Structure-property relationships in phosphoric acid-doped polybenzimidazole membranes and their application in a high temperature electrochemical purification device for hydrogen

by

Kelly A. Perry

An Abstract of a Thesis Submitted to the Graduate

Faculty of Rensselaer Polytechnic Institute

in Partial Fulfillment of the

Requirements for the degree of

DOCTOR OF PHILOSOPHY

Major Subject: Chemistry

The original of the complete thesis is on file
In the Rensselaer Polytechnic Institute Library

Examining Committee:

Prof. Brian C. Benicewicz, Thesis Adviser

Prof. Leonard V. Interrante, Member

Prof. James A. Moore, Member

Dr. Karren L. More, Member

Dr. Lisa Xiao, Member

Rensselaer Polytechnic Institute
Troy, New York

December, 2009

ABSTRACT

Structure-property relationships of phosphoric acid (PA)-doped polybenzimidazole (PBI) membranes that are used in high temperature fuel cells and hydrogen pumps have been investigated as a function of process, polymer rigidity, and dihydroxy functionalization. PA-doped PBI membranes were characterized by compositional analyses to determine acid doping levels and solids content, a four-probe ac impedance method to monitor ionic conductivity, tensile testing, wide angle X-ray scattering (WAXS) to investigate bulk structural ordering, and electron microscopy. Initial structural validation studies found that to ensure retention of the structural integrity of PA-doped PBI membranes, the phosphoric acid should not be removed from the membranes. Heat treatments at 120ºC for 5days were conducted to simulate a membrane exposed to elevated temperatures and caused a reduction in the acid doping level of all PA-doped PBI membrane, regardless of process or polymer chemistry.

It was found that PA-doped PBI membranes with the same polymer chemistry (*m*-PBI) were able to retain higher acid doping levels and achieve higher ionic conductivities when prepared by the sol-gel process, rather than conventional acid immersion. Heat treatment of conventional membranes with ≥6PA/rpu caused a significant reduction in mechanical performance; conversely, the sol-gel membrane exhibited an enhancement in mechanical properties. From WAXS studies and atomistic simulations, both conventional and sol-gel membranes exhibited d-spacings of 3.5 and 4.6Å, which was attributed to parallel ring stacking and staggered side-to-side packing, respectively.

Comparing low and moderate ionic-conducting sol-gel PA-doped PBI membranes, the more rigid polymer (*p*-PBI) achieved a higher acid doping level and higher ionic conductivity than *m*-PBI. The ability for *p*-PBI membranes to accommodate more total acid and a larger range of acid doping levels compared with sol-gel *m*-PBI membranes suggested that the *p*-PBI structure accommodated the acid differently than *m*-PBI. With similar compositions, a heat-treated membrane based on the more rigid *p*-PBI exhibited an average conductivity of 0.01±0.001S/cm higher from 100-180ºC and a more drastic change in modulus than *m*-PBI that correspond with increased structural ordering. The higher modulus of the *p*-PBI may result from stronger intermolecular interactions within

the membrane achieved by closer staggered side-to-side packing determined by atomistic simulations and WAXS studies.

Comparing moderate and high ionic-conducting sol-gel PA-doped PBI membranes, dihydroxy-functionalization of *p*-PBI had minimal effect on the solids content, acid doping levels, and mechanical properties after equilibration in the same concentration phosphoric acid bath. For all compositions, heat-treated dihydroxy-PBI membranes achieved 0.05±0.01S/cm higher ionic conductivities from 120-160ºC than *p*-PBI membranes. From the structural studies of heat-treated membranes with similar compositions, the dihydroxy-PBI had a slightly closer isotropic ring stacking than *p*-PBI. Dihydroxy-functionalization of sol-gel PA-doped PBI membranes permits higher ionic conductivities, preservation of mechanical integrity, and slightly closer spacings of both isotropic ring stacking and anisotropic staggered side-to-side packing.

Electrochemical hydrogen pumping using a high-temperature (>100ºC) sol-gel PA-doped *p*-PBI membrane was demonstrated under nonhumidified and humidified conditions at ambient pressures. Relatively low voltages were required to operate the pump over a wide range of hydrogen flow rates. Gas purity measurements on the cathode gas product were conducted and significant reductions in gas impurities were detected. Additional hydrogen pumps composed of PA-doped PBI membranes of different process and polymer chemistry were tested. The voltage requirements of humidified hydrogen pumps were directly related to the acid doping level and ionic conductivity of the PA-doped PBI membranes.