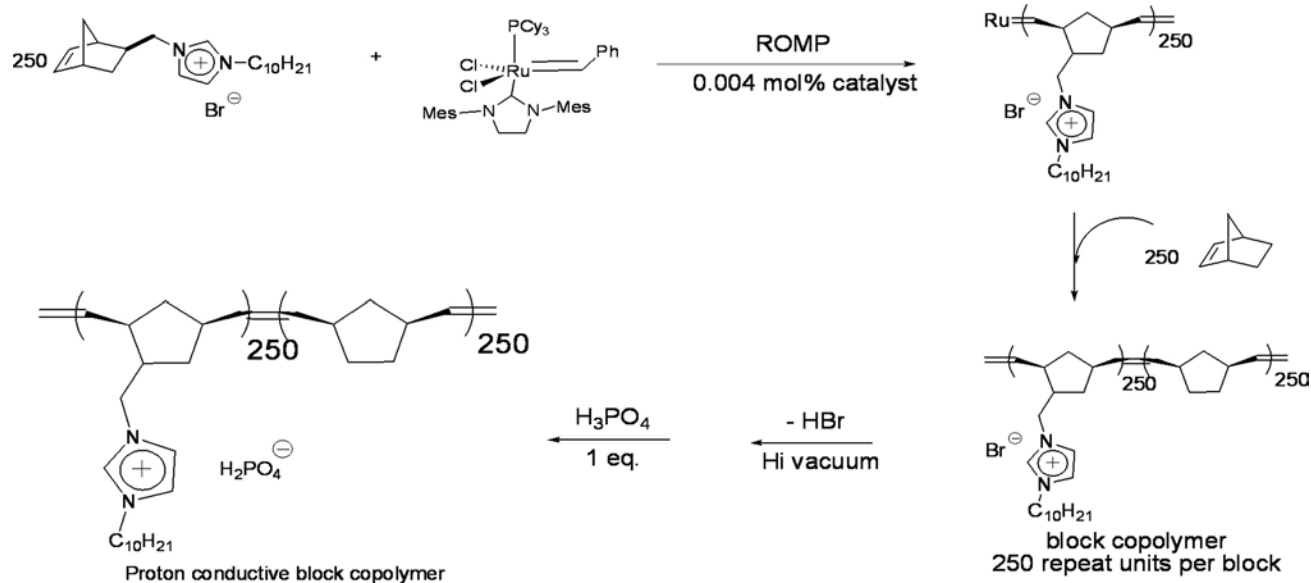


FIGURE 1. Conductivity of an Imidazolium Homopolymer



**FIGURE 2.** Synthesis of Norbornene-Imidazolium Block Co-Polymer

The difference between the volumes of the imidazolium blocks and the norbornene blocks is responsible for the lack of well-defined structural domains in these materials. The synthesis of co-polymers having block volumes that are matched has been accomplished by adjusting the relative block sizes. The resultant polymer films have been cast and are currently being characterized.

The initial results of this research suggests that phase separation which segregates a proton-conducting domain from a structural domain in a membrane yields materials that possess conductivities that are greater than Nafion<sup>®</sup> under the same (low RH) conditions. While the hydrocarbon polymers that have been studied so far will not possess the necessary durability to function as working proton exchange fuel

cell membranes, the information concerning phase separation will be especially useful in designing new membrane materials that will achieve the conductivities at low RH that will meet the DOE technical targets.

### FY 2006 Publications/Presentations

1. M. Hickner and B. Pivovar, "The Chemical and Structural Nature of Proton Exchange Membrane Fuel Cell Properties," *Fuel Cells Fund. to Sys.*, 2005, 5, 213.
2. J. M. Boncella "A Discussion of Conductivity Testing in High Temperature Membranes (lessons learned in assessing transport)" Presented at the High Temperature Membrane working group meeting at the Electrochemical Society Meeting, October 20, 2005.