

# Improvement of Surface Proton Conductivity for Three-Dimensionally Ordered Macroporous Silica Membrane

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## Introduction

Direct methanol fuel cells (DMFCs) have been expected as portable power sources for various kinds of mobile tools because they can utilize methanol without reforming equipment of methanol to hydrogen. However, DMFC has some problems for practical applications. For example, it is necessary to restrain methanol cross-over caused by swelling of ion exchange membrane.<sup>[1]</sup> Cross-over leads to a voltage drop of fuel cell and lowers fuel utilization.<sup>[2]</sup> Recently, we reported a composite electrolyte membrane prepared by using an ordered porous silica membrane whose pores were filled by gel polymer electrolyte. It exhibited an excellent low methanol cross-over due to a suppression of polymer expansion by the silica matrix.

It is well known that silanol groups (Si-OH) react with various organosilane compounds. So, one can introduce desired properties on glass surfaces. In this study, we developed new conductive path for protons by surface modification of porous silica membrane.

## Experimental

Three dimensionally ordered porous silica membrane was prepared on a membrane filter by filtration of suspension containing colloidal polystyrene beads and silica particles at optimized ratio. After filtration, the polystyrene/silica membrane was heated at 450 °C to remove polystyrene beads. Then, the obtained porous silica membrane was sintered to improve a mechanical strength at 880 °C for 1 hour and then at 980 °C for 10 min. The surface modification of the ordered porous silica membrane was performed by oxidation method or direct reaction method. In order to increase silanol group which is reactive point to introduce sulfonic acid group on silica surface, a hydrothermal treatment was conducted at 170 °C for 3-12 hours. In the case of oxidation method, porous silica membrane was soaked for 24 h in 2.6 wt% 3-mercaptopropyltrimethoxysilane aqueous solution in order to introduce mercapto groups (-SH) on silica surface. Then, SH groups was converted to sulfonic acid groups (SO<sub>3</sub>H) by oxidation with H<sub>2</sub>O<sub>2</sub> solution at 70 °C for 2 hour. In the latter method, silica membrane was refluxed in toluene solution containing 0.12 mol dm<sup>-3</sup> 1,3-propanesultone for 48 hours. The amount of silanol groups was analyzed by Fourier transform infrared spectroscopy (FT-IR). The amount of S atom was evaluated with energy dispersive X-ray spectroscopy (EDX). From X-ray photoelectron spectroscopy analysis (XPS), it was confirmed that detected S atom was derived from sulfonic acid groups or mercapto groups.

## Results and Discussion

**Figure 1** shows FT-IR spectra of the porous silica membrane obtained before and after the hydrothermal

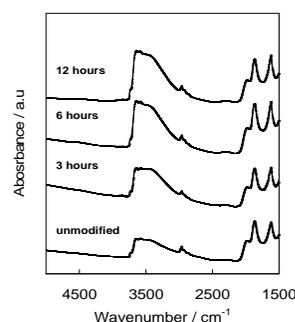
treatment. Each spectrum shows a broad peak at 3200-3700 cm<sup>-1</sup> due to silanol group. The peak intensity of silanol group was increased with increasing duration for hydrothermal treatment time. **Figure 2** shows EDX spectra of sulfonated silica membranes modified by (a) oxidation method and (b) direct reaction method. The larger amount of S atom, about 9.9 atom %, was detected in the case of silica membrane prepared by direct reaction method. **Figure 3** shows XPS spectra for S 2p of sulfonated silica membranes. Each spectrum had a peak at 168 eV which was attributed to S atom in sulfonic acid groups. A peak around 163 eV due to mercapto groups was not detected in both cases. Further optimizations of preparing conditions are now underway. The proton conductivity of composite electrolyte membrane with gel polymer and this sulfonated silica membrane will be also reported.

## Acknowledgement

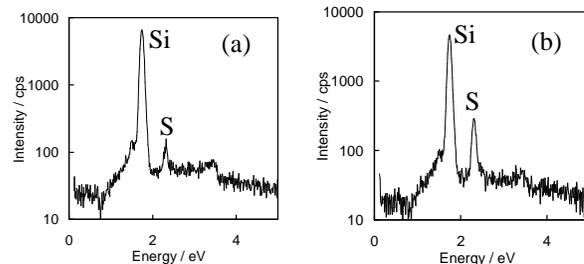
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## References

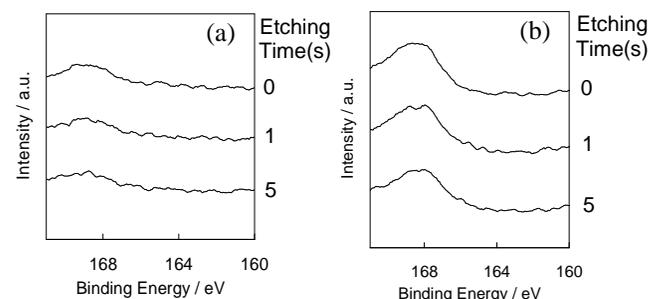
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**Figure 1.** FT-IR spectra of porous silica membranes of various hydrothermal treatment time.



**Figure 2.** EDX spectra of sulfonated silica membranes modified by (a) oxidation method, and (b) direct reaction method



**Figure 3.** XPS spectra for S 2p of sulfonated silica membranes by (a) oxidation method, and (b) direct reaction method.