

Novel Sulfonated Polybenzimidazole Derivatives for High Temperature Fuel Cell Applications

by

Jordan A. Mader

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. Chang Y. Ryu, Member

Prof. Linda B. McGown, Member

Prof. Glenn A. Eisman, Member

Rensselaer Polytechnic Institute
Troy, New York

January, 2010
(For Graduation May 2010)

ABSTRACT

Polymer electrolyte membrane fuel cells (PEMFCs) have garnered much attention recently as clean power sources for a variety of applications, such as portable, residential and automotive devices. High temperature operation ($>100\text{ }^{\circ}\text{C}$) is highly desired due to the benefits of faster electrode kinetics, increased tolerance to fuel impurities (such as carbon monoxide), simpler water management and smaller radiators, and utilization of waste heat. Polybenzimidazoles (PBIs) have emerged as the most prominent candidate for application in high temperature PEMFCs.

The relationship between polymer chemical structure and properties was explored through synthesis and characterization of a functionalized PBI derivative (sulfonated PBI, s-PBI). The PPA Process was used to produce high molecular weight ($IV's=1.2-1.8\text{ dL/g}$), highly phosphoric acid (PA)-doped ($>20\text{ mol PA/PBI}$) gel films. The polymer and sulfonic acid moiety were shown to be thermally stable over fuel cell operating temperatures ($120-180\text{ }^{\circ}\text{C}$) via thermogravimetric analysis, with decomposition of the sulfonic acid group beginning at $\sim 425\text{ }^{\circ}\text{C}$. The homopolymer showed improved properties over sulfonated PBI and *m*-PBI membranes in the literature, especially in terms of phosphoric acid doping and conductivity. While there are few reports of fuel cell performance in the literature, the s-PBI membranes produced via the PPA Process show great performance improvements. Phosphoric acid doping levels of the homopolymer were shown to have an effect on conductivity and fuel cell performance. A membrane with 52 mol PA/PBI showed a conductivity improvement of 47 mS/cm and fuel cell performance improvement of $\sim 41\text{ mV}$ ($160\text{ }^{\circ}\text{C}$, 0.2 A/cm^2) over a s-PBI membrane with 30 mol PA/PBI . The water retention of membranes doped only with water was also studied, with unprecedented initial lambdas (number of water molecules per sulfonic acid group) in the triple digits, and equilibrium lambdas (after being removed from water and placed in a humidified environment) in the 30's. For comparison to the conventionally produced PBI membranes, s-PBI polymer was redissolved in N,N-dimethylacetamide and cast as a thin film. The membrane properties were compared to the PPA Process membranes and showed acid doping levels of $\sim 12\text{ mol PA/PBI}$ and lambdas of 50-80 (water exchanged), with lambda equilibriums of 5-10. The fuel cell performance of the PA-doped membranes was extensively investigated

with various fuels and oxidants. The long term durability of the membrane was explored, with very low degradation rates measured over ~2900 hours of testing.

The s-PBI homopolymer was also doped with sulfuric acid to determine its applicability in a hybrid sulfur dioxide electrolyzer (SDE). The films were stable in sulfuric acid concentrations of 30 and 50 wt% at room temperature or heated (~90 °C) for over eight months. The conductivities of the films were tested up to 100 °C and found to be extremely high (0.24-0.54 S/cm, doping level and bath temperature dependent).

A series of random copolymers of s-PBI with poly(2,2'-(*p*-phenylene)-5,5'-bibenzimidazole) (*p*-PBI) were prepared and studied as membrane materials for high temperature fuel cell use. The random copolymer properties were highly dependent on the s-PBI content in the polymer, but all compositions were thermally stable beyond fuel cell operating temperatures. Increasing the s-PBI content led to decreased IV's, lower acid loading, and generally lower conductivity values. The polymer properties, in general, were an average of the two homopolymer systems. The 25/75 *s/p*-PBI random copolymer showed the best performance, with higher conductivity than the homopolymers. The acid doping and conductivity values were greatly improved over the sulfonated PBI random copolymers in the literature. Incorporating even a small amount of *p*-PBI into the random copolymer improved the membrane mechanical properties. The lambda and lambda equilibrium values of the random copolymers after water exchange were improved over Nafion® and the s-PBI homopolymer ($\lambda_{\text{initial}}=757-146$, composition dependent, vs. 10 and 183, respectively; $\lambda_{\text{equilibrium}} \sim 30$ vs 5 and 5-10, respectively), and are higher than previous literature reports for sulfonated hydrocarbon polymers. All random copolymer membranes doped with PA showed lower fuel cell performance than the *p*-PBI homopolymer membrane, while the 25/75 *s/p*-PBI random copolymer membrane performance was improved over the s-PBI homopolymer membrane.

A series of segmented block copolymers of s-PBI with *p*-PBI was prepared and characterized as fuel cell membrane materials. The segmented block copolymers were prepared in a two stage polymerization process. Oligomers of each homopolymer were prepared using specific time and temperature profiles to control the IV, and then

combined with further polymerization to produce high molecular weight, highly phosphoric acid-doped gel films. The membranes were shown to be thermally stable over typical fuel cell operating temperatures via thermogravimetric analysis. It was found that moderate incorporation of s-PBI (40-60 mol%) yielded the segmented block copolymers with the best properties. There were no direct correlations between s-PBI content and membrane properties for acid doping, conductivity, and mechanical properties. The lambda values of water-exchanged membranes showed an exponential relationship of water content compared to s-PBI content. While there were no direct correlations between membrane composition and properties, all segmented block copolymer membranes showed improved acid loading, conductivities, and mechanical properties compared to the s-PBI homopolymer and random copolymer membranes and were greatly improved over literature reports for conventionally prepared PBI block copolymers. The fuel cell performance was extensively investigated. In general, hydrogen-air performance was better than the s-PBI homopolymer and random copolymers membranes, but poorer than the *p*-PBI homopolymer membrane. Performance was greatly increased when oxygen was used as the oxidant gas. The long term durability of all the block copolymer membranes was excellent over the periods tested.