

## Preparation and Characterization of Polymer-Mica Composite Cation-Exchange Membranes

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Composite cation-exchange membranes composed of organic material polysulfone and inorganic material mica were prepared. Mica crystals show a layered structure. The structure consists of negatively charged silicate layers and interlayer cations. Therefore, mica has ion-exchangeability of interlayer cations. Fine particles of mica were added to polysulfone solutions of *N*-methyl-2-pyrrolidone so as to the weight ratio mica/polysulfone becomes 0/100 – 60/40. After the solutions were poured onto glass plates, they were dried in an oven. The properties of membranes, ion-exchange capacity, water content and transport number of counterions were measured. The transport number of cations estimated from concentration membrane potential in KCl solution system and ion-exchange capacity increased with increasing the mica content. The membrane resistance measured in 0.01 mol kg<sup>-1</sup> HCl aqueous solution decreased with mica content, and the membrane resistance of H<sup>+</sup>-form mica/polysulfone (60/40) membrane was lower than that of Nafion 117. Significant DSC peaks were not observed below 160 °C for the composite membranes.

Key words: composite cation-exchange membrane, organic/inorganic material, ion transport, DSC, fuel cell

### 1. INTRODUCTION

Much attention has been paid to the polymer electrolyte fuel cells (PEFCs) for future energy needs and cleaner environment for decade [1]. Perfluoro-sulfonic acid-type cation-exchange membranes have been widely used for the fuel cells as the proton conducting membranes, however, there are several obstacles in using the membranes, such as high cost, poor thermal stability and volume change of the membrane between swollen and dry situation.

Many approaches have been carried out to improve these weaknesses. From a cost perspective, it is interesting to investigate fluorine-free or partially fluorinated membranes instead of perfluorosulfonic acid-type membrane. It has been reported about composite membranes of perfluorosulfonic acid and porous substrate of polytetrafluoroethylene by some researchers [2,3,4]. Kim et al. investigated partially sulfonated polystyrene-block-poly(ethylene-ran-butylene)-block-polystyrene copolymer membranes[5]. However, these attempts are not satisfactory.

There are some reports about organic-inorganic composite membranes. H. Y. Chang and C. W. Lin have reported a series of organic/inorganic composite materials based on polyethylene glycol/SiO<sub>2</sub> synthesized through sol-gel processes [6]. Yamaguchi et al. have been reported pore-filling membranes on inorganic substrates [7]. But these types of membranes are fragile because of the characteristic properties of inorganic material. It is considered that embedding an inorganic ion-exchangeable material in heat-stable polymer matrix conquers these disadvantages.

Mica is an inorganic material with a layered structure.

An example of mica crystal structure is shown in Fig. 1. The structure consists of negatively charged silicate layers and interlayer cations, therefore, the mica has ion-exchangeability of interlayer cations.

In this work, composite cation-exchange membranes composed of organic material polysulfone and inorganic material mica were prepared by dispersing the mica powder randomly in polysulfone matrix. Membrane resistance and concentration membrane potential were measured to discuss the ion transport phenomena across the membranes. The morphology and thermal stability of the membranes were also discussed.

### 2. EXPERIMENTAL

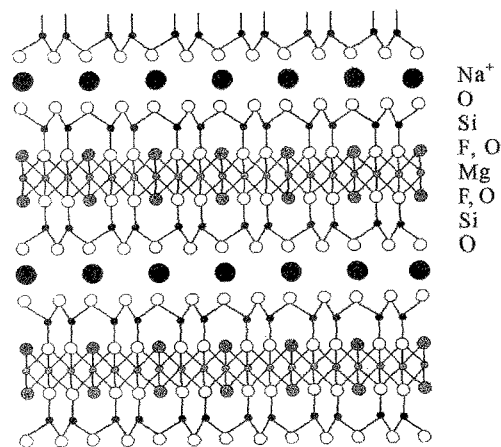


Fig. 1. An example of structure of mica crystal [8].

## 2.1 Preparation of membranes

Appropriate amount of polysulfone (PS, Aldrich, Av Mw = 26000) was dissolved in *N*-methyl-2-pyrrolidone (NMP, Wako Pure Chem. Ind., Ltd.) to prepare 20 wt% solution. Mica powder (MC, Topy Ind., Ltd., DMA-80E) was added to the solution so as to the weight ratio MC/PS becomes 0/100 – 60/40. After the mixture was well mixed by magnetic stirrer it was cast on the glass plate.

It was immersed in coagulation water bath immediately to obtain PS-MCw (*x*) membranes. On the other hand, it was dried in a oven at 50°C for 0.5 h and at 100°C for 4 h. After drying, it was immersed in water to obtain PS-MCd (*x*) membranes. *x* shows mica content.

Commercially available perfluorosulfonic acid-type Nafion 117 was also used.

## 2.2 Properties and characterization of membranes

### 2.2.1 Ion-exchange capacity

Ion-exchange capacity was measured by titration method. It was expressed by the unit mmole of ion-exchange groups per gram of the dry membranes without the weight of anhydrous counterions.

### 2.2.2 Water content

A membrane equilibrated with pure water was sandwiched between additional two pieces of wet filter equilibrated with water, and then the excess water on the surface of two wet filter papers on both side of the membrane was blotted with dry filter paper. The weight of the wet membrane was measured as soon as the wet filter paper was separated from the membrane [9].

### 2.2.3 Concentration membrane potential

The concentration membrane potential was measured

Table I. Properties of membranes.

Membrane	Thick-ness (mm)	Ion-exchange capacity <sup>a)</sup>	Water content <sup>b)</sup>
PS-MCd (0)	0.07	0	0.03
PS-MCd (5)	0.13	1.5	0.01
PS-MCd (10)	0.13	4.9	0.04
PS-MCd (20)	0.18	2.8	0.05
PS-MCd (30)	0.09	3.5	0.07
PS-MCd (50)	0.10	2.9	0.15
PS-MCd (60)	0.22	4.1	0.37
PS-MCw (0)	0.10	0	1.96
PS-MCw (2)	0.20	9.4	1.89
PS-MCw (25)	0.21	7.1	1.79
PS-MCw (50)	0.23	9.7	1.89
Nafion 117	0.53	0.6	0.23

a) mmol per g-dry membrane without counterions.

b) g-H<sub>2</sub>O per dry membrane without counterions.

in KCl ( $c_1$  mol kg<sup>-1</sup>) /membrane/ KCl ( $c_2$  mol kg<sup>-1</sup>) system, where  $c_2/c_1 = 2$  and  $c_1$  varied from 0.001 to 0.1. The membrane potential cell was constructed from two sections made of poly(methyl methacrylate) resin, and a calomel electrode was connected to each section. The membrane, whose effective area was 0.78 cm<sup>2</sup>, was mounted between the half-cells. The solution inlet and outlet were inserted in each half of the cell to disturb a diffusion layer on the membrane surface. The transport number of counterions ( $t_+$ ) was estimated by the membrane potential using the equation:

$$-\Delta\psi = -(2t_+ - 1)(RT/F) \ln(a_+'/a_+'' ) \quad (1)$$

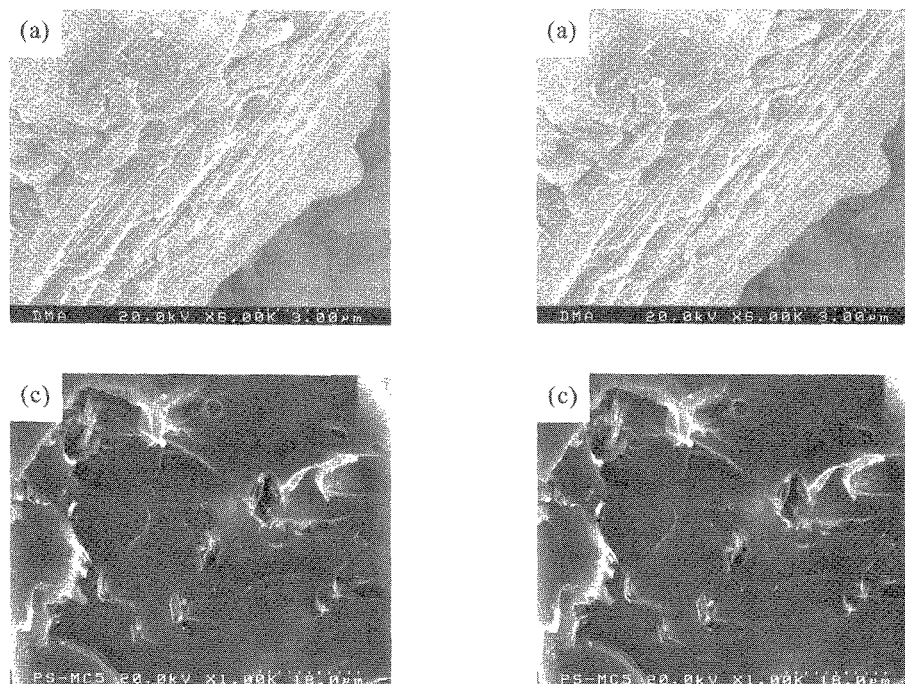


Fig. 2. SEM photographs of (a) mica powder and cross-sections of (b) PS-MCd (0), (c) PS-MCd (5) and (d) PS-MCd (50) membrane.

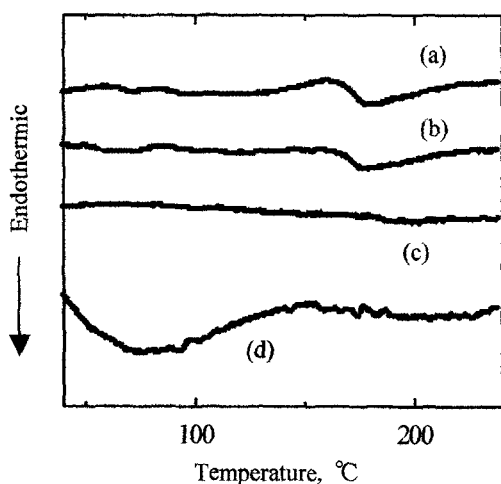


Fig. 3. DSC heating curves of (a) PS-MCd (5), (b) PS-MCd (20), (c) PS-MCd (50) membrane and (d) Nafion 117.

where,  $R$  and  $F$  are gas and Faraday constants, respectively,  $T$  the absolute temperature,  $a_{\pm}'$  and  $a_{\pm}''$  are the activities of the KCl solutions of both side of the membrane.

#### 2.2.4 Membrane resistance

Membranes were equilibrated at 0.01 mol kg<sup>-1</sup> HCl solution. Two flat, impervious carbon electrodes were directly connected to both sides of the membrane equilibrated with the solution, and the membrane resistance was measured at 298 K using an impedance analyzer 4192A (Yokogawa-Hewlett-Packard, Ltd.). The effective area of membrane was 1 cm<sup>2</sup>.

#### 2.2.5 Scanning electron microscopy (SEM)

The structure of mica powder and the morphologies of the composite membranes were examined using a SEM (S-4100, Hitachi). The sample membranes were immersed in liquid nitrogen and fractured to expose the cross-sectional areas. The mica powder and sample membranes were dried and sputtered with gold using sputtering device and viewed with the SEM at 20 kV.

#### 2.2.6 Differential scanning calorimetric (DSC) measurement

DSC measurements were performed to estimate the thermal stability of the membranes with DSC 6200 (Seiko Instruments). All DSC experiments were carried out over the temperature range 40 – 250°C at a rate of 5 K min<sup>-1</sup>. All the specimens were dried more than 24 h before measurement.

### 3. RESULTS AND DISCUSSION

Table I shows the properties of PS-MCd membranes, PS-MCw membranes and Nafion 117. The water contents of PS-MCw membranes were higher than those of PS-MCd membranes due to their porous structure. Because of the high water content, the mica powder sometimes came out from the membrane matrix of PS-MCw membranes.

In general, the water content and the ion-exchange

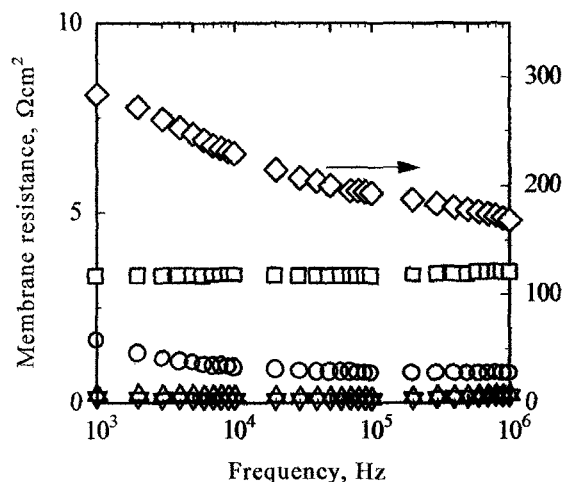


Fig. 5. The dependence of the membrane resistance in 0.01 mol kg<sup>-1</sup> HCl aqueous solutions on frequency. Membranes:  $\diamond$ , PS-MCd(10);  $\square$ , PS-MCd(20);  $\triangle$ , PS-MCd(50);  $\nabla$ , PS-MCd(60);  $\circ$ , Nafion 117.

capacity of PS-MCd membranes increased with increasing the mica content of the composite membranes.

Figure 2 shows the SEM photographs of the (a) mica powder and the cross-sections of (b) PS-MCd (0), (c) PS-MCd (5) and (d) PS-MCd (50). The layered structure of the mica powder was observed in Fig. 2 (a). Relatively dense structure of PS matrix was observed in Fig. 2 (b).

Figure 3 shows the DSC heating curves of PS-MCd (5), PS-MCd (20), PS-MCd (50) membranes and Nafion 117. The endothermic peaks around 190°C were observed for PS-MCd membranes due to the glass transition behavior of polysulfone[10], however, significant peaks were not observed below 160°C. The PS-MCd membranes were stable below glass transition

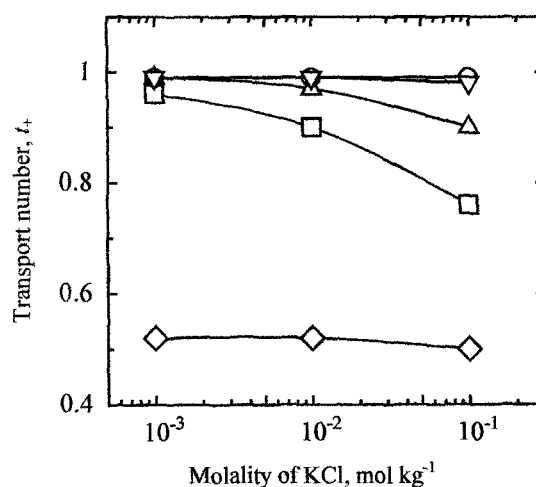


Fig. 4. The relationships between the transport numbers of cations and the lower molality of the KCl solutions. Membranes:  $\diamond$ , PS-MCd(0);  $\square$ , PS-MCd(5);  $\triangle$ , PS-MCd(10);  $\nabla$ , PS-MCd(50);  $\circ$ , Nafion 117.

temperature of PS.

In Fig. 4, transport numbers of cations estimated from the concentration membrane potential across PS-MCd (0), PS-MCd (5), PS-MCd (10), PS-MCd (50) and Nafion 117 were plotted against the lower molality of the KCl solutions. Permselectivity was not observed for PS-MCd (0) membrane. The transport number increased with increasing the mica content and PS-MCd (50) membrane showed an ideal permselectivity below  $0.1 \text{ mol kg}^{-1}$ .

Figure 5 shows the dependence of the membrane resistance in  $0.01 \text{ mol kg}^{-1}$  HCl solutions across PS-MCd (10), PS-MCd (20), PS-MCd (50), PS-MCd (60) and Nafion 117 on frequency. The membrane resistance decreased with increasing the mica content. The membrane resistances of PS-MCd (50) and (60) were lower than that of Nafion 117.

#### 4. REFERENCES

- [1] J. Larminie and A. Dicks, *Fuel Cell Systems Explained*, Wiley, Great Britain, 2000.
- [2] K.M. Nouel and P.S. Fedkiw, *Electrochim. Acta*, **43**, 2381 (1997).
- [3] C. Liu and C.R. Martin, *J. Electrochem. Soc.* **137**, 510 (1990).
- [4] R.M. Penner and C.R. Martin, *J. Electrochem. Soc.* **132**, 514 (1985).
- [5] J. Kim, B. Kim and B. Jung, *J. Membrane Sci.* **207**, 129 (2002).
- [6] H. Y. Chang and C. W. Lin, *J. Membrane Sci.*, **218**, 295 (2003).
- [7] T. Yamaguchi, M. Ibe, B.N. Nair and S. Nakao, *J. Electrochem. Soc.* **149**, 1448 (2002).
- [8] K. Kitajima, *Hyoumen*, **19**, 83 (1981) (in Japanese).
- [9] R. Kiyono, Y. Tanaka, O. Sekiguchi and M. Tasaka, *Colloid Polym. Sci.*, **271**, 1183 (1993).
- [10] M. Mulder, "Basic Principles of Membrane Technology, 2nd Ed., Kluwer Academic Pub., Dordrecht / Boston / London (1996) p 36.

(Received October 13 2003; Accepted March 31, 2004)