

Anion Conductive Aromatic Block Copolymer Membranes Containing Diphenyl Ether or Diphenyl Sulfide Moieties

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There has been a much interest in alkaline fuel cells (AFCs) that utilize anion exchange membranes (AEMs) as the electrolyte. The advantages of AFCs over proton exchange membrane fuel cells (PEFCs) include better kinetics of the oxygen reduction reaction and more options for cathode catalysts based on abundant transition metals such as nickel, resulting in higher performance and lower cost fuel cells. Since the existing AEMs are not as ion conductive and stable as the proton exchange membranes, efforts have been devoted to developing better AEM materials. One of the attractive candidates is aromatic polymers substituted with anion exchangeable functional groups.^{1,2} We have recently reported that aromatic multiblock copolymers, poly(arylene ether)s containing quaternized ammonio-substituted fluorene groups (Fig. 1a), showed considerably higher hydroxide ion conductivities, up to 144 mS/cm at 80 °C, than those of existing anion conductive ionomer membranes.³ A noble metal-free direct hydrazine fuel cell was operated with the AEM. In this communication, we report advanced version of our multiblock copolymer AEMs, which replace fluorenyl groups with diphenyl ether or diphenyl sulfide groups for further improving the hydroxide ion conducting properties.

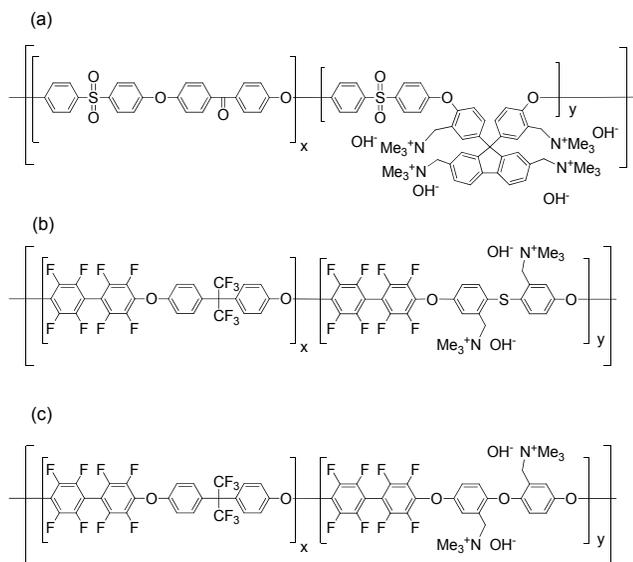


Fig. 1 Chemical structures of quaternized multiblock poly(arylene ether)s; (a) QPE-bl-1, (b) QPE-bl-5, and (c) QPE-bl-6.

In Fig.1b and c are shown the chemical structures of the quaternized block copolymers. The precursor block copolymers were synthesized by the typical polycondensation reactions. Oligomers for hydrophilic blocks were synthesized from bis(4-

hydroxyphenyl)sulfide or ether and decafluorobiphenyl. Similarly, oligomers for hydrophobic blocks were synthesized from 2,2-bis(4-hydroxyphenyl)hexafluoropropane (hexafluorobisphenol A) and decafluorobiphenyl. The block copolymerization proceeded well under mild conditions to provide high molecular weight precursor block copolymers (PE-5, and 6). A series of block copolymers with X = 5 and Y = 4 or 11 with different ion exchange capacity (IEC) values were synthesized. The chloromethylation reaction with chloromethyl methyl ether followed by quaternization with trimethylamine gave the title AEMs. The membranes were ductile and flexible under dry or wet conditions. The IECs of the QPE-bl-5 and QPE-bl-6 membranes ranged from 0.95 to 1.91 meq/g, assuming the quantitative quaternization reaction of the chloromethyl groups.

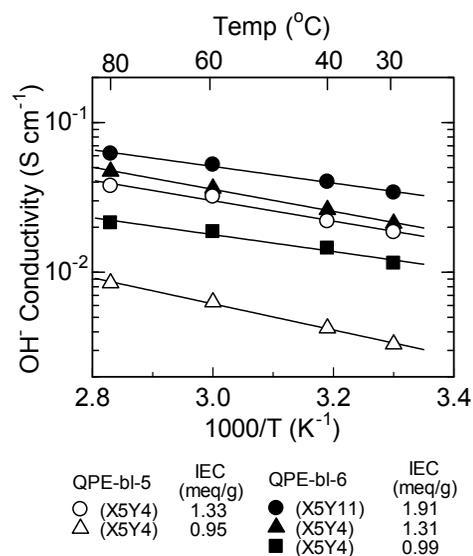


Fig. 2 Temperature dependence of hydroxide ion conductivity of QPE-bl-5 and QPE-bl-6 membranes in water.

The QPE-bl-5 and QPE-bl-6 membranes showed high hydroxide conductivity in water. The QPE-bl-6 membrane with IEC = 1.91 meq/g showed 34 mS/cm of the conductivity at 30 °C, which increased with the temperature up to 62 mS/cm at 80 °C. There were no obvious degradations observed in water at 80 °C.

The QPE-bl-6 membrane was subjected to accelerated stability test under basic conditions. After soaking in 1M KOH containing 5wt% hydrazine at 80 °C for 500 h, the membrane showed minor weight loss, however, lost hydroxide ion conductivity and water uptake capability to certain extent. The results indicate that the trimethylbenzylammonium groups were not stable under the harsh basic conditions.

References

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