Sulfonic group를 갖는 PVA/silica hybrid membrane의 제조 및 응용

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Preparation and application of PVA/silica hybrid membrane containing sulfonic group

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1. Introduction

A direct methanol fuel cells (DMFCs) using polymer electrolyte membranes are one of the most attractive power sources for a wide range of application from vehicles to portable utilities due to the stable operation at a rarely low temperature, the high energy generation yield and energy density, the simplicity of system. The preparation of hybrid organic-inorganic composites has attracted much attention because such hybrids may show controllable properties such as optical, electrical and mechanical behaviors by combining the properties of both organic polymer and inorganic compound [1,2]. As hydrophilic polymer materials swell in aqueous media, the membranes would loose their mechanical resistance if they were too hydrophilic. A compromise needs to be found for each type of application by balancing hydrophilicity -hydrophobicity. One way to do this is to copolymerize monomers with hydrophilic and hydrophobic groups. Several organic groups like

hydroxyl, amine, carboxylate, sulfonate, quaternary ammonium can be used to impart hydrophilicity to a polymer[3]. However, the procedure used to incorporate these hydrophilicity groups in their structures were generally not simple and the reaction conditions are sometimes extreme. Thus, the synthesis of sulfonated polymer using monomer containing sulfonic group is the most favorable owing to easily controlling.
In this study, the PVA/SiO_2 nanocomposites hybrid membranes containing sulfonic groups have been synthesized through sol-gel processes in order to improve ion conductivity and reduce the methanol permeability.

2. Experimental

Materials and Preparation of hybrid Membrane

PVA was dissolved in pure water at 90°C with a concentration of 10wt% and was stirred constantly to ensure homogeneity.
A homogeneous tetraethyl orthosilicate (TEOS) mixture was prepared using hydrochloric acid, sulfosuccinic acid (SSA) and TEOS. TEOS solution was dropped to PVA solution while stirring to homogeneous mixtures. The homogeneous solution was poured into a Petri dish. The membranes were allowed to dry in air at room temperature, and completely dried membranes were then peeled off. The dried membranes were heated in a thermostated oven at 120°C for 1hr. The PVA/SiO_2 hybrid film containing sulfonic group was obtained.

3. Results and discussion

Organic-inorganic hybrids, based on PVA/SiO_2 hybrid membranes containing sulfonic acid groups, were successfully prepared via in situ polymerization of TEOS and sulfosuccinic acid using the sol-gel process. The hybridization of TEOS and SSA proceeds through an esterification reaction between the silanol groups of the hydrolyzed TEOS and OH groups of SSA. The total water content decreased with increasing SSA content up to 20 wt%, but increased at 25 wt% SSA.

This result indicated that an increase in the crosslinking density of the membranes up to 20 wt% SSA makes the polymer structure more compact and decrease free volume. The free volume decreased and SO_3H content increase with increasing SSA content. The water content more depend on crosslinking density rather than SO_3H content up to 20 wt% SSA. But, from 20 wt%, the water content depend on SO_3H content. The prepared ion exchange membranes at each preparation condition possessed the IEC in the range of 0.2 ~ 1.02 meq./g-dry membrane. These results confirmed that experimental IEC values by a titration fit well. The ion conductivity of the membranes containing equilibrated water was measured as a function of the SSA concentration and temperature. As shown in Fig. 1, the conductivity decreased with increasing SSA content up to 20 wt%, but increased at 25 wt% SSA. This behavior shows the same tendency of water content

4. References

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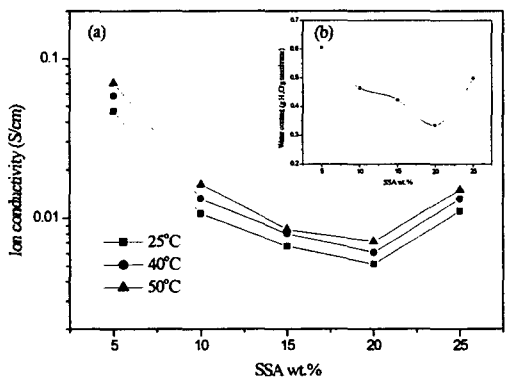

Fig. 1 (a) ion conductivity versus SSA concentration (b) water content versus SSA concentration