Sulfonated Polyimide Multiblock Copolymer Membranes for Fuel Cell Applications

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Proton exchange membranes (PEM) are one of the key components of fuel cells. From viewpoint of practical applications, an ideal PEM must meet the requirements of high proton conductivity, long-term durability, low swelling ratio, high mechanical strength and good barrier properties to fuels and oxygen. In the past two decades a large number of sulfonated polymers have been developed as potential PEMs for fuel cell applications and among them sulfonated polyimides (SPI) have been identified to be one of the most promising PEM candidates. Proton conductivity, being one of the most important properties of PEMs, is closely related to fuel cell performance. To achieve high proton conductivity, PEMs are generally required to have high IEC. However, too high IEC often cause excessive swelling ratio or even dissolution of the PEM. Recently block copolymerization has been reported to be an effective way to enhance proton conductivity while swelling ratio can be suppressed to some extent. To further investigate the effects of both the hydrophilic block and the hydrophobic block on membrane properties and fuel cell performance, in this presentation a series of sulfonated multiblock copolyimides (SPIs) with varied hydrophobic blocks and hydrophilic blocks were synthesized. The effects of the structure and length of hydrophilic/hydrophobic blocks on membrane properties and fuel cell performances were investigated.

The synthesis of the multiblock SPIs was achieved by a three-step procedure. First, the anhydride-terminated aliphatic hydrophobic oligomers were synthesized by condensation polymerization of *non*-sulfonated diamines with excess 1,4,5,8-naphthalenetetracarboxylic dianhydride (NTDA) in *m*-cresol in the presence of benzoic acid and isoquinoline at 180 °C for 24 h. Then in another port an amine-terminated hydrophilic block was synthesized by condensation polymerization of NTDA with excess 4,4'-bis(4-aminophenoxy)-3,3'-biphenyldisulfonic acid (BAPBDS) in *m*-cresol under similar conditions in the presence of triethylamine. Finally, the hydrophobic oligomers were further reacted with the hydrophilic oligomer to give a series of SPI multiblock copolymers. The averaged block length was controlled at X = 5 and 10 for the hydrophobic oligomer and Y = 10, 15, 20 and 30 for the hydrophilic oligomer. The resulting SPI membranes showed high tensile strength in the range of 53-86 MPa and the elongation at break of 42-90% indicating that high molecular weight polymers were obtained. The IEC values are in the range 1.30-2.22 meq/g (theoretical) or 1.19-2.16 meq/g (titrated) depending on the content of the hydrophilic blocks. TEM images suggest good microphase-separated morphologies of the multiblock copolymers. Preliminary H_2/O_2 fuel cell test (Fig. 1) revealed that the fuel cell with the one of the SPI block copolymer X10Y30 exhibited good performance at 50% relative humidity and varied temperatures (80-110 °C).

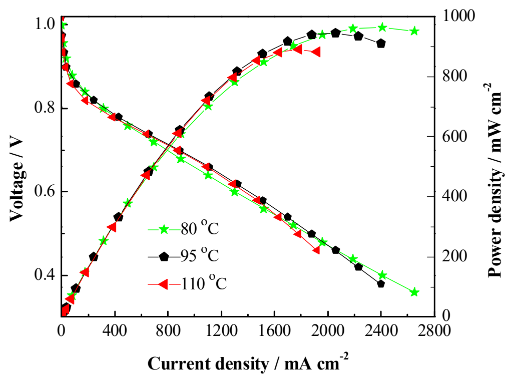

Fig. 1 Single cell performance of the fuel cell equipped with the sulfonated polyimide multiblock copolymer membrane X10Y30 operated at 50% relative humidity and varied temperatures.

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