High Temperature Polymer Membranes for Fuel Cells and Sustainable Energy Devices

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Introduction

There have been major efforts for more than a decade to increase the operating temperature of polymer based membrane fuel cells above the traditional operating temperature of approximately 85˚C. This temperature limitation is derived from the use of water to assist proton conduction in perfluorosulfonic acid based membranes or sulfonated aromatic polymer membranes that have been used in fuel cell devices. Polybenzimidazole (PBI) polymers are excellent candidates for PEM fuel cell membranes capable of operating at temperatures up to 200˚C. One of the more important benefits of PBI polymers doped with phosphoric acid is the ability to operate efficiently without the need for external humidification and the related engineering hardware to monitor and control the hydration levels in the membrane. This feature has been widely explored for portable and stationary PEM fuel cell devices, and numerous companies are developing systems based on PBI MEA's.

In the mid-1990's, it was shown by Savinell et al.[1-3] and others[4] that polybenzimidazole doped with phosphoric acid could operate at temperatures up to 200˚C. It was reported that these membranes exhibited high ionic conductivities at high temperatures, low gas permeability, excellent chemical and thermal stability in the fuel cell environment, and nearly zero water drag coefficient. Furthermore, PBI polymer (the meta-PBI variant) is a polymer that is commercially available, has been well characterized and methods of synthesis have been developed thoroughly. However, some of the perceived problems with using PBI for fuel cell

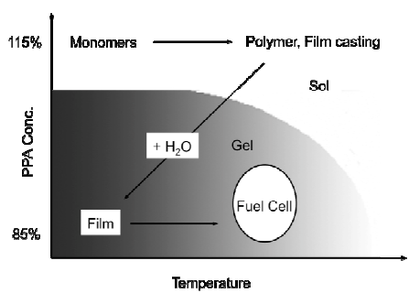

Figure 1. State diagram of the PPA Process for producing membranes doped with phosphoric acid.

membranes were the low molecular weights (IVs of 0.5 – 0.8 dL/g), low phosphoric acid loading (6-10 moles/repeat unit), phosphoric acid retention, and membrane durability.

Several years ago, a sol-gel process was developed to produce PBI membranes loaded with high levels of phosphoric acid.[5,6] This process, termed the PPA process, uses polyphosphoric acid as the condensing agent for the polymerization and the membrane casting solvent. After casting, absorption of water from the atmosphere causes hydrolysis of the polyphosphoric acid to phosphoric acid (Fig. 1). The change in the nature of the solvent induces a sol-to-gel transition that produces membranes with high loadings of phosphoric acid and a desirable suite of physical and mechanical properties. Membranes produced from this process showed the ability to maintain high levels of phosphoric acid (PA) and high proton conductivities while simultaneously exhibiting low levels of PA loss during operating conditions.[7-9] The membranes were characterized by acid doping levels, ionic conductivity, mechanical properties and fuel cell testing. The durability of these new membranes in multiple operating environments is of particular importance for the further development of practical fuel cell devices.[10-12] Testing protocols have been developed to examine the behavior of PBI membranes under both static and cyclic conditions which will also be presented.

We have been exploring PBI chemical variants to understand the effect of chemical structure on the basic membrane properties, as well as issues of stability and durability of the membranes produced by the PPA Process. In this presentation, we will review the historical development of polymer-acid complexes with a focus on polybenzimidazole polymers. Additionally, some recent results will be used to describe correlations between polymer structure and properties which provide valuable insights for designing membranes with extended durability tailored to devices and specific applications.[13] We will also discuss the use of PBI membranes in electrochemical hydrogen pumping and purification devices which may play an important role in current and future hydrogen based technologies.

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