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# Properties of composite membrane based on sulfonated poly(arylene ether sulfone): effect of functional groups in phosphotungstic acid particles prepared by sol–gel method

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ABSTRACT

Sulfonated poly(arylene ether sulfone)/modified phosphotungstic acid containing amine group membranes was fabricated in order to evaluate the effect of introduced functional groups for use as polymer electrolyte membrane fuel cells. In order to resolve the inherent solubility problem of phosphotungstic acid particles, the sol–gel method was used to prepare the modified phosphotungstic acid particles, which have an insoluble property in solar solvents such as water. The sulfonated poly(arylene ether sulfone)/phosphotungstic acid composite membrane was prepared via solution casting and evaporation of the solvent. The mechanical and thermal property performances of the membranes prepared for use in fuel cells were investigated using their water uptake, water retention, and proton conductivity properties. The mechanical and thermal properties of the composite membranes were improved with the introduction of functional sites such as amine and silanol groups in the modified phosphotungstic acid. The proton conductivity of the nano-composite membranes at 100% relative humidity was increased due to the creation of a proton-conducting path through the amine–sulfonic acid group networks between the modified nanoparticles and the polymer. The functional group in the polymer matrix was also presumed to provide molecular water absorption ability, which resulted in an increase in the proton conductivity. These composite membranes can be used as a proton conductivity membrane for fuel cell applications.

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## 1. Introduction

Proton exchange membrane fuel cells (PEMFCs) are considered to be one of the most promising power sources due to their extensive potential applications [1]. Proton exchange membrane (PEM) is a key component in fuel cells for the transfer of protons and inexpensive materials; they have high chemical, mechanical, and thermal stabilities, as well as excellent electrochemical properties [2,3]. Sulfonated perfluorinated copolymers, such as DuPont's Nafion®, are the most commonly used PEM materials due to their excellent chemical and mechanical stabilities as well as high proton conductivity. Despite their high conductivities at room temperature and other advantages, they still have problems in commercialization as a result of their high cost, high fuel permeability, and reduced conductivity at high temperatures. For these reasons, various attempts have been made to overcome the drawbacks of Nafion® membranes for fuel cell applications [1]. Recently, polymer materials based on the arylene main chain, such as poly(ether sulfone), have been fabricated for use as electrolytes in fuel cell systems as a result of their availability, processability, options for chemical modification, anticipated stability, and good performance as polymer electrolytes in fuel cell systems [4].

A number of preparation methods have been developed to enhance the performance of fuel cell membranes: sulfonation of aromatic polymers, blending, crosslinking, and addition of inorganic materials. Among the available preparation methods used to obtain improved properties, the method of preparing inorganic–organic composite membranes is relatively convenient compared with the other methods. Furthermore, a composite system has the potential to provide a unique combination of two component properties. In hybrid organic–inorganic membranes, the inorganic part provides good mechanical and thermal stabilities with the organic functional group or compound presenting a specific chemical reactivity. Consequently, the inorganic–organic composite membrane is considered to be a promising method of developing proton conductive electrolytes in fuel cell applications. The materials that are used extensively for nano-composite fabrication include phosphotungstic acids (PWAs) such as solid acids, silica, metals, clays, and blending using second polymers due to their unique properties and surface chemistry as well as their excellent mechanical strength for long-term use [5–8].

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However, pristine PWAs are usually soluble in water, intractable, and decompose before testing in fuel cell applications. Therefore, they cannot be mixed with other polymers in the preparation of polymer hybrid membranes using conventional material processing techniques. Furthermore, it drastically decreases fuel cell performance. In order to overcome this problem, the chemical modification of PWAs has become important and essential [9–11]. A notable example is an incorporated host material such as a silica hybrid network with PWA clusters that can be stabilized through strong Coulombic interactions and the inorganic part of the hybrid framework [12]. Aparico et al. fabricated hybrid organic–inorganic nanostructured membranes incorporating hydroxyl groups and PWAs that exhibited increased proton conductivity as a result of a high concentration of hydroxyl groups in the PWA phase [13]. In this study, a sol–gel method was used to prepare PWA–silica–$NH_2$ (PWA–NH series) particles as constituents of composite membranes. Then, the effect of the interaction between the functional groups in the PWA–silica–$NH_2$ nanoparticles and the ionic site in the sulfonated poly(arylene ether sulfone)(SPAES) as a proton conducting material for PEMFCs was evaluated in terms of morphology, water behavior, mechanical properties, and proton conductivity.

## 2. Experimental details

### 2.1. Materials

4,4′-Biphenol and 4,4′-dichlorodiphenyl sulfone (DCDPS) were obtained from Tokyo Chemical Industry (TCI, Japan). Fuming sulfuric acid, potassium carbonate, phosphotungstic acid, 3-aminopropyl triethoxysilane (APTES), and anhydrous toluene were purchased from Aldrich (USA). Sodium chloride, sodium hydroxide, 1-methyl-2-pyrrolidinone (NMP), and sulfuric acid were obtained from Daejung Chemicals (Korea). Deionized water was produced using Aquamax™ equipment (Younglin Instruments, Korea). The DCDPS and sulfonated DCDPS were recrystallized from isopropyl alcohol (IPA) and dried in a vacuum oven for a minimum of 12 h at 120 °C. The DCDPS was converted to 3,3′-disulfonate-4,4′-dichlorodiphenylsulfone (SDCDPS; yield: 91.4%) using fuming sulfuric acid (28% free $SO_3$). The PWA was obtained commercially and used without further purification or modification. The SPAES copolymers were synthesized using the reference method [14]. The prepared copolymers had a sulfonation degree of 50.1%.

### 2.2. Preparation of PWA–silica–$NH_2$ particles using the sol–gel method and an organic–inorganic composite membrane

The sol–gel method was used to prepare the PWA–silica nanoparticles in this research. The PWA and APTES were mixed with a mixture of isopropyl alcohol, hydrochloric acid, and water in a weight ratio of 1:1–3:8:8:2. The mixture was stirred at 60 °C for 12 h. The prepared PWA–silica–$NH_2$ particles were filtered and washed several times with deionized water and then dried at 120 °C for 12 h in a vacuum oven. The SPAES–PWA–silica–$NH_2$ sol–gel composite membranes were prepared as follows: SPAES in sodium form was dissolved in NMP at 60 °C for 24 h to prepare a 5 wt.% solution. Then, a controlled amount of PWA–silica–$NH_2$ particles suspended in the NMP was added to the prepared SPAES solution and vigorously stirred for 1 day in order to obtain homogeneous solutions. The composite membranes were fabricated using a process that involves the evaporation of a cast solution. The solution was poured on a glass plate guided with silicon rubber (size: 6 cm × 6 cm). The solution was evaporated at 80 °C for 2 days with an infrared lamp. Finally, the prepared membrane was immersed in a boiling 1 N sulfuric acid solution for 2 h in order to chemically convert the $-SO_3Na$ groups in SPAES to $-SO_3H$ groups. The membranes were rinsed repeatedly with distilled water to remove any excess acid. The membrane samples were stored in deionized water until testing. The resulting membranes had a thickness of 80 ± 10 μm. In this study, the relative weight ratios of the PWA and APTES (1:1, 1:2, and 1:3) are referred to as N1, N2, and N3, respectively.

### 2.3. Characterization

The infrared spectra of the PWA and modified PWA particles were measured using the KBr method and were scanned between the wavelengths of 400 and 4000 $cm^{-1}$ using a VERTEX 80/80v Fourier transform infrared spectroscopy (FT-IR; Bruker Optics, Germany). A thermogravimetric analyzer (TGA; Q50, TA Instruments, USA) was used to study the thermal stability of the prepared membrane and the effect of the functional group between the PWA–silica–$NH_2$ particles. Samples of 10 mg to 20 mg were heated to 800 °C at a rate of 10 °C/min in a nitrogen atmosphere. The morphology of the composite membrane and the distribution of the inorganic particles were observed under the same magnification (×1000) at 15.0 kV using a field emission scanning electron

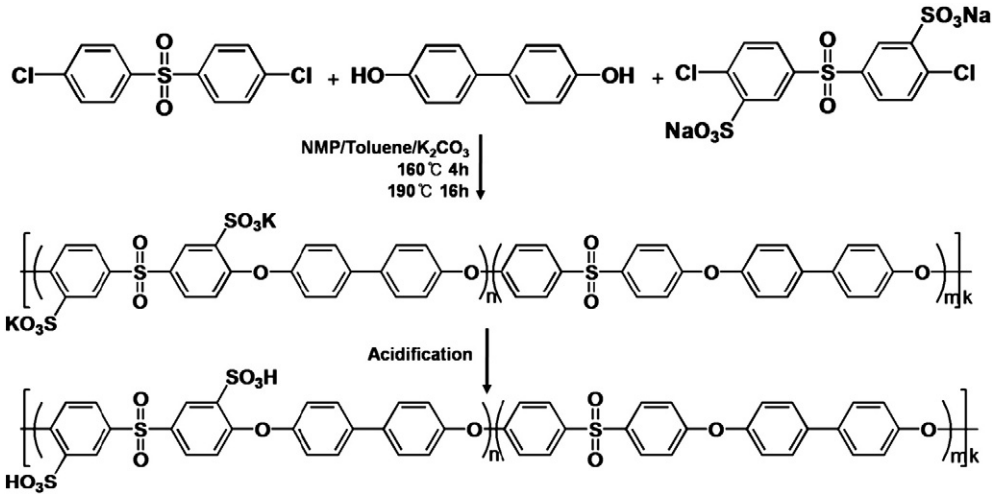


**Fig. 1.** Synthesis process of SPAES copolymers.

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