

술폰화 Poly(phthalazonone ether sulfone ketone) (PPESK)/실리카막의 제조 및 특성

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Preparation and Characterization of Sulfonated Poly(phthalazonone ether sulfone ketone) (PPESK)/Silica

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1. Introduction

A direct methanol fuel cells (DMFCs) using polymer electrolyte membranes has gained much interest over the last decade [1-2]. Most DMFC research has concentrated on polymer electrolyte membrane fuel cells (PEMFC) fed directly with methanol [3].

The PPESK family of polymers has high glass transition temperatures and excellent physical properties and thermostability. Membranes made from PPESK have shown good separation and permeation properties for gas and liquid separation. Sulfonated PPESKs (SPESK) has been prepared from previously synthesized polymers to improve the polymers' hydrophilicity and thereby utilize this type of polymer for membranes for application in ion exchange membrane [4].

In the operation of a DMFC, membrane hydration is critical to the fuel cell performance and influences proton conductivity. The state of water is generally defined as follows[5]: (a) nonfreezing bound water, water that is strongly bound to the polymer chain. (b) freezing bound water, water that is weakly bound to the polymer chain or interacts weakly with nonfreezing bound water and displays relatively broad melting endotherms. (c) free

water, water that is not intimately bound to the polymer chain and behaves like bulk water.

In this study, the proton exchange membranes were prepared using PPESK as the base materials. The introduction of sulfonic acid group into polymer matrix was achieved by the sulfonation with concentrated sulfuric acid under a variety of conditions. Here, we might expect that the introduction of sulfonic group might lead to both high proton conductivity. The state of water in membrane was quantified by differential scanning calorimetry (DSC) and water vapor sorption.

Their water swelling, ion exchange capacity, proton conductivity and methanol permeability were investigated in an attempt to characterize membranes for DMFC application.

2. Experimental

Polymer used in this study was PPESK ($M_w = 39000$; Polymer New Material Co., Ltd. China). The PPESK random copolymer used in this study has a sulfone/ketone ratio of 1:1. PPESK was dried in a vacuum oven at 120°C for 24h. PPESK and concentrated sulfuric acid were placed in a three-neck reaction vessel equipped with a mechanical stirrer. SPPEKs with different degrees of sulfonation were obtained at certain reaction temperatures (60°C) and times (6-50hr). The polymers were precipitated in ethanol and then filtered. The polymers were washed with ethanol/water to remove acid until pH was neutral, then swelled and washed with water. All the polymers were filtered and then dried in a vacuum oven at 120°C for 24hr.

Sulfonated PPESK membrane was obtained by solution casting methods. The sulfonated polymer (10wt%) was dissolved in NMP. The sulfonated polymer solution was poured into a glass plat. The sulfonated PPESK solution was poured into a glass plat. Freshly cast films were initially heated at 80°C for 24h, then 100°C for 24h. A homogeneous tetraethyl orthosilicate (TEOS) mixture was prepared using HCl, H_2O and TEOS. TEOS solution was dropped to SPPEK solution while stirring to homogeneous mixtures. The homogeneous solution was poured into a Petri dish.

3. Results and discussion

All the sulfonated membranes have higher inherent viscosity than the PPESK, probably because the introduction of $-\text{SO}_3\text{H}$ groups leads to enhancement of interchain interactions with a consequent higher resistance to the stretching of the main chains. The prepared proton exchange membranes at each preparation condition possessed the IEC in the range of 0.3 - 1.1 meq./g-dry membrane. The IEC values increased with the sulfonation degree of PPESK due to the increasing charged portion ($-\text{SO}_3\text{H}$) in membranes.

The freezing bound water and non freezing bound water is affected by interactions with the polymer chain. However, the free water is seemingly unaffected by the polymer matrix. Therefore, we expected that the water content would be maintained in high temperature due to high freezing bound water content and also, the proton conductivity would be maintained in high temperature. The water content of the membranes decreased in the order freezing bound water > free water > non freezing bound water as shown Fig 1.

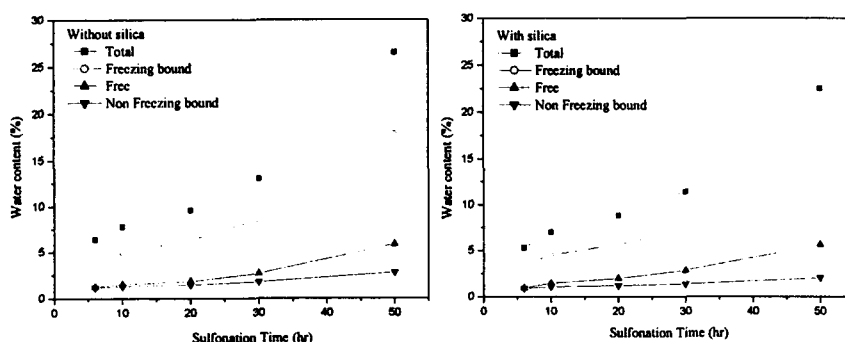


Fig. 1. State of water in SPPEK membranes

Water vapor sorption properties of solid polymer electrolyte membranes have significant effects on their proton conductivity and are very important in view of their application in polymer electrolyte fuel cells. When a small amount of water is absorbed by the polymer, the water molecules primarily associate with the polar and ionic groups present on the polymer chain. At a certain amount of absorbed water, the polar and ionic groups are saturated with water. This saturated water is non freezing bound water. Water absorbed in

amounts higher than this saturation level will have a lower degree of interaction with the polymer and will be consequently freezable. This absorbed water is freezing bound water. After freezing bound water is absorbed, water absorbed is free water. Therefore, we expected that the distinguish between diffusion coefficients of state of water will be possible. As shown Fig. 2, the sorption ratio curve of SPPEK 6 at RH 90 was shown three slopes. The first slope (a) is water vapor sorption due to non freezing bound water that is bound by hydrogen bonding with SO_3H . The second slope (b) is due to freezing bound water that is bound by hydrogen bonding with neighboring water molecules. Last slope (c) is due to free water that is not bound by hydrogen bonding. The highest diffusion coefficient and water absorbed content is shown in freezing bound water (b).

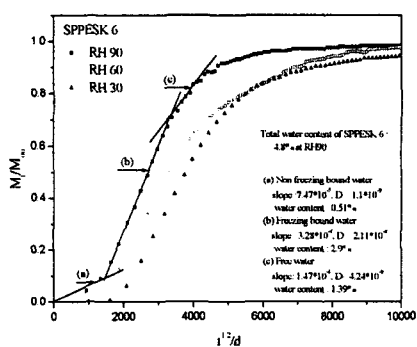


Fig. 2 Water vapor sorption

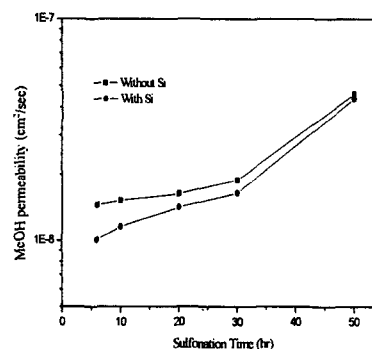


Fig. 3 Methanol permeability

The water vapor sorption of the membranes decreased in the order freezing bound water > free water > non freezing bound water. This result is corresponding with the state of water test using DSC.

The proton conductivity of sulfonated PPESK membranes are in the range from $10^{-3} \sim 10^{-2}$ S/cm. It was found that proton conductivity was dependent on the sulfonation degree due to hydrophilic group (SO_3H) and state of water. In particular, the silica particle embedded in crosslinked polymer matrix was act as a methanol barrier by hindering pathway to pass methanol molecules. Consequently, methanol permeability reduced without lost proton conductivity as shown in Fig. 3.

References

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