

A study of new electrode binder for DMFC

직접 메탄올 연료전지를 위한 새로운 전극 바인더에 관한 연구

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1. Introduction

Membranes currently used in DMFC are perfluorinated polymers such as Nafion, because Nafion (Du Pont) has high hydrolytic and oxidative stability and excellent proton conductivity. However, Nafion has some drawbacks such as the high cost, loss of conductivity at high temperature (>80°C) and high methanol permeability, which are still the barriers against practical applications. Therefore, searching for alternative materials is important. In view of this, there is widespread effort to develop alternative more economical non-perfluorinated polymer electrolyte membranes [1-3]. Among these polymers, poly(arylene ether sulfone) (PAES) has been studied as an alternative to Nafion due to their good mechanical properties, thermal stability and conductivity [2]. However, the performance of DMFCs is strongly affected by the electrode as well as the membrane. To enhance the electrochemical active surface area and compatibility on the electrode, an ionomer should be impregnated. The ionomer plays an important role in determining the performance of a DMFC catalyst layer because it serves both as a binder and a proton conductor [4]. However, the binder which could be compatible with the sulfonated-PAES (s-PAES) membrane has not been investigated. To enhance the compatibility between the electrode and the s-PAES membrane, appropriate binder should be applied to the electrode. In this paper, we investigated the effect of binder for the compatibility between the electrode and the s-PAES membrane.

2. Experimental

The sulfonated comonomer, 3,3'-disulfonate-4,4'-dichlorodiphenylsulfone (SDCDPS) was synthesized from 4,4'-dichlorodiphenyl sulfone (DCDPS) with fuming sulfuric acid [5]. All other reagents were obtained from Aldrich.

PAES polymers were synthesized with DCDPS, 4,4'-biphenol (BP) and SDCDPS in the presence of potassium carbonate in NMP with toluene, as reported previously [2].

Membranes were prepared by dissolving the polymer in DMAc and casting directly onto clean glass substrates. The polymers were characterized with ^1H NMR and FT-IR.

An electrochemical impedance spectroscopy for the DMFC was carried out at 0.4 V. The cell was operated at 30°C. The binder was made by mixing the dry PAES polymer (5wt.%) with solvents. The electrodes were prepared using a brushing technique on carbon paper (TGPH090, Toray). The catalyst content was maintained constant at 5 mg/cm² for both the anode and the cathode electrode. The MEAs were characterized in a 2 cm² single cell.

3. Results and discussion

The sulfonation of monomer was confirmed using ^1H NMR spectrum [5] as shown in Fig. 1. In the ^1H NMR spectrum of S-DCDPS, there are three different aromatic protons. The ortho-proton peak to sulfonate group was appeared at the most down field, which could attribute to two electron-withdrawing groups, such as sulfone and sulfonate.

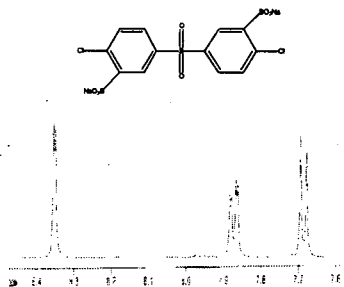


Fig. 1. ^1H NMR spectrum of SDCDPS in DMSO-d₆

To apply PAES to the electrode binder, PAES was sulfonated with the introduction of SDCDPS. First evidence of sulfonation is given by the infrared spectroscopy. Fig. 2 shows spectra of PAES with the degree of sulfonation (DS). Upon sulfonation, a new absorption band at 1030 and 1098 cm⁻¹ in PAES was assigned to symmetric and asymmetric stretching of the sodium sulfonate groups [2]. The successful sulfonation of PAES was confirmed. It has known that the sulfonated PAES with moderate degree of sulfonation (<40%) may be suitable for operation of fuel cell [6]. Therefore, the 40% sulfonated PAES was applied to membrane and electrode binder in this study.

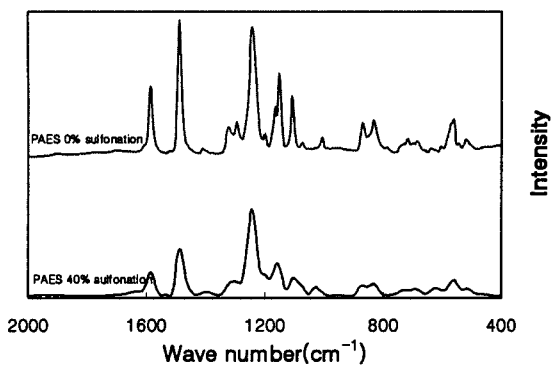


Fig. 2. FT-IR spectra

Cell voltage and power density versus current density plots are given in Fig. 3. The performance of s-PAES binded cell (B-PAES) was better than that of Nafion binded cell (B-Nafion) at lower cell potential. The B-Nafion cell showed good performance at higher cell potential but markedly reduced at lower cell potential. This is because the B-Nafion cell may encounter large cell resistance due to the poor adhesion between s-PAES membrane and Nafion binded electrode, resulting in a cell performance worse than the s-PAES binder based cell.

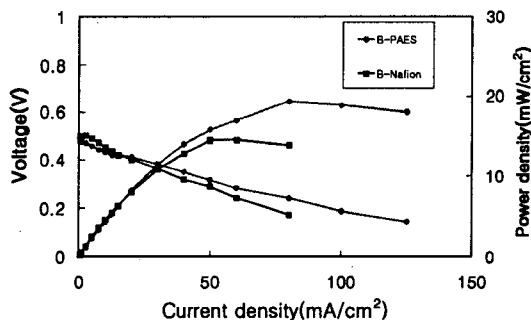


Fig. 3. Cell performances

Fig. 4 shows scanning electron micrographs of the cross section of the MEA, after the use in the cell, for B-Nafion and B-PAES cells, respectively. The catalyst layer of the B-Nafion cell was separated from the membrane while the catalyst layer of B-PAES cell was not separated from the membrane. In the B-Nafion cell, the poor adhesion between membrane and electrode increased the cell resistance. In the B-PAES cell, the adhesion between membrane and electrode was sustained. This result suggested that s-PAES binder could be proper for enhancing the adhesion between the s-PAES membrane and the electrode as well as long-term stability.

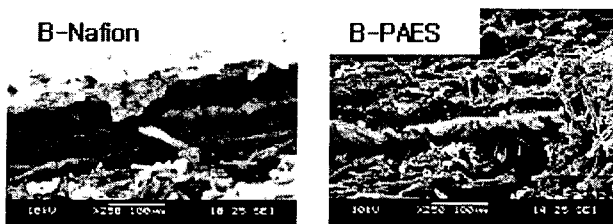


Fig. 4. SEM images

4. Conclusion

The s-PAES were prepared and applied to the membrane as well as the electrode binder for DMFC. The cell performance of B-PAES was better than that of B-Nafion. This seems to be closely related to the adhesion between the membrane and electrode binder. The B-PAES cell showed a good adhesion of the electrode binder and the membrane. From these results, it is suggested that s-PAES binder can be a proper candidate for enhancing the adhesion between the s-PAES membrane and the electrode and the consequent long-term stability.

Acknowledgement

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