

Short communication

The effect of sulfonated poly(ether ether ketone) as an electrode binder for direct methanol fuel cell (DMFC)

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Abstract

Poly(ether ether ketones) (PEEKs) are sulfonated and used as a binder in the electrode for DMFC studies. The effect of sulfonated PEEK (s-PEEK) binder in the catalyst layer on the cell performance is investigated. The s-PEEK binder in the electrode is found to be more efficient in maintaining long-term stability of the cell performance than the conventional Nafion binder. The cell based on electrode having s-PEEK as a binder showed a good adhesion between electrode and electrolyte (s-PEEK membrane), while the electrode based on Nafion binder was delaminated from the s-PEEK membrane after supplying the fuel for a prolonged time.

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1. Introduction

Nafion (Du Pont) has been demonstrated to be an excellent proton exchange membrane, but the high cost, loss of conductivity at high temperature ($>80^{\circ}\text{C}$), and high methanol permeability are still barriers against successful commercialization. Concerned on this, there have been various efforts to develop more economical non-perfluorinated polymer electrolyte membranes typically based on poly(ether ether ketone) [1], poly(arylene ether sulfone) [2], and polybenzimidazole [3]. Sulfonated aromatic poly(ether ether ketone) has been much studied as one of the important alternatives to Nafion due to their good mechanical properties, thermal stability, and conductivity [4,5].

The performance of DMFC is strongly affected by the electrode as well as the membrane and also by their adhesion. As the electrode of DMFC requires platinum (Pt) catalyst as an active material, it is also important to increase the reaction sites in the catalytic layer. Since the polymer electrolyte membrane is in its solid state, it is rather difficult to penetrate sufficiently into the electrode. Therefore, the reaction area is usually limited to contact surface between the electrode and membrane. To

increase the contact surface area, the ionomer membrane should be impregnated to the electrode. The ionomer plays another important role in determining the performance of DMFC catalyst layer because it serves as a binder, holding the catalyst/carbon clusters together to form a porous layer with structural integrity, and also as a proton conductor, allowing proton migration [6].

Several groups have been studying the effect of electrode composition on the overall performance of the cell [7–9]. Most of their studies are based on Nafion membrane system and focused on optimization of Nafion binder content to achieve maximum performance of the cell. However, little attention has been paid so far to the electrode binder compatible with the alternative electrolyte membranes. In this work, the effect of new electrode binder on the performance of the s-PEEK membrane-based DMFC was investigated.

2. Experimental

2.1. Materials

The Nafion solution is purchased from DuPont with a specified concentration of 5 wt.%. Concentrated (95 wt.%) sulfuric acid is provided by JUNSEI, Japan. The PEEK, dimethylacetamide (DMAc), *N*-methyl-2-pyrrolidone (NMP),

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deuterated dimethyl sulfoxide (DMSO-d6), isopropyl alcohol (IPA) and methanol are procured from Aldrich.

2.2. Sulfonation of PEEK and membrane preparation

Typically 2 g of PEEK is dried in a vacuum oven at 90 °C and then dissolved in 50 ml of concentrated (95%) sulfuric acid at 50 °C under vigorous stirring for a predetermined time, ranging from 6 to 24 h. The sulfonated polymer is recovered by precipitating the acid polymer solution into an excess quantity of ice water. The precipitated polymer is filtered and washed several times with deionized water until the pH of the polymer reaches 6–7. The recovered s-PEEKs are dried at 50 °C for 24 h, and dried in a vacuum oven at 50 °C for 2 days.

Solution casting method [10] was used to prepare membranes. The dry s-PEEK polymer is first dissolved (10 wt.%) in *N*-methyl-2-pyrrolidone (NMP), and cast onto a clean glass plate. The cast membrane is dried at 50 °C for 24 h and dried again under vacuum at 140 °C for the following 2 days.

2.3. Characterization of s-PEEK

Degree of sulfonation (DS) is determined by ¹H NMR method [11]. NMR spectra are recorded on a FT-500 MHz NMR spectrometer (BRUKER AMX500). FT-IR spectra are acquired on a Bomem 102 Fourier transform spectrometer with thin polymer films.

The glass transition temperature (T_g) of s-PEEK is measured by differential scanning calorimetry (DSC) using TA instrument DSC2010 in a nitrogen atmosphere from 50 to 250 °C with a heating rate of 10 °C min⁻¹.

All the samples are dried in a vacuum oven at 80 °C for 3 days prior to measurements of water uptake. The proton conductivity is determined using an AC impedance spectroscopy.

2.4. Impedance spectroscopy

An electrochemical impedance spectroscopic measurement for DMFC is performed under the following conditions: the ac amplitude is 10 mV, and the frequency is typically varied from 0.05 to 5000 Hz. The cell is operated at 30 °C. The flow rates of oxygen and methanol solution (2 M) are 200 and 1 cc min⁻¹, respectively.

2.5. Preparation of binder and electrode

The binder is prepared by mixing the dry s-PEEK polymer (5 wt.%) with DMAc, IPA, methanol, and deionized water. Black catalysts are used in this study, and they were supplied by E-TEK. The active materials for anode and cathode are Pt/Ru and Pt black, respectively. Catalyst inks are prepared by dispersing appropriate amounts of catalyst, deionized water, IPA, and 5 wt.% s-PEEK as a binder.

The electrodes are prepared by using a brushing technique on carbon paper (TGPH090, Toray) and the obtained electrodes are dried at 70 °C. The catalyst content is maintained constant at a 5 mg cm⁻² for both the anode and cathode.

2.6. MEAs (membrane electrode assembly) preparation and their performance

The MEAs are prepared by hot-pressing the electrodes onto s-PEEK membrane at 130 °C for 3 min and they are characterized with a 2 cm² single cell. Methanol solution (2 M) and oxygen are supplied to both the anode and cathode, respectively.

3. Results and discussion

3.1. Characterization of s-PEEK

FT-IR spectra of s-PEEK showed a new absorption band at 1080 cm⁻¹ corresponding to sulfur-oxygen symmetric vibration O=S=O. The new absorptions at 1255, 1080, and 1020 cm⁻¹ are assigned to the vibrations of the sulfonic acid group in s-PEEK [12].

The degree of sulfonation (DS) with reaction time is listed in Table 1. When the DS is over 40%, the s-PEEK polymers are found to be soluble in normal organic solvents such as DMF, DMSO, NMP, however, when the DS is above 70%, they are soluble in methanol, and for 100% sulfonation, they can be dissolved in hot water. Based on these results, s-PEEK with the DS of 60% was selected as the material for the membrane and electrode preparation.

3.2. Proton conductivity and water uptake

Proton conductivity usually depends on the number of acid groups and their association and dissociation capability in water. Water molecules dissociate the acid functional groups and facilitate proton transport, and therefore the water uptake is an important parameter in determining the proton conductivities of polymer electrolyte membranes. The proton conductivity and water uptake of the s-PEEK membranes are listed in Table 1. As expected, the conductivity and water uptake of the s-PEEK membrane increased with increase of DS. The s-PEEK membranes with high DS showed high proton conductivities comparable to Nafion 117.

3.3. MEA processing condition

From the DSC results, T_g of the dried s-PEEK is found to be 139 °C and that of the hydrated one is 128 °C. To make the membrane/electrode assembly (MEA), the hydrated membrane is normally hot-pressed with two electrodes. For effective physical contact between the membrane and the electrodes,

Table 1
DS, proton conductivity, and water uptake of s-PEEK

	Sulfonated PEEK				Nafion 117
Sulfonation time (h)	6	9	12	24	
DS (%)	50	60	70	90	
Proton conductivity (S cm ⁻¹)	1 × 10 ⁻²	9 × 10 ⁻²	1 × 10 ⁻¹	–	1.3 × 10 ⁻¹
Water uptake (%)	33.5	42.3	115.4	–	24.7

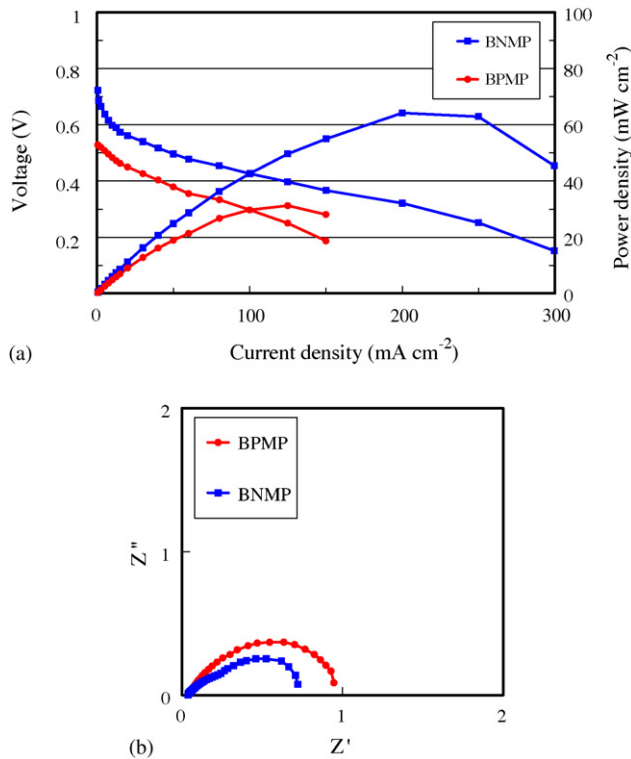


Fig. 1. (a) Polarization Curves of BNMP and BPMP after 3 days operation of continuous fuel supply (BNMP: binder is Nafion and membrane is s-PEEK, and BPMP: binder is s-PEEK and membrane is s-PEEK). (b) Impedance spectra of BNMP and BPMP cells after 3 days operation of continuous fuel supply.

hot-pressing temperature of MEA is set at 130 °C which is close to the T_g value of the hydrated s-PEEK.

3.4. Cell performance

For the comparative studies of the cell performance, the s-PEEK membrane is used as electrolyte membrane for both cells having s-PEEK and Nafion as an electrode binder. Cell voltage and power density versus current density plots are given in Fig. 1(a). The cell performance data of the MEAs are recorded at 30 °C after 3 days operation of continuous fuel supply. Fig. 1(a) shows that the cell performance based on BNMP (binder: Nafion, membrane: s-PEEK) is superior to that based on BPMP (binder: s-PEEK, membrane: s-PEEK). This is closely related to the fact that the cell resistance of BNMP after 3 days of continuous fuel supply is quite lower than that of BPMP as shown in Fig. 1(b).

On the contrary to the result above, Fig. 2(a) shows that the cell performance based on BPMP is higher than that based on BNMP after 10 days operation with continuous fuel supply. Fig. 2(b) also shows that the cell resistance of BPMP after 10 days of continuous fuel supply is quite lower than that of BNMP. The cell performance based on BPMP after feeding the fuel for 10 days is even higher than that of BNMP at a lower cell potential. The BNMP cell showed good performance at a higher cell potential but its performance is much degraded at a lower cell potential compared to BPMP cell. It is thus, very noticeable that the cell performance based on BNMP is significantly deteriorated,

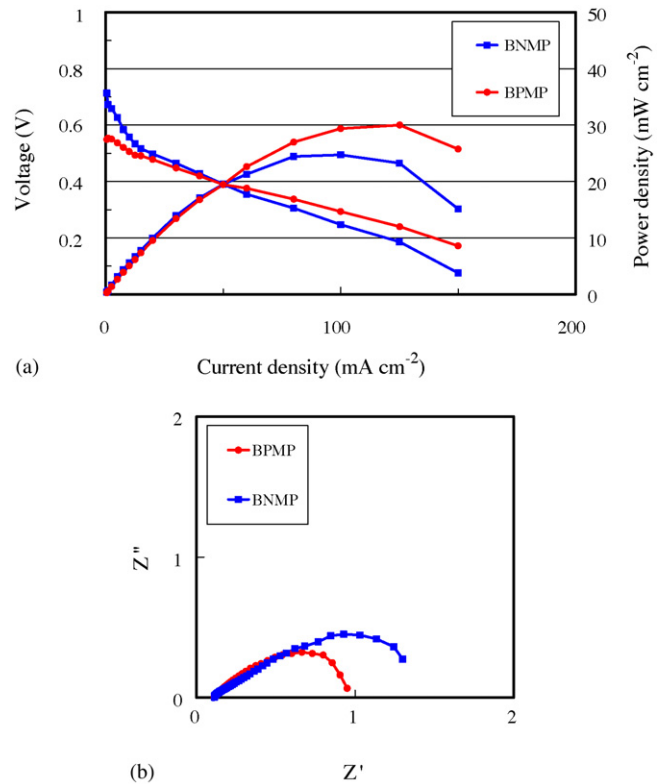


Fig. 2. (a) BNMP and BPMP-based cell performance after 10 days operation of continuous fuel supply. (b) Impedance spectra of BNMP and BPMP cells after 10 days operation of continuous fuel supply.

while the BPMP cell showed less decay in performance with a prolonged fuel supply.

Fig. 3 shows the cell resistance of BNMP as a function of fuel supply time. The cell resistance of BNMP is drastically increased with a prolonged fuel supply, which is attributed to the poor adhesion between s-PEEK membrane and the electrode using Nafion binder. Fig. 4 shows scanning electron micrographs of cross section of the MEAs after operation of BNMP and BPMP cells, respectively. The catalyst layer of the BNMP cell is clearly observed to delaminate from the membrane while it maintains a good adhesion to the membrane for BPMP cell. Poor adhesion

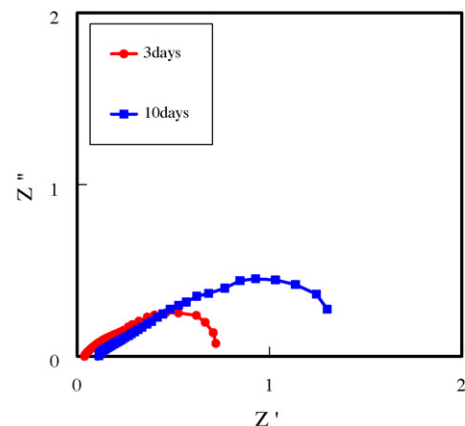


Fig. 3. Cell resistance of BNMP with fuel supply time.

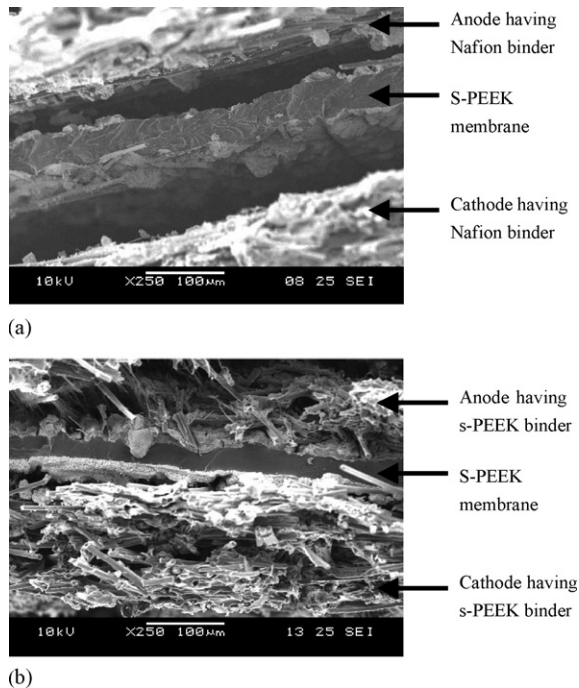


Fig. 4. Scanning electron micrographs of the (a) cross section of BNMP cell, (b) cross section of BPMP cell.

between the membrane and electrode for BNMP cell led to the increase in cell resistance, resulting in a poor performance of the cell with continued operation.

4. Conclusion

Sulfonated PEEKs (s-PEEKs) are prepared and used as membrane and binder to the electrode for DMFC applications. With continued fuel supply, the BNMP cell exhibited a significant decay in the cell performance, while the BPMP cell could operate rather in a stable way. This is largely related to the extent of adhesion between the membrane and electrode binder. The

BPMP cell showed a good adhesion of the electrode binder and membrane after a prolonged time of operation. From these results, it is suggested that s-PEEK binder can be a proper candidate for enhancing the adhesion between the s-PEEK membrane and the electrode and the consequent long-term stability.

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References

- [1] S. Kaliaguine, S.D. Mikhailenko, K.P. Wang, P. Xing, G. Robertson, M. Guiver, *Catal. Today* 82 (2003) 213.
- [2] F. Wang, M. Hickner, Y.S. Kim, T.A. Zawodzinski, J.E. McGrath, *J. Membr. Sci.* 197 (2002) 231.
- [3] S.R. Samms, S. Wasmus, R.F. Savinell, *J. Electrochem. Soc.* 143 (1996) 1225.
- [4] K.D. Kreuer, On the development of proton conducting materials for technological applications, *Solid State Ionics* 97 (1–4) (1997) 1.
- [5] K.D. Kreuer, On the development of proton conducting polymer membranes for hydrogen and methanol fuel cells, *J. Membr. Sci.* 185 (1) (2001) 29.
- [6] J. Xie, F. Garzon, T. Zawodzinski, W. Smith, *J. Electrochem. Soc.* 151 (7) (2004) A1084.
- [7] S.C. Thomas, X. Ren, S. Gottesfeld, *J. Electrochem. Soc.* 146 (12) (1999) 4354.
- [8] E. Passalacqua, F. Lufrano, G. Squadrito, A. Patti, L. Giorgi, *Electrochim. Acta* 43 (24) (1998) 3665.
- [9] S.J. Lee, S. Mukerjee, J. McBreen, Y.W. Rho, Y.T. Kho, T.H. Lee, *Electrochim. Acta* 43 (1998) 3693.
- [10] M.D. Kurkuri, J.-R. Lee, J.H. Han, I. Lee, *Smart Mater. Struct.* 15 (2006) 1.
- [11] G.P. Robertson, S.D. Mikhailenko, K. Wang, P. Xing, M.D. Guiver, S. Kaliaguine, *J. Membr. Sci.* 219 (2003) 113.
- [12] P. Xing, G.P. Robertson, M.D. Guiver, S.D. Mikhailenko, K. Wang, S. Kaliaguine, *J. Membr. Sci.* 229 (2004) 95.