

**NOVEL POLYBENZIMIDAZOLE DERIVATIVES FOR HIGH  
TEMPERATURE PEM FUEL CELLS**

by

Seonghan Yu

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Examining Committee:

Prof. Brian C. Benicewicz, Thesis Adviser

Prof. James A. Moore, Member

Prof. Chang Y. Ryu, Member

Prof. Linda S. Schadler, Member

Prof. Glenn A. Eisman, Member

Rensselaer Polytechnic Institute  
Troy, New York

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Polymer electrolyte membrane fuel cells (PEMFCs) have recently received much attention as power sources in a wide range of applications such as residential, automotive and portable devices. High temperature ( $> 120\text{ }^{\circ}\text{C}$ ) PEMFCs have been extensively studied because they have many benefits such as faster electrode kinetics, simpler water management and smaller cooling systems, increased tolerance of impurity gases (eg. CO), and better utilization of generated heat. Polybenzimidazoles (PBI) are one of the most prominent candidates for membranes of high temperature PEMFCs.

The relationship between the chemical structures of PBIs and their properties were explored by studying two broad polymer areas, segmented block copolymers and functionalized PBI derivatives. A series of segmented block copolymers containing blocks of poly(2,2'-(*p*-phenylene)-5,5'-bibenzimidazole (*para*-PBI) and poly(2,5-benzimidazole) (AB-PBI) were prepared and studied as membrane materials in fuel cells. The solubility of the homopolymers and their blocks in phosphoric acid had a major effect on the membrane properties. When processed using the PPA process, AB-PBI was found to be too soluble to obtain a gel membrane even when high I.V. ( $\sim 10\text{ dL.g}$ ) polymers were prepared. However, segmented block copolymers of AB-PBI and the less soluble *para*-PBI formed mechanically stable films at both room and elevated temperatures. The segmented block copolymer membranes of AB-PBI and *para*-PBI showed comparable membrane properties to *para*-PBI homopolymer membrane.

The introduction of functional groups on PBI polymers was also studied in this work. PBI polymers containing dihydroxy groups (2OH-PBI) were successfully synthesized and studied as membrane materials. The polymerizations were conducted at lower monomer concentrations than *para*-PBI to prevent gelation during the polymerization. Carefully designed acid doping level control experiments showed that 2OH-PBI membranes had a higher conductivity ( $\sim 0.43\text{ S/cm}$  at  $160\text{ }^{\circ}\text{C}$ ) than *para*-PBI ( $\sim 0.25\text{ S/cm}$  at  $160\text{ }^{\circ}\text{C}$ ) membranes with a similar acid doping level. Random copolymers of 2OH-PBI and *para*-PBI were also prepared which showed that the conductivity of the membranes scaled with the amount of 2OH-PBI units in the copolymer. Studies on the 2OH-PBI polymers, coupled with a model compound study, confirmed that the 2OH-PBI polymers formed in the polyphosphoric acid

polymerization were composed of lower molecular weight main chains cross-linked through phosphoric acid ester bridges. A fuel cell performance comparison with different cathode catalysts (Pt and Pt-Ni alloy) showed that fuel cell performance depended not only on membrane properties such as acid doping level and proton conductivity, but also on the catalyst materials, especially those in the cathode electrode. The fuel cell performance of 2OH-PBI membranes with a Pt-Ni alloy cathode catalyst was 0.69 V at 0.2 A/cm<sup>2</sup> and 0.49 A/cm<sup>2</sup> at 0.6V at 180 °C under H<sub>2</sub>/air operation and ambient pressure.

Although PBI membranes prepared by the PPA process showed high proton conductivity and good fuel cell performance at high temperatures and dry conditions, there are some concerns about long-term durability and mechanical properties such as creep or compression stress relaxation due to the membrane's gel structure. Silica (SiO<sub>2</sub>) nanoparticles were uniformly dispersed in PBI membranes up to ~ 30 wt% to polymer without any sacrifice of proton conductivity and fuel cell performance. The tensile strengths of the nanoparticle filled membranes slightly increased at ~10 wt% and ~20 wt% SiO<sub>2</sub> nanoparticle loadings. The compression modulus was not affected by the presence of the SiO<sub>2</sub> nanoparticles at loading levels investigated in this work.

The durability of high temperature PEM fuel cells using PBI-based membranes was studied by measuring cell voltage degradation and analyzing phosphoric acid loss. New test protocols were proposed for steady-state operation and dynamic long term durability tests for PBI-based high temperature PEM fuel cells. Fuel cell performance degradation was measured by monitoring fuel cell voltage over time and cycles. Phosphoric acid loss was analyzed using ion chromatography to understand the relationship between fuel cell performance degradation and phosphoric acid loss rate. PBI-based PEM fuel cells could be operated at constant current density (0.2 A/cm<sup>2</sup>) with 5 – 60 μV/hour voltage degradation rates over wide range of operating temperatures (80 – 190 °C). In the typical operating range of high temperature PEM fuel cells (120 – 160 °C), the fuel cell voltage degradation was as low as ~5 μV/hour. The dynamic durability tests (load, thermal and shutdown-startup cycling tests) showed similar to or higher voltage degradation rates than steady-state operation. The highest PA loss rates occurred at high

temperature (190 °C (static) or 180 °C (cyclic)) and were substantially higher than the loss rates measured at lower temperatures. When the fuel cell was operated in a temperature range of 80 – 160 °C, PA loss from the membranes is not the main factor of the fuel cell failure.