Preparation of Proton Conductive Polymer/ Ion Exchange Fiber Sheet Composite Membranes

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Proton conductive polymer membranes such as perfluoro-sulfonic acid membranes have been noticed as polymer electrolyte membranes (PEM) for the Polymer Electrolyte Fuel Cell (PEFC) and the Direct Methanol Fuel Cell (DMFC). However, perfluoro-sulfonic acid membranes have some disadvantages using as PEM because of the high cost of membranes and the low operational temperature of the fuel cell that results in electrode poisoning of carbon monoxide (CO) [1]. Therefore, it is required that the membranes are prepared in low cost, and the fuel cell operates over 100 °C for reducing electrode poisoning due to CO [2].

In this study, we selected polysulfone (PSf), which is thermal resistance engineering plastics and its glass transition temperature is approximately 190 °C, and provided sulfonic acid into the structural unit of it (sulfonic acid concentration 34.6 % to 95.4 %). We investigated the fabrication of membranes and proton conductivity of these materials. Moreover, sulfonated PSf (SPSf)/ion exchange fiber (IEF) sheet composite membranes were investigated for the purpose of improving membrane mechanical strength and proton conductivity.

SPSf was synthesized from the commercial PSf Udel® (Solvay Advanced Polymers) and chlorosulfonic acid (Kanto Chemical Co., Inc.) [3]. Then, SPSf was dissolved in N,N-dimetylacetamide (Tokyo Kasei Kogyo Co., Ltd.) to prepare casting solution of SPSf, and was cast on petri dish to prepare SPSf membranes. On the other hand, SPSf/IEF sheet composite membranes were prepared by immersing of IEF sheet into SPSf casting solution. Proton conductivity was measured by using AC impedance spectroscopy technique at 80 °C in 80 % relative humidity.

Proton conductivity of SPSf membranes increased with increasing sulfonic acid concentration. That of composite membranes (IEF sheet: 70 % blended sulfonic acid bonded polyvinylalchol (PVA) fiber sheet) also increased with increasing sulfonic acid concentration, and it was higher than that of SPSf membranes (Fig. 1). On the other hand, proton conductivity of composite membranes (IEF sheet: 70 % blended sulfonic acid bonded PVA sheet) increased with decreasing SPSf concentration of casting solution (Fig. 2).

In addition, we investigated the effect of ion exchange ability in the sheet for the proton conductivity of composite membrane. Two kinds of sheet were used. One type of IEF sheet was the strong acid bonded PVA (PVA-SO_3H) sheet which contains 60 % blended sulfonic acid, and the other type was the weak acid bonded PVA (PVA-COOH) sheet which contains 60 % blended carboxylic acid. Proton conductivity of composite membranes using IEF sheet based on PVA-SO_3H sheet (1.82×10^{-1} S/cm) was higher than that of composite membranes using IEF sheet based on PVA-COOH sheet (1.13×10^{-1} S/cm). From these results, it is considered that the membranes which compose SPSf and IEF sheet are expected as PEM for PEFC.

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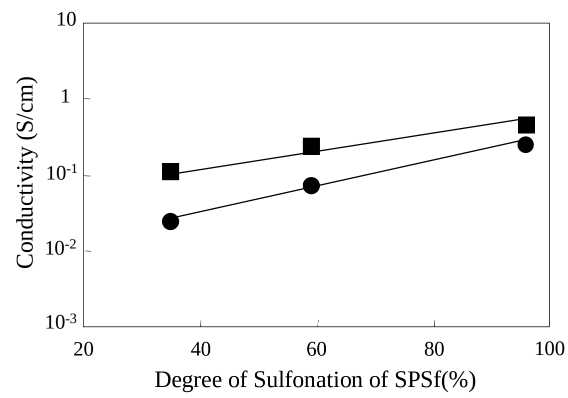

Fig. 1 Conductivity of SPSf membranes and composite membranes versus degree of sulfonation of SPSf.
●: SPSf membranes, ■: composite membranes, SPSf concentration of casting solution: 10 wt%, IEF sheet: 70 % blended sulfonic acid bonded PVA sheet, Humidity: 80 %, Temperature: 80 °C.

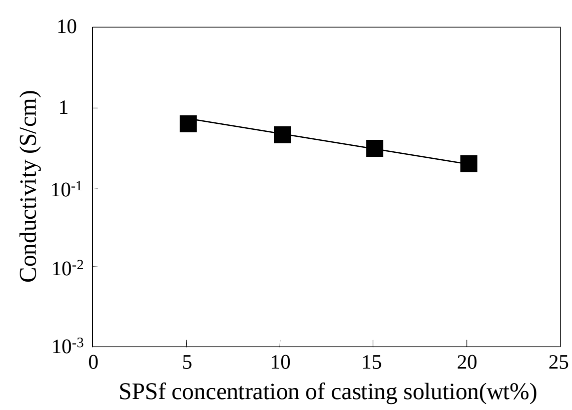

Fig. 2 Conductivity of composite membranes versus SPSf concentration of casting solution.
Degree of sulfonation of SPSf: 95.4 %, IEF sheet: 70 % blended sulfonic acid bonded PVA sheet, Humidity: 80 %, Temperature: 80 °C.