NMR Studies Of Mass Transport In High Acid Content Fuel Cell Membranes Based On PBI/Phosphoric Acid

S.H. Chung[#], Lisa Durantino[#], J.R.P. Jayakody*, H. Zhang[‡], L. Xiao[‡], B. Benicewicz[‡], and S.G. Greenbaum*

[#] William Paterson University of New Jersey, Wayne, NJ 07470 USA

*Hunter College of CUNY New York, NY 10021 USA

[‡]Rensselaer Polytechnic Institute, Troy, NY 12180 USA

Acid doped polybenzimidazole (PBI) has emerged as a promising candidate for a low-cost and high performance fuel cell membrane material. It has been shown that this polymer electrolyte membrane exhibits high ionic conductivity at temperatures up to 200^{o}C.[1] However, additional progress is still needed for the large-scale application of PBI in fuel cells. Furthermore, the conventional method to prepare acid doped PBI membranes involves a multi-step process while the mechanical properties of the resulting membranes are largely limited by the low molecular weight of PBI used in previous studies. A novel process, previously reported and termed as the PPA process, has been developed to prepare pyridine-based PBI (PPBI) membranes loaded with high levels of phosphoric acid by direct casting of the PPA polymerization solution without isolation or redissolution of the polymers, followed by a sol-gel transition induced by the hydrolysis of PPA into phosphoric acid.[2]

In an attempt to understand the ion dynamics in these membranes, two samples of this material prepared in a different manner have been examined by using nuclear magnetic resonance (NMR) techniques over a range of temperatures from 290 to 383 K. The first sample BB1 was prepared by soaking the PBI films in phosphoric acid solutions whereas the second sample BB2 was produced by the new sol-gel process which allows for greater levels of phosphoric acid loading. Using experimental techniques described elsewhere[3], ^{1}H (I=½) and ^{31}P (I=½) NMR linewidths, spin-lattice relaxation times T_1, and self-diffusion coefficients D for these materials are reported. To obtain consistent and reproducible data, the samples were dried at 423K for 90 minutes. Significant differences in the diffusion coefficients and relaxations times before and after drying are noted. For all samples a single ^{31}P peak centered close to the reference signal from 85% H_3P0_4 was observed. There were no spectral indications of condensed phosphates. In BB1 the linewidths and relaxation times show weak temperature dependence in contrast to the data for BB2 where there were indications of motional narrowing and a well-defined T_1 minimum. The diffusion data show that protons diffuse faster than the phosphorus carrying species, which means that the inter-phosphate proton transfer is important in these materials. Proton NMR diffusion and T_1 data for BB2 are shown at right.

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Proton NMR Self Diffusion and Spin-lattice Relaxation