High temperature proton exchange membranes based on poly(arylene ether)s with benzimidazole side groups for fuel cells

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Introduction

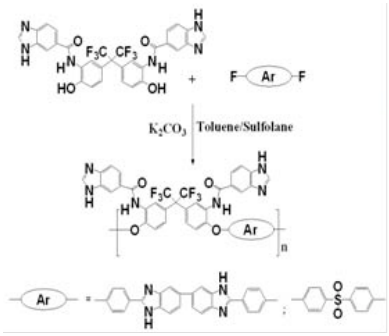
In this study, we combined the characteristics of PBI and poly(arylene ether)s, and synthesized new polymers containing benzimidazole on the side chains through aromatic nucleophilic substitution polymerization. The benzimidazole groups played an important role in the polymer. They served as the phosphoric acid doping site, and underwent proton transfer via the Grotthuss mechanism at high temperatures. These polymers can be used to fabricate membranes for high temperature polymer electrolyte membrane fuel cell application.

Results and discussion

A new benzimidazole containing monomer has been synthesized for the preparation of poly(arylene ether sulfone) (PAES) and poly(arylene ether benzimidazole) (PAEB) with benzimidazole side groups by nucleophilic substitution polymerization. PAES and PAEB had inherent viscosities of 0.56 and 0.93 dL/g, respectively, measured in N,N-dimethylacetamide (DMAc) at a concentration of 0.5 g/dL. The structures of the benzimidazole containing monomer, PAES and PAEB were characterized by FTIR, 1H-NMR, and elemental analysis. These polymers showed excellent solubility in common organic solvents, such as DMAc, dimethyl sulfoxide (DMSO), and N-methyl-pyrrolidinone (NMP) at room temperature. Due to the strong intermolecular hydrogen bonding from the amide and imidazole groups in the side chains, the PAES and PAEB had unusually high Tg's at 374 and 381 oC, correspondingly. The 5% weight loss temperatures of PAES and PAEB were around 472 and 522 oC in air, respectively. The phosphoric acid doping levels of PAES and PAEB membranes were 5.6 and 15.3. The proton conductivity of phosphoric acid doped membranes increased with increasing temperatures, and reached to a range of 10^{-3} to 10^{-2} Scm^{-1} at 160 ^{o}C.

Conclusions

A new benzimidazole containing monomer has been synthesized for the preparation of PAES and PAEB by nucleophilic substitution polymerization. Both PAES and PAEB had good mechanical properties, thermal stability, and excellent solubility in common organic solvents. Due to the introduction of benzimidazole side groups in the polymers, their membranes had high proton conductivity after phosphoric acid doping. The proton conductivity of phosphoric acid doped polymer membranes increased with increasing temperatures and reached to a range of 10^{-3} to 10^{-2} Scm^{-1} at 160 ^{o}C. In addition to that, the new PAES and PAEB membranes were easy to prepare compared to the conventional PBI membranes.



Scheme 1. Synthesis of poly(arylene ether)s.

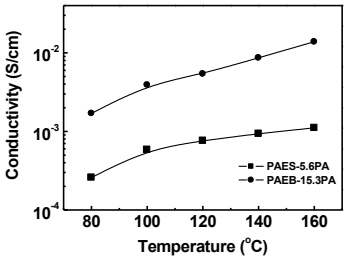


Fig. 1 Proton conductivity of PAES and PAEB membranes doped with phosphoric acid at different temperatures.