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Direct Methanol Fuel Cell Using Sulfonated Phenol Polymer Membrane and Carbonized Silk Cloth

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Nafion® 117 shows very high proton conductivity, because water is taken in the ion cluster area of Nafion. But, when it was used for direct methanol fuel cell (DMFC), methanol permeation (crossover) of the membrane is a major problem. The methanol that permeated the membrane reacts with oxygen, and causes the decline of the cathode electric potential, and decreases the total fuel efficiency of DMFC.

Phenol resins are thermosetting resins with cross-linked network structure. Phenol resins are generally resistant to thermal and chemical degradation. Membrane of sulfonated phenol resins has a possibility of the repression of the methanol crossover without decline of the proton conductivity.

In the present paper, the repression of the methanol crossover and the DMFC performance of the preparation of sulfonated phenol resin (SPR) membrane are reported. The membrane was characterized in terms of swelling, methanol permeability, proton conductivity, and thermal stability. The electrolyte membrane - electrode assembly (MEA) was made by using carbon fiber clothes, which was obtained by carbonaizing of silk clothes.

The sulfonated phenol resins were synthesized in the through holes with a diameter of 5 µm of the isoporous membrane filters. The ion-exchange capacities (IEC) of the sulfonated phenol resins (SPR27, SPR30, and SPR36) were 2.7, 3.0, and 3.6 mmol g^{-1}.

The MEAs with a geometric area of 5.0 cm^2 were prepared using Pt/C (Metal cont. *ca.* 50 wt%, TANAKA) and Pt-Ru(1:1)/C (Metal cont. *ca.* 50 wt%, TANAKA) as the cathode and anode catalysts, respectively. MEA inks were painted onto carbon cloth (CC) electrodes (#16, carbonized at 1400°C, Shinano Kenshi Co., Ltd.) for SPR MEAs, and onto carbon paper (CP) electrodes (TGP-H-060, Toray) for a Nafion MEA. The catalyst / carbon cloth anode and cathode were hot-pressed onto a SPR membrane at 120°C and 3 MPa for 3 min. Steady-state current density / cell voltage data were collected using a single cell DMFC test station (Scribner 890B-100/10). The DMFC was operated at 60°C, with 1.5M methanol (at a flow rate of 2.8 mL min^{-1}) and humidified air (at 60°C and flow rate of 500 sccm at ambient pressure).

Proton conductance (G_{film} [S cm^{-2}]) and methanol crossover rate (MCO [mol cm^{-2} min^{-1}]) of three SPR membranes that varied in their IEC, from 2.7 to 3.6 mmol g^{-1} are contrasted with those of Nafion 117 in Fig. 1. The methanol crossover rate in the SPR membranes were lower than that in Nafion 117; 1.32, 2.37, and 3.91 times lower for the SPE36, SPR30, and SPR27, respectively. This result is given the fact that the content of phenol unit that forms cross-linkage is higher in the SPR membrane with lower IEC. The proton conductance was 1.7 times higher in SPR36, then 1.35 and 2.18 times lower in SPR30 and SPR27, respectively, than that of Nafion 117. This ranking of the proton conductance was attributed to the order of IEC in the SPR membranes. DMFC tests were performed with three SPR/CC MEAs that varied in their IEC, from 2.7 to 3.6 mmol g^{-1}. The DMFC current density / cell voltage or power density curves for MEAs containing these membranes are shown in Fig. 2. The maximum power density in the SPR27/CC MEA was slightly lower than that in the Nafion 117/CP MEA. In the SPR30/CC and SPR36/CC MEAs, the maximum power density was greater than that in the Nafion 117/CP MEA; 1.25 and 1.28 times greater for the SPR30/CC and SPR36/CC MEAs, respectively. The gentle slope in the current density / cell voltage curves for the SPR30/CC and SPR36/CC MEAs was attributed to the higher proton conductance of the membranes and the lower contact resistance between the membrane and catalyst/CC electrodes. Adjustment of the catalyst binder amount and the texture type of the carbon fiber electrode minimize this contact resistance. The DMFC performance of the SPR36/CC MEA that the Pt-loading was enriched to 0.5 mg cm^{-2} (anode) and 1.0 mg cm^{-2} (cathode) is shown in Fig. 3. Both the open-circuit potential and the maximum power density for the SPR36/CC MEA in Fig. 3 were higher than those for the SPR36/CC MEA in Fig. 2; 0.12 V higher in the potential and 1.42 times higher in the power density.

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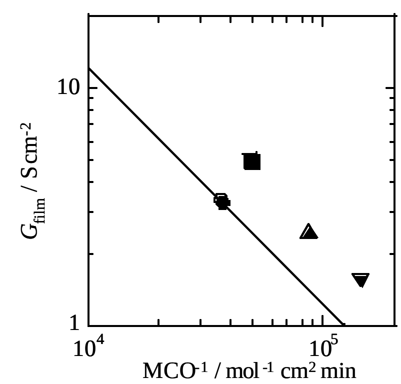

Fig.1. Proton conductance (G_{film}) and Methanol crossover rate (MCO) in SPR membranes. ● Nafion 117; ▼ SPR27; ▲ SPR30; ■ SPR36.

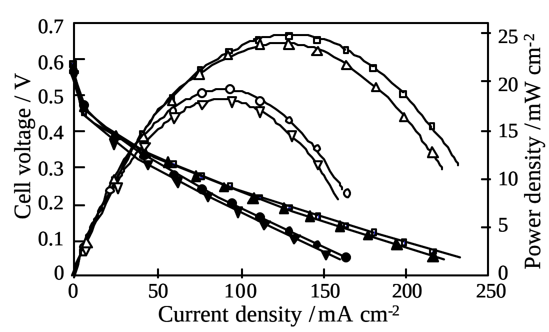

Fig. 2. DMFC performance with SPR/CC MEAs. Operating conditions: Pt-loadings were 0.27 mg cm^{-2} (anode) and 0.52 mg cm^{-2} (cathode). ●○ Nafion 117/CP MEA ; ▼▽ SPR27/CC MEA ; ▲△ SPR30/CC MEA : ■□ SPR36/CC MEA.

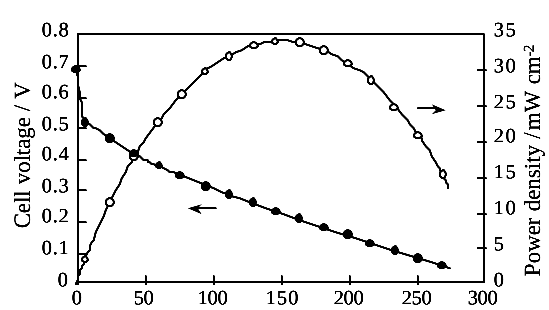

Fig. 3. DMFC performance with the SPR36/CC MEA. Pt-loadings were 0.5 mg cm^{-2} (anode) and 1.0 mg cm^{-2} (cathode).