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Electrical Conductivity and Water-Methanol Uptake of Proton Conducting Nafion®117 Membrane

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The electrical conductivity of Nafion®117 membrane in water-methanol mixture liquid and gas was measured by ac impedance technique and the solvent uptake from the mixture liquid was investigated. In the liquid mixture, the conductivity of the Nafion® film decreased with increasing the methanol content and the activation energy for the electrical conduction ranged from 0.14 to 0.17eV with the negligible dependence on the methanol content. As to the solvent uptake, the Nafion®117 membrane showed the preference for methanol to water. These results indicates that the contribution of methanol to the proton carrier generation is much smaller that that of the water. In the gas mixture, the electrical conductivity of the Nafion® membrane showed no dependence on the gas composition below 20 mol% methanol content.
Key words: Nafion, electrical conductivity, water-methanol uptake

1. INTRODUCTION

Direct Methanol Fuel Cells (DMFCs) have attracted many interests as stationary, portable and vehicle power source due to its simple design and high reliability. DMFCs employ as electrolyte the perfluorosulphonate proton exchange membrane like Nafion®. The polymer membrane, however, is highly permeable to methanol, causing methanol cross-over from anode to cathode during operation. This results in the loss of fuel and cathode depolarization, which finally causes the decrease of power efficiency. To improve this problem, the basic knowledge on the electrochemical properties of the polymer membrane in the presence of methanol should be available. Till now, however, most studies on the polymer electrolyte had been focused on its electrochemical properties in humidified conditions.(for example, Ref. [1-3]) Thus, this work is aimed to construct the database on the electrochemical property of the polymer electrolyte membrane in water-methanol mixed condition. In the present work, the electrical conductivity of Nafion®117 membrane was measured in water-methanol mixture liquid and gas, and water and methanol uptake of Nafion®117 film from the mixture liquid was investigated.

2. EXPERIMENTAL

2.1 Membrane pretreatment

The Nafion®117 membrane from E. I. Du Pont de Nemours and Company has the specification of 0.18mm thickness and 1100 equivalent weight. For conductivity measurement, Nafion® membranes were cut and pretreated in the conventional way [4]. The membranes were boiled in 3% H_2O_2 aqueous solution for 1h, rinsed in boiling deionized water to remove the organic impurity and, subsequently, boiled in 0.5M H_2SO_4 for 1h to make them a protonic form, and finally rinsed in deionized water. After treatment, the membranes were maintained in deionized water.

2.2 Conductivity measurement

In liquid state: The conductivity of Nafion®117 membrane in liquid state was measured by 2-probe ac method as a function of water/methanol mixing ratio and temperature. The pretreated membranes were first submersed in water and methanol mixture liquid for more than 24h to fully saturate the membranes with mixture liquid. The volume ratios of methanol to water in liquid mixtures were 0, 0.2, 0.4, 0.6, 0.8, and 1. The saturated membrane, then, was inserted between two Teflon blocks, in the middle of which cavities were made to keep contacts between membrane and liquid. As electrodes, the blackened Pt foils welded with ϕ0.2mm Pt lead wires were inserted between Teflon block and the membrane, and Teflon blocks were joined with screws. Figure 1(a) illustrates a schematic of a cell after assembly. The whole assembly was submersed in the same water/methanol mixture. Then, the ac impedance was measured using frequency response analyzer (Solatoron Model 1260 H. F. frequency analyzer) combined with potentiostat (Solatoron Model 1286 electrochemical interface) in the frequency ranges from 1Hz to 300kHz. The temperature was controlled using thermostatic water bath in range from 30°C to 70°C.

The conductivity of the membrane,σ, was calculated from the membrane resistance, R , using the equation as

$$\sigma = \frac{1}{R}\cdot\frac{L}{A}, \qquad (1)$$

where L, A are the inter-electrode distance and the area of sample perpendicular to an electric field, respectively. Even though the membrane swelled due to uptake of solvent, its dimensional change was neglected in conductivity calculation.

In gas state: The conductivity of Nafion®117 in gaseous condition was measured by 4-probe ac method as function of water/methanol mixing ratio and relative humidity at 50°C. The pretreated membrane was first fixed to a cell (Fig. 1(b)) and dried in the vacuum oven

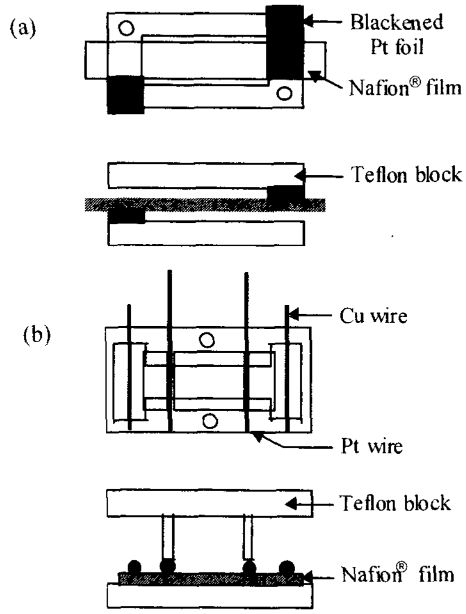

Fig. 1. Schematics of cells for the measurement of electrical conductivity (a) in liquid state, (b) in gas state

at 100°C for 24h. The cell consists of two Cu wires 3 cm apart to feed current to the membrane, and two Pt wires 1 cm apart to measure the potential drop near the center. After drying, the cell was placed in a glass bottle, around which the heating wire was wound to keep the sample at desired temperature. The humidified gas was supplied by flowing the dry Ar gas to a bubbling bottle, which was filled with water-methanol mixture liquid and maintained in thermostatic water bath. The humidity was controlled by varying the temperature of the water bath.

2.3 Measurement of water/methanol uptake from liquid mixture

The amount of absorbed solvent was measured at room temperature as a function of water/methanol mixing ratio. The pretreated Nafion® film was immersed to the liquid mixture for over 24 hr to obtain fully saturated membranes. The wet weight of the film, W_{wet} was measured after the free liquid on the surface of membranes was blotted on a filtering paper. Then, the film was fully dried in a vacuum oven at 100°C for 24h, quickly moved to a weighing bottle and the dry weight, W_{dry} was measured. The amount of solvent uptake, $W_{wet}-W_{dry}$ is normalized to the dry weight of the film, W_{dry}.

3. RESULTS AND DISCUSSION

3.1 Electrical conductivity of Nafion®117

In liquid state: Figure 2 shows a typical impedance spectrum plotted on the complex plane. The highest frequency of this experiment was too low to obtain full spectrum corresponding to the film. Alternatively, the resistance of the membrane was determined from the intercept on the real axis. The position of the intercept was experimentally confirmed to vary by such an extent as the change in sample dimension. The conductivity of Nafion® membrane determined as such was 8.8×10^{-2} Scm^{-1} in pure water at 30°C, which agrees well with the

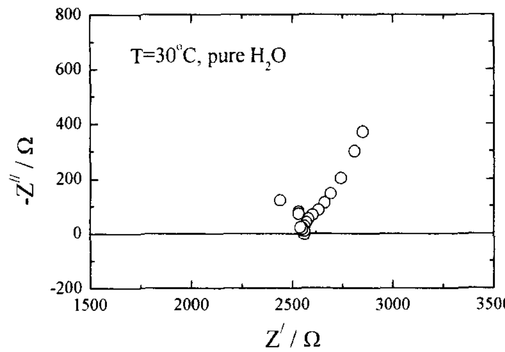

Fig. 2. Typical impedance spectrum of the cell in the liquid mixture; T=30°C in pure H_2O

described in catalogue specification, 8.3×10^{-2} Scm^{-1} at 25°C.

The variation of the conductivity of Nafion® 117 membrane against the volume percent of methanol in the water/methanol liquid mixture was shown in Fig. 3. The conductivity decreased with increasing the methanol content in liquid mixture.

In Figure 4 was represented the logarithms of the membrane conductivity against the inverse temperature at various water-methanol liquid mixture. Figure 4 shows clearly that the electrical conduction in Nafion® membrane is thermally activated process. The activation energy of the electrical conduction, E_a was obtained by fitting the result to the Arrhenius relation,

$$\sigma = A\exp\left(-\frac{E_a}{kT}\right). \tag{2}$$

The values of E_a's were listed in Table 1 along with those of the pre-exponential factor, A. The E_a's have the value of about 0.15eV. It is well known that the proton conduction in the low temperature proton conductor takes place via the Grothuss mechanism. In this mechanism, the activation energy of the proton conduction ranges from 0.15eV to 0.42eV [5]. The good agreement of the obtained E_a with those expected

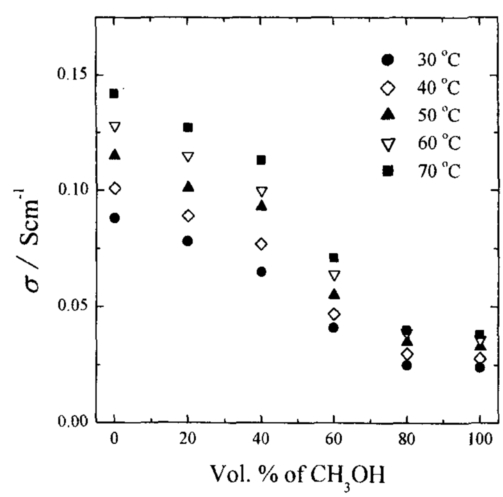

Fig. 3. Conductivity against volume % of methanol in liquid mixture.

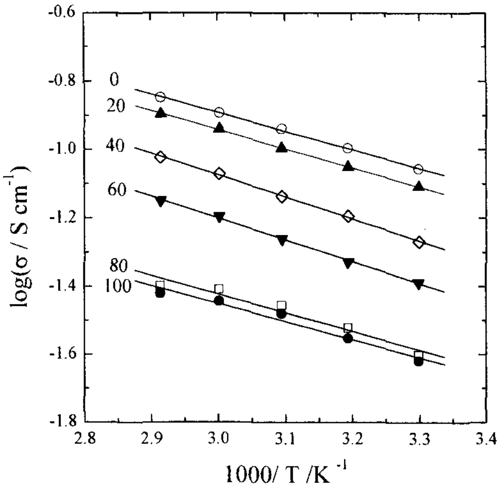

Fig. 4. The logarithms of conductivity against the inverse temperature of the water-methanol liquid mixture. The numerals left the line indicate volume % of methanol in liquid mixture.

suggests the Grothuss mechanism for conduction in Table 1. Activation energy, E_a for the electrical conduction and pre-exponential factor, A in Eq. (2) as function of the methanol content in liquid mixture

Vol. % of CH_3OH	E_a / eV	Log (A/Scm^{-1})
0	0.145	-0.540
20	0.145	-0.557
40	0.168	-0.639
60	0.141	-0.636
80	0.151	-0.716
100	0.122	-0.677

Nafion® 117 in the liquid state.

According to Table 1, the E_a shows no significant dependence on the methanol content in liquid mixture. This indicates that the decrease in conductivity with increasing methanol content shown in Fig. 3 may be due to the decrease in concentration of the charge carrier, proton with replacement of water by methanol.

In gas state: Figure 5 shows the logarithms of the film conductivity against the relative humidity (R.H.). The liquid mixtures used to introduce the gas mixture were pure water and 20 mol% methanol, respectively. It is likely that the conductivity in both conditions shows no difference, which is different from the results in liquid state. Further experiment is needed to elucidate this observation.

3.2 Water and methanol uptake of Nafion® membrane from liquid mixture.

It has been well known that the physical and transport properties of polymer membrane electrolyte are closely related to the solvation process [6]. In Fig. 6 was shown the amount of liquid absorbed into Nafion® membrane from liquid mixture. The solvent uptake shows a maximum around in 80 vol% methanol liquid mixture.

The amount of solvent uptake has conventionally been expressed by the number of solvent per sulphonate ionic group calculated as :

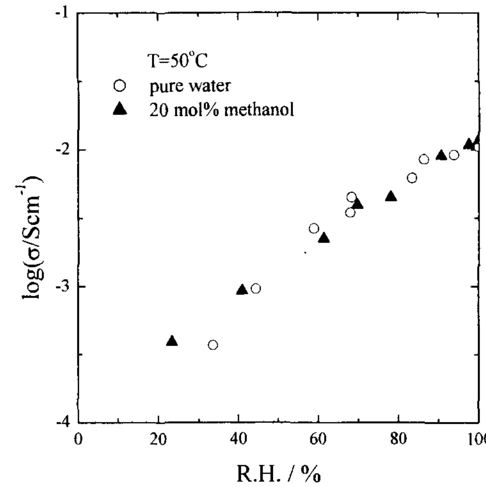

Fig. 5. The logarithms of conductivity against the relative humidity at T=50°C. The composition in the text box indicates that of the liquid mixture used to introduce the gas mixture.

$$N(mol_{solvent}/mol_{SO_3H}) = \frac{(W_{wet} - W_{dry})}{M_{eq}} \cdot \frac{EW}{W_{dry}}, \quad (3)$$

where M_{eq} is the equivalent molar weight of liquid mixture absorbed and EW denotes the equivalent weight of membrane. The values of N's are 19 and 29 for the water-saturated and methanol-saturated membrane, respectively. This result means that the amount of solvent uptake in the methanol-saturated membrane is 1.6 times larger than that in the water-saturated one. This result is different from the reported by E. Skou *et al.* [7] that Nafion®117 has no preference for either water or methanol. It would be proper to mention that, in the present stage, the normalization of solvent uptake per sulphonate group can not be conducted for the liquid mixture saturated membrane because the composition of the absorbed liquid in the membrane is not known.

In Fig. 3 was noted the decrease of the conductivity with increasing the methanol content in the liquid

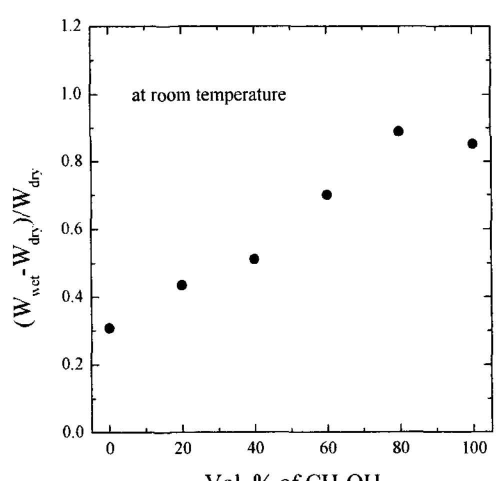

Fig. 6. The amount of solvent uptake in Nafion® 117 from the water-methanol liquid mixture.

mixture. This indicates together with the result of solvent uptake that, even though the Nafion® film prefer methanol to water, the contribution of methanol to the generation of the proton carrier is much smaller than that of the water.

4. SUMMARY AND CONCLUSION

Electrical conductivity of Nafion®117 membrane in water-methanol mixture liquid and gas was measured by ac impedance technique, and solvent uptake from the mixture liquid was investigated. In the liquid mixture, the conductivity of the Nafion® film decreased with increasing the methanol content. The activation energy for the electrical conduction was 0.14-0.17eV with negligible dependence on the methanol content. The solvent uptake in the methanol-saturated membrane is 1.6 times larger than that in the water-saturated one, and the solvent uptake showed a maximum around 80% methanol liquid mixture. It could be concluded from the above results that the contribution of methanol to the proton carrier generation is much smaller than that of the water. In the gas mixture, the electrical conductivity of the Nafion® membrane shows no dependence on the gas composition below 20 mol% methanol content.

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