Permeation Evaluation of Charged-Membranes Prepared for Direct Methanol Fuel Cell

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Direct Methanol Fuel Cells (DMFCs) are promising power sources for vehicular and portable applications. In this work, membranes for the DMFC electrolyte were prepared and evaluated to suppress the methanol crossover flux which lower the efficiency of DMFC. The permeation control by the method for modifying fixed charge of surface and inside of a Nafion membrane was tried.[1] The methanol permeability for as-received Nafion® 117 (Aldrich), Aciplex®-S (Asahi Chemical) and modified Nafion were evaluated.

Table 1 shows experimental conditions for modification. For charging Nafion membranes with long-chained counter ion, each sample was boiled for 10min and immersed in tetraoctylammonium bromide $(C_8H_{17})_4NBr$ (Aldrich) or tetramethylammonium bromide $(CH_3)_4NBr$ (Aldrich) solutions for 1 min or 24 h. Partial modified samples were prepared by using 0.1 M HCl with $(C_8H_{17})_4NBr$ or $(CH_3)_4NBr$ solutions for the conductivity improvement. Moreover, sandwich-type membranes were also investigated. A modified membrane was put by a as-received Nafion membrane from both sides, and then a sandwich-type membrane was prepared by heat treatment. The microstructure in as-received Nafion and modified Nafion membranes were evaluated by a small angle X-ray diffraction (SAXRD) measurement using a RIGAKU RU300. Figure 1 shows a schematic diagram of the experimental apparatus. The sample was set in the H-type cell, and 5 M methanol and 0.5 M sulfuric acid mixed solution were put into one side, and the sulfuric acid was put into the other side at 298 K and 343 K. The fixed current was run using the electrochemistry measuring system (HOKUTO DENKO HZ-3000), and quantitative analysis of the permeate methanol was carried out by the gas chromatography (SHIMADZU GC-14B). Conductivity of the membranes measured in the 0.5 M sulfuric acid solution at 1 kHzAC.

The methanol crossover flux for modified Nafion membranes were lower than that for Nafion, and the number of. methanol molecules following the proton calculated from the results of the methanol crossover flux decreased by 24 % with Methyl-1 at 298 K. The effect of cluster diameter on methanol crossover flux at 298 K is shown in Fig. 2 The cluster diameter was estimated from the results of SAXRD measurement. The methanol crossover flux was decreased with reducing the cluster diameter. In case of immersing in 0.1 M $(C_8H_{17})_4NBr$ for 1min (Octyl-1), the cluster diameter was reduced to 42.8 Å and the flux was decreased less than 1/10. The relationship between conductivity and flux at 343 K are shown in Fig. 3, and the region surrounded in the line means the target area as a temporary standard. The conductivity was not decreased drastically and the permeate flux was suppressed by preparing the sandwich-type modified membrane. The proton conductivity was 4.2 S/m and the permeate flux was decreased 43 % for Octyl-s1.

1) S. P. Kusumocahyo and M. Sudoh, J. Membr. Sci., 161 77 (1999).

Table 1 Experimental conditions for modification.

Abbre-viation	$(C_8H_{17})_4NBr$ [mol/l]	$(CH_3)_4NBr$ [mol/l]	HCl [mol/l	Treated temp.	Treated time
Modified membranes					
Octyl-1	0.1	-	-	298	1min.
Octyl-2	0.01	-	0.1	298	1min.
Octyl-3	0.1	-	-	343	1min.
Octyl-4	0.1	-	-	298	24h.
Methyl-1	-	0.1	0.1	298	1min.
Sandwich-type modified membranes					
Octyl-s1	0.1	-	-	298	1min.
Octyl-s2	0.01	-	0.1	298	1min.
Octyl-s3	0.1	-	-	343	1min.

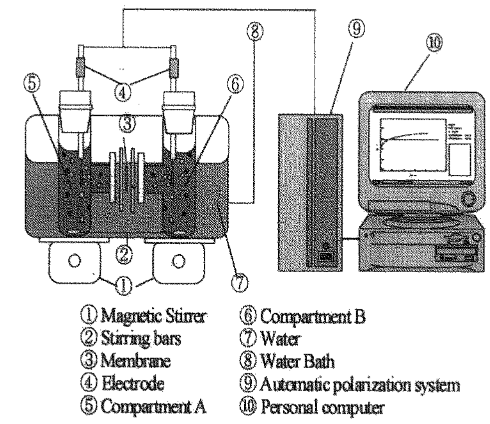

Fig. 1 Schematic diagram of the experimental apparatus.

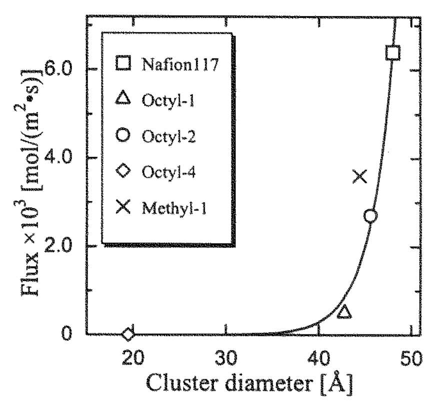

Fig. 2 Effect of cluster diameter on methanol crossover flux at 298 K.

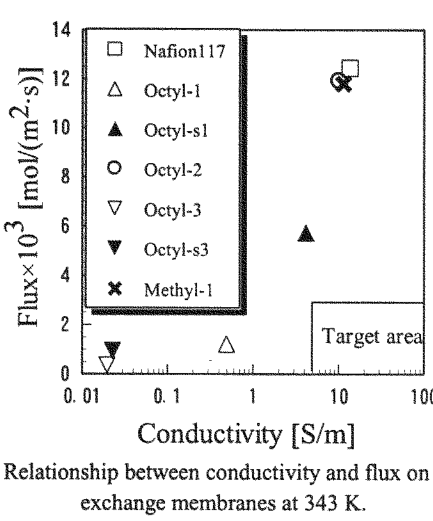

Fig. 3 Relationship between conductivity and flux on proton-exchange membranes at 343 K.