ORGANIC – INORGANIC COMPOSITE MEMBRANE FOR POLYMER ELECTROLYTE MEMBRANE FUEL CELL

Yong Gun Shul *, Hyun Jong Kim, Ji Eun Ahn, Hak Soo Han

Dept. Chem. Eng., Yonsei Univ., Seodaemun-Gu, Shinchon-Dong, 134 Seoul, Korea
*Corresponding author
Fax: 02-312-6401 E-mail: shulyg@yonsei.ac.kr

ABSTRACT

Mesoporous zeolite - heteropolyacid – polymer hybrid membrane was prepared by sol-gel processes to make a proton conducting membrane. The crystallinity of mesoporous zeolite in composite membrane was increased with contents of heteropolyacid. Proton conductivity obtained from impedance measurements increases with contents of heteropolyacid, about 10^{-3} S/cm in ca. 1.5 wt% heteropolyacid.

INTRODUCTION

The proton conductor has been studied in fields of inorganic and polymer materials because of the technological potential for application in fuel cells, hydrogen separation, water electrolysis and other electrochemical devices[1, 2]. Especially, zeolite materials can give proton or electron conducting route, water path, mechanical stability for solid electrolyte at high temperature, because it has rigid porous channel structure. Therefore, zeolite has attracted increasing attentions for polymer electrolyte membrane fuel cell (PEMFC). However, applications of zeolite materials for PEMFC are quite limited due to the low ionic conductivities and poor material processibility.

The sol-gel hybrid inorganic-organic matrix of our membrane is constructed by using a reactive silicon alkoxide (tetramethyl orthosilicate) precursor containing heteropoly acid and poly(vinyl alcohol) for application of direct methanol fuel cell(DMFC). Heteropoly acids(HPA)-phosphotungstic acid(PWA) and silicotungstic acid(SiWA)-have showed high proton conductivity at room temperature from 0.02 to 0.1 S/cm[3] and a high solubility in water and in many organic solvents. PWA in aqueous solution has been already used in low-temperature fuel cells[4] with an excellent performance, but the risk of its continuous leakage during cell operation is not negligible. To overcome this problem and to increase the lifetime of the cell, PWA or PMoA[5] was immobilized in polymer and silica gel[6, 7].

In our study, Silica mesoporous material/heteropoly acid (HPA)-poly(vinyl alcohol) (PVA) hybrid membrane was prepared by sol-gel processes to make a proton conducting membrane. The method involves stabilization of HPA in inorganic-organic hybrid membrane. And we crosslinked PVA modified with sulfosuccinic acid(SSA), which contains SO_3OH by heat treatment.

EXPERIMENTAL

To prepare mesoporous silica, tetramethoxysilane was partially hydrolyzed by a substoichiometirc amount of water under acid conditions for 2hr. Various concentrations of phosphotungstic acid are used as proton conductor in the mesoporous silica matrix. cetyltrimethyl-ammoniumchloride as a template for the formation of mesoporous structure was mixed with poly(vinyl alcohol) solution. Then silica precursor was dropped into the mixture of surfactant and poly(vinyl alcohol) solution with stirring very vigorously. After aging in room temperature, we prepared mesoporous zeolite – heteropolyacid – poly(vinyl alcohol) hybrid membrane by casting onto a glass plate.

X-ray diffraction (XRD) patterns of mesoporous silica /HPA-PVA hybrid membrane were obtained with a Cu-Kα X-ray source using a Rigaku instrument at room temperature. Scanning Electron Micrograph (SEM) images of the membranes were taken to show to the surface and cross-section with JEOL instrument. The proton conductivity was measured by impedance spectroscopy using a Autolab(AUT30.FRA2) spectrometer working in the frequency range between 0.1 and 100 000 Hz. The measuring cell consisted of two electrodes made of platinum. The membrane to be tested was placed between the two electrodes. Two electrodes were connected through platinum wires to a frequency response analyzer. The conductivity was calculated from the impedance data, using the relation.

$$\sigma = d/RS$$

where d and S are the thickness and area of the membrane, respectively, and R was derived from the low intersect of the high-frequency semicircle on a complex impedance plane with the Re(z)-axis. This was performed in a 0.1M HCl electrolyte solution at a temperature of 25°C.

Fuel cell performance was measured by unit cell test station with cross-sectional area of 1cm^2 for direct methanol fuel cell. The used fuel cell consisted of two housings containing a variable flow field stamp in the center. The flow field consisted of channels, which were parallel oriented to the inlet and outlet for the gases, respectively, methanol. The membrane was placed between the two housings. On each side layer was attached with its catalyst side facing the membrane.

RESULTS AND DISCUSSION

Mesoporous silica/heteropoly acid (HPA)-poly(vinyl alcohol) (PVA) hybrid membrane was prepared successfully. To make a membrane, optimal point of the meoporous silica/HPA-PVA hybrid solution for membrane casting was about 4 hours after mixing. For convincing the mesoporous structure, crystallinity of mesoporous silica/HPA-PVA/SSA hybrid membranes were measured by X-ray diffraction patterns. As shown in figure 1, the prepared membranes showed typical low angle (110) diffraction associated with the nature of mesoporous structure. And the peaks intensities of mesoporous material increase as increasing the HPA loading. It suggests that crystallinity of mesoporous structure is influenced by the HPA contents.

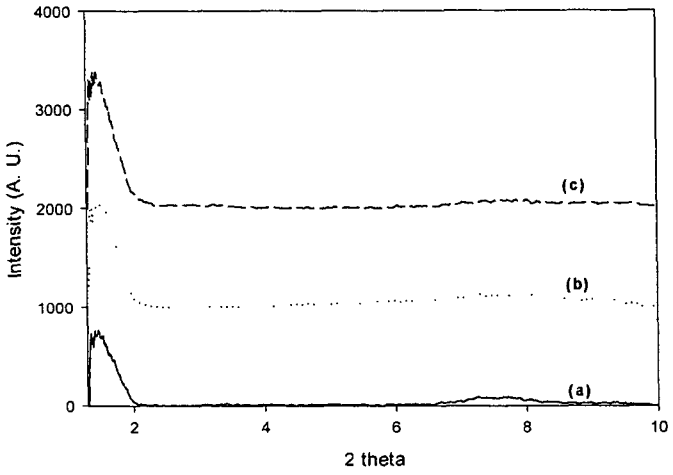

Figure 1. X-ray diffraction patterns of mesoporous silica/HPA-PVA membranes with various contents of SiWA ; (a) 0.49 %, (b) 0.98 %, (c)1.47 %

Figure 2 shows proton conductivities of hybrid membrane containing HPA. The conductivity increased from 9.130 $\times 10^{-4}$ to 2.930 $\times 10^{-3}$ S/cm with increasing the HPA contents from 0.49 % to 1.47 %, respectively. It also shows that the conductivity changes with composition of HPA. It is noteworthy that the HPA contents of mesoporous film were limited up to ca. 1.5 % since further increase in HPA contents resulted in mesoporous silica in powdery form. Conductivity of PWA component is some little change which is 1.80×10^{-4} S/cm in proportion to contents as compared with that of SiWA which is 5.87 $\times 10^{-4}$ S/cm. Lavrencic Stangar et al. reported that the better conductivity of SiWA/organically modified silica gels can be explained by higher proton concentration in the material compared to PWA/organically modified silica. But they tested the conductivity of HPA/ organically modified silica gels containing HPA content from equal mole up to 50 times in proportion of silica contents. HPA content range of our materials is from 0.49 to 1.47 %. If one can increase the HPA contents up to 30-50 % by wt. in mesoporous structure, high proton conductive membrane will be introduced to DMFC successfully. Further work is underway now. At present the conductivity of 10^{-3} S/cm order is due to the loading of HPA in the mesoporous matrix enabling transport of protons through mesoporous pore.

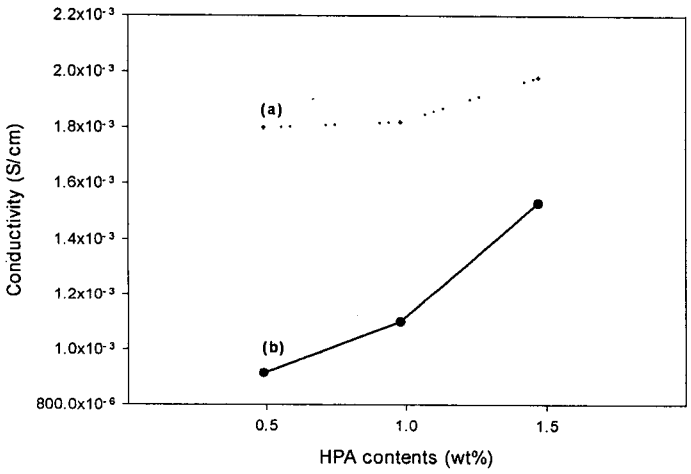

Figure 2. Conductivity changes of mesoporous silica/HPA PVA/SSA membranes as a function of HPA contents ; (a) PWA, (b) SiWA

Preliminary results of the fuel cell measurements carried out with the experimental fuel cell setup are presented figure 3. The current-voltage characteristics were obtained for methanol/oxygen fuel cell utilizing the mesoporous silica-PVA hybrid membranes which contains 1.47% of HPAs. The experiments were performed at 80 °C. The highest current densities obtained for the fuel cell studied were approximately equal to 16mA/cm^2 for PWA and 6mA/ cm^2 for SiWA.

REFERENCES

1. Kesege, C. T., Leonowicz, M. E., Vartuli, J. C., Beck, J. S., *Nature*, 359,710,1992
2. Beck, J. S. et al., *J. Am. Chem. Soc.*, **114**,10834,1992
3. U. Mioc, M. Davidovic, N. Tjapkin, Ph. Colomban, A. Nobak, *Solid State Ionics*, **46**, 103 (1991)
4. P. Stati, A.S. Arico, S. Hocevar, V. Antonucci, *J. New Mater. Electrochem. Syst.*, **1**, 1 (1998)

5. Min Woo Park, Jae Choon Yang, Hak Soo Han, Yong Gun Shul, Tea Hee Lee, Yong Il Cho, *Denki Kagaku*, **64**, 743 (1996)
6. I. Honma, Y. Takeda, J.M. Bea, *Solid State Ionics*, **120**, 255 (1999)
7. P. Staiti, S. Freni, S. Hocevar, *J. Power Source*, **79**, 250 (1999)

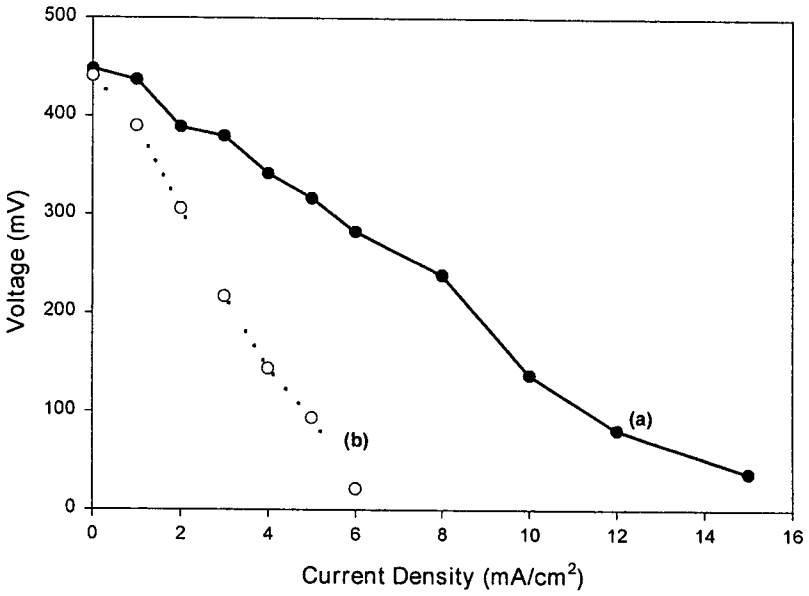

Figure 3. Polarization curves for mesoporous silica/HPA-PVA membrane from DMFC measurements at 80 °C ; (a) PWA, (b) SiWA