DIRECT METHANOL FUEL CELL USING SULFONATED PHENOL POLYMER MEMBRANE AND CARBONIZED SILK CLOTH

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Performance of the DMFCs with sulfonated phenol resin electrolyte membranes was evaluated. The electrolyte membranes were synthesized in the through holes with a diameter of 5 μm of the isoporous membrane filters. The membrane-electrode assembly was made from the membrane and two carbon knitted cloth electrodes that coated with Pt/C (Pt 0.54 mg cm⁻²) and Pt-Ru/C (Pt 0.34 and Ru 0.26 mg cm⁻²). The maximum power density of the DMFC was 11.2 mW cm⁻² at current density of 57.3 mA cm⁻². Higher-density crosslink of the phenol polymer was more effective to repress methanol crossover in the electrolyte membrane. Higher-density sulfonation was more effective to enhance proton-conduction and improve DMFC performance. By using the carbon knitted clothes instead of the carbon papers, electrode exfoliation from the thermosetting electrolyte membrane was improved remarkably. Knitted fabric texture of the carbon fiber electrode was effective to adhere on the membrane strongly, and to improve DMFC performance.

INTRODUCTION

Nafion¹ 117 shows very high proton conductivity, because water is taken in the ion cluster area of Nafion¹. But, when it was used for direct methanol fuel cell (DMFC), methanol permeation (crossover) of the membrane is a major problem². The methanol 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 crosslinked 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 and electrode assembly (MEA) was prepared by using carbon knitted cloth, which was obtained by carbonizing of silk knitted clothes.

EXPERIMENTAL

Figure 1 shows the synthesis scheme of pre-polymers (preSPR). PreSPR were synthesized from phenolsulfonic acid, phenol, and formaldehyde in several molar ratios.
PreSPR were thermally condensed and crosslinked using a hot press at 110 °C for 5 hours in the through holes with a diameter of 5 μm of isoporuous membrane filters. Obtained sulfonated phenol resin (SPR) membranes in the isoporuous membrane filter were acidified with 1.0 N hydrochloric acid. Proton conductance \( G_{\text{film}} \) of the SPR membranes was determined by the complex impedance method using an impedance/gain phase analyzer (Solartron 1260). Methanol crossover rate \( \text{MCO} \) was determined using an H-type cell and a gas chromatograph. The ion-exchange capacities (IEC) of the SPR membranes were determined by pH titration. MEAs with a geometric area of 5.0 cm² 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 for cathode and anode were prepared with mixing of each catalysts, 5 wt% Nafion solution, iso-propanol, and pure water, as showed in Table I. Weight ratio \((I/C)\) of the ionomer to the catalyst in the dried MEA ink was varied to 0.1, 0.2, and 0.3. MEA inks were painted onto carbon knitted cloth (CC) electrodes (supplied by Shinanokenshi Co., Ltd.) for SPR/CC MEAs, and carbon paper (CP) electrodes (Toray TGP-H-060) for SPR/CP MEAs. The catalyst-loaded electrodes 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 solution (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).

![Figure 1. Synthesis of Pre-polymer of sulfonated phenol resin (preSPRxy).](image)

| Electrode | Mixing ratio / wt% |
|-----------|-------------------|
|           | Catalyst a) | 5wt% Nafion sol. | \(I/C\) b) | \((\text{CH}_3)_2\text{CHOH}\) | \(\text{H}_2\text{O}\) |
| Anode     | 4           | 8              | 0.1       | 44       | 44       |
| Anode     | 4           | 16             | 0.2       | 44       | 44       |
| Anode     | 4           | 24             | 0.3       | 44       | 44       |
| Cathode   | 4           | 4              | 0.05      | 37       | 55       |

a) Anode catalyst: Pt-Ru(1:1)/C (Pt+Ru ca.50 wt%), Cathode catalyst: Pt/C (Pt ca.50 wt%), b) \(I/C\) = (Ionomer weight)/(Catalyst weight)
RESULTS AND DISCUSSION

Characteristics of SPR membranes

Figure 2 shows SEM images of cross sections of the SPR membranes. These SEM images indicate that the through holes of IMF were filled with SPR almost perfectly. And, even in the hole with diameter of 1.2 \( \mu \text{m} \), the filling up was completed. Figure 3 shows swelling ratios of SPR membranes in directions of thickness and surface. The swelling ratio in the direction of the thickness depended on the values of IEC. However, in the direction of surface was repressed. The repression of swelling in a direction of film surface was effective in the higher methanol concentration. From these results, the contribution to the repression of methanol crossover was expected\(^3\). As shown in Table II, IEC of SPR membranes (SPR34, SPR33, and SPR32) were 2.7, 3.0, and 3.6 \( \mu \text{mol g}^{-1} \). The observed values of IEC were close to the theoretical values of 2.79, 3.12, and 3.53 \( \mu \text{mol g}^{-1} \), respectively. IEC was controlled by molar ratio of the phenol units. Proton conductance (\( G_{\text{film}} \) [S cm\(^{-2}\)]) and methanol crossover rate (MCO [mol cm\(^{-2}\) min\(^{-1}\)]) of

![Figure 2. SEM images of the cross section of SPR membranes](image)

![Figure 3. Swelling characteristic of the SPR membranes](image)
three SPR membranes that varied in their IEC, from 2.7 to 3.6 \( \mu \text{mol g}^{-1} \) are contrasted with those of Nafion 117 in Table II. 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 SPR32, SPR33, and SPR34, respectively. This result is given the fact that the content of phenol unit that forms crosslinkage is higher in the SPR membrane with lower IEC. The proton conductance was 1.7 times higher in SPR32, then 1.35 and 2.18 times lower in SPR33 and SPR34, respectively, than that of Nafion 117. This ranking of the proton conductance was attributed to the order of IEC in the SPR membranes.

**DMFC performance of SPRxy membranes**

The Nafion membrane is thermoplastic film. However, the SPR membrane is the thermosetting film. Carbon paper has uniform thickness and enough strength. But its surface carbon fiber is detachable easily. Carbon knitted cloth has un-uniform thickness and insufficient strength. However, strong adhesion with the SPR membrane can be expected. Then, a SPR33/CC MEA using the carbon knitted cloth electrode was prepared, to compare with a SPR33/CP MEA. Figure 4 shows the DMFC current

![Figure 4. Effects of the carbon knitted cloth electrode on DMFC performance.](image)

**Figure 4.** Effects of the carbon knitted cloth electrode on DMFC performance. Pt-loading [mg cm\(^{-2}\)] SPR33 CC: 0.50 (Anode), 0.71 (Cathode), SPR33 CP: 0.46 (Anode), 1.00 (Cathode).

![Figure 5. DMFC performance with the SPR/CC MEAs.](image)

**Figure 5.** DMFC performance with the SPR/CC MEAs. Pt-loadings of anode and cathode were 0.27 and 0.52 mg cm\(^{-2}\), respectively. IEC [\( \mu \text{mol g}^{-1} \)] SPR32: 3.63, SPR33: 3.00, SPR34: 2.69, and Nafion 117: 0.93. ▪ Nafion 117/CP MEA ; ▼ ▼ SPR27/CC MEA ; ▲ ▼ SPR30/CC MEA : □ □ SPR36/CC MEA.
density / cell voltage or power density curves for SPR33/CC MEA and SPR33/CP MEA. When the carbon knitted cloth electrode was used, the maximum power density reached to 34 mW cm\(^{-2}\). DMFC performance using SPR membranes could be improved remarkably. It was demonstrated that the carbon knitted cloth electrode is suitable to SPR membranes.

The DMFC current density / cell voltage or power density curves for MEAs using three SPR/CC MEAs that varied in their IEC, from 2.7 to 3.6 \(\mu\text{mol g}^{-1}\), are shown in Figure 5. The maximum power density in the SPR34/CC MEA was slightly lower than that in the Nafion/CP MEA. In the SPR33/CC and SPR32/CC MEAs, the maximum power density was greater than that in the Nafion/CP MEA; 1.25 and 1.28 times greater for the SPR33/CC and SPR32/CC MEAs, respectively. The gentle slope in the current density - cell voltage curves for the SPR33/CC and SPR32/CC MEAs was attributed to the higher proton conductance of the membranes and the lower contact resistance between the membrane and catalyst/CC electrodes. Figure 6 shows effects of I/C ratio on DMFC performance. The DMFC performance was depended on I/C ratio and maximized at I/C of 0.2. Therefore, by adjustment in amount of the catalyst binder, the contact resistance of the interface between membrane and catalyst could be minimized. The DMFC performance of the SPR32/CC MEA that the Pt-loadings of anode and cathode were enriched to 0.5 and 1.0 mg cm\(^{-2}\), respectively, is shown in Figure 7. Both the open-circuit voltage and the maximum power density for the SPR32/CC MEA in Figure 7 were higher than those for the SPR32/CC MEA in Figure 5; 0.12 V higher in the voltage and 1.42 times higher in the power density.

In conclusion, higher-density crosslink of the phenol polymer was more effective to repress methanol crossover in the electrolyte membrane. Higher-density sulfonation was more effective to enhance proton-conduction and improve DMFC performance. Knitted fabric texture of the carbon fiber electrode was effective to adhere on the membrane strongly, and to improve DMFC performance. In addition, adjustment of the catalyst binder amount and selection of the texture type in the carbon fiber electrode improved the DMFC performance.
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