Novel Sulfonated Polyimide Membranes Containing Aliphatic Groups For High Temperature PEFC Applications

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Introduction

In order to improve the performance of PEFCs, it is desirable to operate them at high temperature above 120 °C. Since the perfluorinated sulfonic acid ionomers such as Nafion are not available for high temperature operation, alternative membrane material with high proton conductivity and durability has been in great demand. We have proposed a series sulfonated polyimide membranes and achieved very high proton conductivity ($1.67 Scm^{-1}$) at 120 °C and 100% RH.[1)-3)]

In this study, we report synthesis and electrolyte properties of novel sulfonated polyimide copolymers (SPI-5) containing aliphatic groups both in the main chain and in the side groups in order to improve the hydrolytic and oxidative stability and the flexibility of the membrane. The electrolyte properties were investigated and compared with those of other SPI membranes and Nafion112.

Experimental

The side chain type sulfonated polyimides (SPI-5) were synthesized by the polycondensation of 1,4,5,8-naphthalene tetracarboxylic dianhydride, 3,3'-bis(sulfoalkopoxy)-4,4'-diaminobiphenyl and α, ω-alkyldiamine. The polymerizaition mixture was cast onto a glass plate, and then heated at 80 °C. The obtained membrane was acidified by soaking into 1N HNO_3/EtOH. The oxidative stability was examined by observing the dissolving time of a small piece of membranes in Fenton's reagent at 80°C. The stability against methanol was examined by observing the dissolving time of a small piece of membranes in 1M MeOHaq at 100 °C. The hydrolytic stability of SPI was evaluated by treating the membrane sample at 140 °C and 100% RH as an accelerated testing. Proton conductivity of SPI was measured by complex impedance analyses using four blocking electrodes.

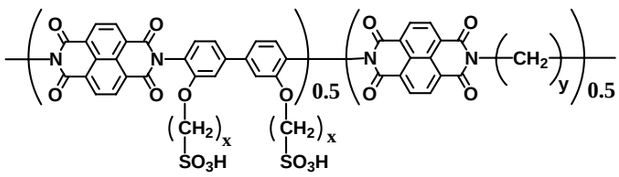

Figure 1 Chemical structure of side chain type SPI-5

Results and discussion

The obtained SPI membranes were tough and transparent and had a typical brown color for polyimides. The membrane was more flexible due to the incorporation of aliphatic groups than the whole aromatic SPI membranes. The SPI-5 membranes containing various alkyl chain lengths in the main chain (x=3,4) and side chain (y=6,10) were synthesized (Figure 1).

During the oxidative stability testing, the membrane without alkyl group (SPI-4, x=3,y=0) in the main chain dissolved in Fenton's reagent within 18min. The SPI-5 membranes were more oxidatively stable; it took 55min for SPI-5 (x=3,y=10) before it started to dissolve (Table 1). SPI-5 membranes showed much better hydrolytic stability without any changes in appearance, flexibility, and toughness even after 24h.

Proton conductivity of SPI-5 was measured 100% RH. Although the conductivity of SPI-5 were lower than Nafion112 at low temperature, high temperature conductivity was comparable (Figure 2). RH dependence of the conductivity and other electrolyte properties will also be reported.

Ref 1) K.Miyatake et al., *Chem.Commun*., 368-369(2003).
2) K.Miyatake et al., *J.Polym.Sci. A;Polym.Chem.* **41**, 3901-3907 (2003).
3) K.Miyatake et al., *Macromolecules* **37**, in press (2004).

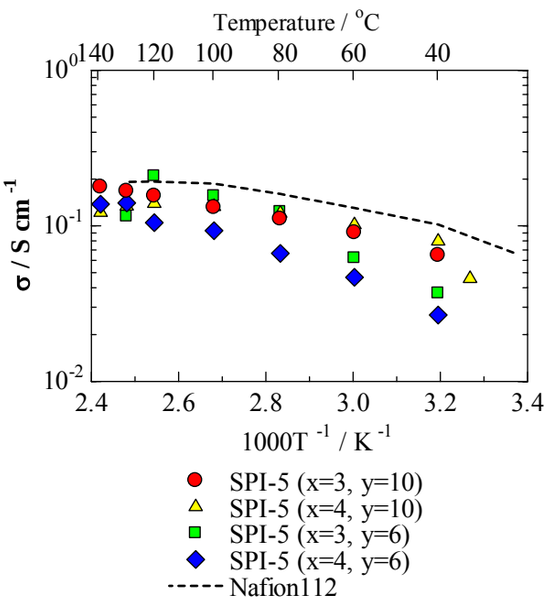

Figure 2 Temperature dependence of the proton conductivity at 100% RH

Table 1 Electrolyte properties of SPIs and Nafion112

Membrane	x,y	EW(g/eq)	σ(S/cm)[1)]	Stability 1[3)]	Stability 2[4)]	Stability 3[5)]
SPI-5	3,6	521	0.21	35min	>1000h	○
SPI-5	4,6	535	0.11	45min	>5000h	○
SPI-5	3,10	549	0.16	55min	>5000h	○
SPI-5	4,10	562	0.14	54min	>5000h	○
SPI-3	-	372	0.21	25min	6h	×
SPI-4	3,0	347	0.23[2)]	18min	55h	○
Nafion112	-	1100	0.16	-	-	-

1)120 °C,100 %RH 2)80 °C,100 %RH
3)Dissolving time of the membrane in Fenton's reagent(3%H_2O_2 aqueous solution containing 2ppm $FeSO_4$)
4)Dissolving time of the membrane in 1M MeOHaq at 100 °C
5)Hydrolytic stability at 140 °C and 100 %RH