

Organic-inorganic Nano Composite Membranes of Sulfonated Poly(Ether Sulfone-ketone) Copolymer and SiO₂ for Fuel Cell Application

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Abstract

Novel bisphenol-based wholly aromatic poly(ether sulfone-ketone) copolymer containing pendant sulfonate groups were prepared by direct aromatic nucleophilic substitution polycondensation of 4,4-difluorobenzophenone, 2,2'-disodiumsulfonyl-4,4'-fluorophenylsulfone (40mole% of bisphenol A) and bisphenol A. Polymerization proceeded quantitatively to high molecular weight in N-methyl-2-pyrrolidinone at 180 °C. Organic-inorganic composite membranes were obtained by mixing organic polymers with hydrophilic SiO₂ (ca. 20nm) obtained by sol-gel process. The polymer and a series of composite membranes were studied by FT-IR, ¹HNMR, differential scanning calorimetry (DSC) and thermal stability. The proton conductivity as a function of temperature decreased as SiO₂ content increased, but methanol permeability decreased. The nano composite membranes were found to posse all requisite properties; Ion exchange capacity (1.2meq./g), glass transition temperatures (164-183 °C), and low affinity towards methanol (4.63-1.08x10⁻⁷ cm²/S).

Keywords : Polymer electrolyte membrane fuel cells, poly(ether sulfone ketone), SiO₂, nano composite

1. Introduction

The polymer-based organic/inorganic nano composites have gained increasing attention in the field of material science. The hydrophilic inorganic material, SiO₂, which is able to uptake water more strongly, was added to the organic polymer solution, making organic-inorganic composite membranes. Water molecules are strongly hydrogen-bonded to the ions or dipoles in the inorganic material. As a result of this, compared with organic polymer membranes, composite membranes showed higher water uptake and better cell performances at high temperature [1-2].

In this study, polyethersulfones (PES) and polyetherketone (PEK) are primarily chosen because they have achieved an excellent position among other thermoplastic polymers by virtue of their superior properties, such as thermal stability, high heat distortion temperature, chemical inertness, electrical performance and flame retardancy [3,4]. To improve the conductivity, water uptake and mechanical properties organic-inorganic nano composite membranes were prepared. In addition, we described our efforts to investigate the relative properties of sulfonated poly(ethersulfone-ketone) copolymer membrane and nano composite membranes. Proton conductivity, water uptake, methanol permeability, and ion exchange capacity (IEC), were evaluated.

2. Experimental and Results

Polymer synthesis: Bisphenol A (7 mmol), 2,2'-disodium-sulfonyl-4,4'-fluorophenylsulfone (2.8 mmol), 2,2'-difluorobenzophenone (4.2 mmol) and K₂CO₃ (8.4 mmol) were dissolved in a mixture of NMP 25 mL and toluene 25 mL. The mixture was refluxed for 4 h at 150 °C, and then excess toluene was distilled off. The mixture was heated at 180 °C for 12 h. The crude product was then washed three times with hot water to remove inorganic salts. The purified polymer was filtered and dried in vacuum at 100 °C for 24 h, and yielded 95%.

Organic-inorganic composite membranes: The composite membranes were prepared by mixing of the copolymer and alternating SiO₂ (4, 7 and 10wt %) in DMSO. The mixed solution was cast at 85 °C for 10 h. Membranes were dried in a vacuum oven at 100 °C for 24 h. The prepared membrane was acidified with 0.1 N HCl solution.

The sulfonated poly(ethersulfone-ketone) copolymer were synthesized by nucleophilic aromatic substitution as shown in Fig. 1. The mole ratio of the disulfonated monomer was chosen 40 mol% of bisphenol A because the copolymer using 50% mole of sulfonated monomer could not obtain high molecular weight. The composite membranes were cast except the composite membrane containing 15 wt%. The glass transition temperatures (*T_g*)

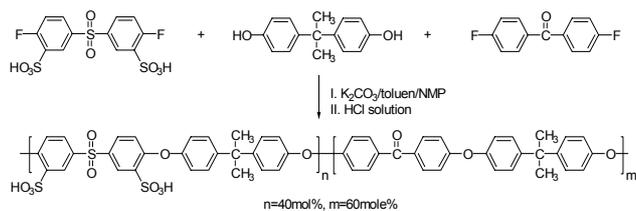


Fig. 1. Synthesis of sulfonated poly(ether sulfone-ketone) copolymer.

of the copolymer and composites evaluated using DSC by heated initially to 200 °C, quenched, and then heated to 250 °C at 10 °C/min. The T_g s of copolymer and composites were ranged from 164 to 183 °C. The T_g s of composites showed lower than that of copolymer (Fig. 2) because of free volume between SiO₂ and polymer chains. Thermo-oxidative stability of the polymer and composites were studied using thermogravimetric analysis (TGA) with results shown in Figure 3. Most of the polymers showed excellent thermal stability at high temperature and are useful for high temperature operation over 100 °C.

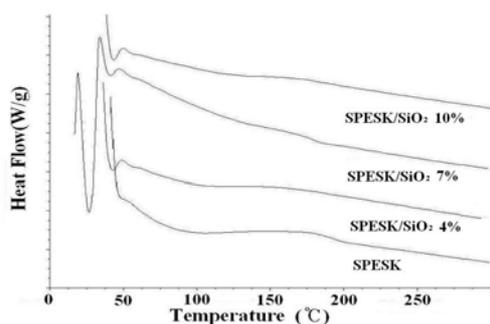


Fig. 2. DSC curves of SPESK and SPESK/SiO₂ membranes.

Fig. 3 is shown ion exchange capacity (IEC) and water uptake. The water uptakes of the samples rose with increasing SiO₂ content. IEC of the composite membranes were lower than that of the copolymer even though they had higher water uptakes than that of copolymer. The difference of this behavior is due to the microstructure of the polymers. Methanol permeabilities of the composite membranes decreased up to 7% SiO₂, and that of 10% SiO₂ composite membrane increased. The downward and upward trends of the methanol permeability have been reported that the function of SiO₂ content arises from two factors: the effect of interaction by the polymer/SiO₂, and the presence of hydrophilic groups (-SO₃H) associated with the polymer and SiO₂ [5]. The effect of interaction dominates methanol transport behavior up to 7% SiO₂ content. Above 10% SiO₂ content, however, the effect of the hydrophilic SO₃H groups exceeds the effect of interaction. Proton conductivities of the copolymer and composites membranes were evaluated as a function of temperature. Although the composite membranes had low proton conductivities relative to

copolymer and Nafion 112, proton conductivities increased to $8.32 \times 10^{-3} \text{ S/cm}^{-1}$ as temperature was increased to 100 °C (Fig. 7). The role of SiO₂ is the strong capture of water to maintain proton conductivity at high temperature [5].

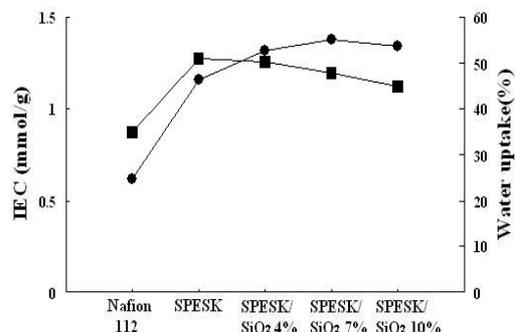


Fig. 3. IEC (■) and water uptake (●) for membranes

3. Summary

The sulfonated poly(ethersulfone-ketone) copolymer has been successfully synthesized by condensation polymerization. The organic-inorganic nano composite membranes were prepared by mixing the copolymer and SiO₂. The copolymer and composites were shown above 160 °C of glass transition temperature, and thermally stable at high temperature (400 °C). The composite membranes were shown higher water uptake compared to the copolymer membrane. The proton conductivities of composite membranes showed lower than that of the copolymer membrane at room temperature, but they substantially improved with elevated temperatures. Methanol permeabilities of the composite membrane were improved. These characteristics of the composite membranes are desirable for future application related to direct methanol fuel cell.

4. References

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