Performance of PEMFC based on Sulfonated Polyimides

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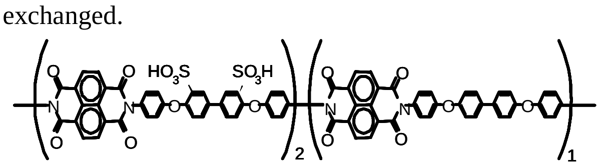
INTRODUCTION

Polymer electrolyte membrane fuel cells (PEMFCs) have attracted the increasing attention as eco-friendly energy sources. Up to now, many kinds of nonfluorinated polymer electrolyte membranes (PEMs) based on sulfonated aromatic hydrocarbon polymers have been developed. Among them, sulfonated polyimides (SPIs) are one of the most promising candidates. We developed novel SPIs with high water-durability and high proton conductivity [1-3] and reported preliminary results about the preparation and fuel cell performance of membrane-electrode assemblies (MEAs) based on these SPIs [4].

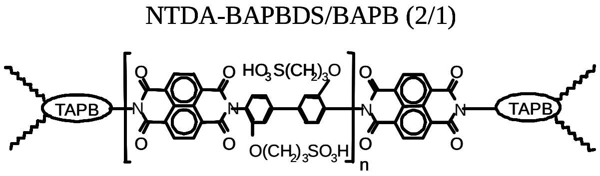
In this paper, we report on further study on PEMFCs based on SPIs.

EXPERIMENTAL

The SPIs used in this study, of which the chemical structure is shown in Fig. 1, are classified into the main-chain type and the side-chain type according to the substituion position of sulfo groups, and also into the linear type and the branched/crosslinked type according to the absence or presence of a triamine, tris(4-aminophenoxy)-benzene (TAPB). 1,4,5,8-naphthalene-tetracarboxylic dianhydride (NTDA) was used as an acid anhydride. 4,4'-bis(4-amino-phenoxy)-biphenyl-3,3'-disulfonic acid (BAPBDS) and 3,3'-bis(3-sulfopropoxy) benzidine (3,3'-BSPB) were used as main-chain type and side-chain type, respectively, of sulfonated diamines. 4,4'-bis(4-aminophenoxy)biphenyl (BAPB) was used as a nonsulfonated diamine. The linear type of SPI was prepared according to the method previously reported [2,3]. The branched/crosslinked type of SPI was prepared as follows. First, the anhydride-terminated oligomer of SPI was prepared in *m*-cresol using a little excess of NTDA in a molar ratio of NTDA/sulfonated-diamine of x/y. Then, a 2(x-y)/3 portion of TAPB was added to the oligomer solution with stirring and heated at 60-80 °C until the solution became highly viscous. The thus-obtained solution was cast on a glass plate. The membrane was heated at 200°C for 10h and then proton-exchanged.



NTDA-BAPBDS/BAPB (2/1)



NTDA-3,3'-BSPB/TAPB (x/y)

Fig.1 Chemical structure of typical SPIs.

Proton conductivity (σ) in plane direction of membrane was measured using a four-point-probe impedance spectroscopy technique with a LCR meter.

Pt/C fuel electrodes (Vulcan XC-72, E-TEK Inc., Pt load: 0.5 mg/cm^2) were impregnated with 1.5 mg/cm^2 of Nafion by applying 0.036 ml/cm^2 of 5 % Nafion (EW: 1100) solution. A MEA was prepared by hot-pressing the electrodes onto a membrane. The MEA was set into single cell (S = 5 cm^2) and humidified O_2 and H_2 gas was supplied to the cathode side and the anode side respectively. PEMFC experiments were carried out at a cell temperature of 90 °C.

Table 1. Basic properties of SPIs

electrolyte Membranes	IEC	WU[g/100g] In water	σ [S/cm] 90 %RH	Δt_c In water	Δl_c
NTDA-BAPBDS	2.63	117	0.16	0.30	0.10
NTDA-BAPBDS/BAPB(2/1)	1.89	80	0.09	0.41	0.086
NTDA-3,3'-BSPB/TAPB (5/4)	2.49	123	0.15	1.23	0.010
Nafion112	0.90	-	0.10		

RESULTS AND DISCUSSION

Table 1 lists the basic physical properties of SPI membranes. They displayed anisotropic membrane swelling. This is due to the orientation of the polymer chain in parallel direction of the membrane surface.

The PEMFC performances in I-V profiles are showed in Fig. 2. In the higher current density region, there was observed a little difference in the performance among these SPIs, whereas the open circuit voltage (OCV) and cell voltage at 1 A/cm^2 load (V_1) are very similar as listed in Table 2. These SPIs showed the high performance of PEMFC, which was comparable to that of NAFION112.

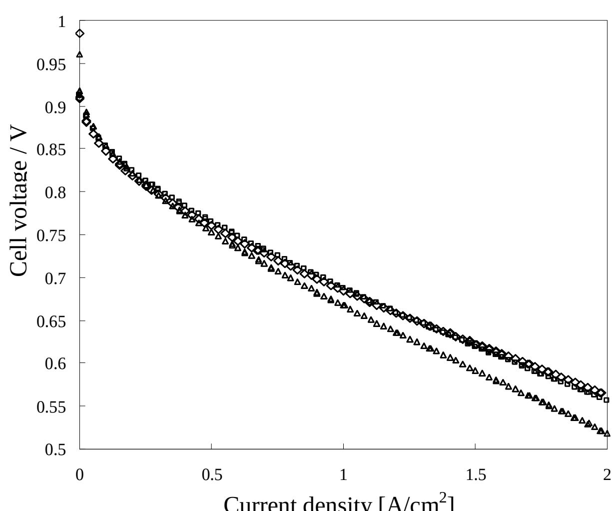


Fig.2 Fuel cell perfomances of SPIs and Nafion112.
□ : NTDA-BAPBDS , △ : NTDA-BAPBDS/BAPB(2/1), ◇ : NTDA-3,3'-BSPB/TAPB(5/4)
Cell temperature : 90 ºC , 0.3 MPa, Anode : H2 150ml/min. (90/90 ºC), cathode:O2 100ml/min. (90/88 ºC)

Table 2. Electrochemical properties of SPIs

Membrane electrolyte	OCV [V]	thickness [μm]	V_1 [V]
NTDA-BAPBDS	1.01	42	0.69
NTDA-BAPBDS/BAPB(2/1)	0.94	25	0.67
NTDA-3,3'-BSPB/TAPB(5/4)	0.98	25	0.69
Nafion112	0.93	55	0.66

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