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Novel composite proton-exchange membrane based on proton-conductive glass powders and sulfonated poly (ether ether ketone)

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HIGHLIGHTS

- The SiO_2–Nafion/sulfonated poly (ether ether ketone) (SPEEK) composite membranes are fabricated.
- The poor miscibility of Nafion with SPEEK is solved by fixing Nafion into the SiO_2 glass powder.
- A maximum of the proton conductivity of 0.018 S cm^{-1} is obtained from the composite membrane.
- A single fuel cell equipped with the composite membrane exhibits a peak power density of 589.2 mW cm^{-2}.

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ABSTRACT

The SiO_2–Nafion/sulfonated poly (ether ether ketone) (SPEEK) composite membranes are fabricated by using the simple mechanical ball-milling process to combine SiO_2 glass powders with small portion of Nafion, in which SiO_2 glass powders are prepared by modified sol–gel progress and Nafion is embedded in situ into a highly porous silica network. The morphology, thermal and mechanical properties, pore structure, proton conductivity and fuel cell performance of the SiO_2–Nafion/SPEEK composite membranes are investigated. The poor miscibility of Nafion and sulfonated aromatic polymer is solved by fixing Nafion into SiO_2 glass powders. The composite membranes perform well even if the proportion of inorganic component in membranes is as high as 40 wt.%. A maximum of proton conductivity, 0.018 S cm^{-1}, is obtained from the membrane of 4(8Si–2N)/6SPEEK at 80 °C and 90% relative humidity, which is owing to its enhanced hygroscopicity and highly dispersed Nafion clusters. In addition, a single fuel cell equipped with the composite membrane shows a peak power density of 589.2 mW cm^{-2} at 70 °C.

1. Introduction

Proton-exchange membrane fuel cells (PEMFCs) are regarded as one of the most promising new energy devices for addressing energy and environmental issues because of their diverse advantages like low operating temperature, high efficiency and environmental friendliness. Proton-exchange membranes (PEMs) are one of the key components in PEMFCs. Among all kinds of proton exchange membranes, perfluorosulfonic acid (PFSA) type membranes such as Nafion® made by DuPont™ have been used extensively in current low-temperature PEMFCs owing to their high proton conductivity and good chemical stability. However, the application of this kind of membrane in fuel cells is restricted by their noticeable disadvantages such as high cost, high fuel permeability and loss of proton conductivity above 80 °C. Accordingly, it's strongly worthwhile to develop an alternative and cost-effective PEMs to promote a wider use of PEMFCs in stationary and vehicular applications.

The feasibility of hydrocarbon-based membranes as a substitute for Nafion has been explored by many researchers in the past few years [1–8]. Of all kinds of hydrocarbon-based membranes, the most studied one is the membrane based on aromatic poly (ether ether ketone) (PEEK), which is a thermally stable polymer with an aromatic, non-fluorinated backbone in which 1,4-disubstituted phenyl groups are separated by ether (–O–) and carbonyl (–CO–) linkages. Compared with PEEK, Sulfonated PEEK (SPEEK) possesses better mechanical properties, thermal stability and higher conductivity, all of which depend on the degree of sulfonation (DS) that can be controlled by changing the reaction time and temperature [5–9].

In addition, inorganic materials have also been widely studied that are used as non-proton-conductive additives or as proton

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conductors in PEMs. Hygroscopic inorganic oxides, such as SiO_2, ZrO_2, and TiO_2, have been incorporated into organic PEMs to increase water retention under low humidity. Among these oxides, SiO_2 is the most important because of its low cost and easy synthesis. When used in a PEM, SiO_2 is usually prepared in situ from alkoxide tetraethylorthosilicate (TEOS) via sol–gel process [10]. The sol–gel-prepared SiO_2 powders have three-dimensional structure and are realistically denoted as $SiO_{2(1-x/4)}(OH)_x$, where x is greater than zero in order to achieve the porous and hygroscopic property desired. Generally, a maximum of ~10 wt.% of oxide can be added to a polymer matrix without reducing proton conductivity. Additionally, all of these oxides can be sulfonated, which makes them acidic and improves their proton conductivity. However, sulfonation is very complicated and doesn't necessarily boost its conductivity significantly and fuel-cell performance [11]. Several inorganic proton conductors can reach high proton conductivities of 10^{-2}–10^{-1} S cm^{-1} under certain conditions, which is comparable to that of Nafion® under proper and favorable conditions. These proton conductors include CsH_2PO_4 at 245 °C and 30% RH [12], $Zr(HPO_4)_2$ at 80 °C and 100% RH [13] as well as P_2O_5–TiO_2 at 80 °C and 100% RH [14]. Nevertheless, the power densities of fuel cells using inorganic proton-conductive membranes as electrolytes are much lower than those of fuel cells based on Nafion® membrane. For example, using phosphotungstic acid (HPW) –P_2O_5–SiO_2 membranes in fuel cells, Nogami et al. obtained a peak power density of 42 mW cm^{-2} in H_2/O_2 at ~30 °C and 30% RH [15]. Lu et al. obtained a peak power density of 95 mW cm^{-2} at 100 °C from the fuel cell using a phosphotungstic acid ($H_3PW_{12}O_{40}$)/mesoporous silica (MCM-41) membrane [16]. Ioroi et al. obtained a peak power density of 45 mW cm^{-2} from the fuel cell using the surface-modified porous glass with SO_3H attached on the surface of the pores [17]. Our group has prepared phosphosilicate (SiO_2–P_2O_5) glass membranes with high proton conductivity of 10^{-1} S cm^{-1} and assembled a fuel cell using that membrane, obtaining a peak power output of 207 mW cm^{-2} [18]. Despite the favorable properties of inorganic membranes such as low cost and high proton conductivity, their widespread applications are seriously hindered by their low power density mainly caused by their inflexibility and brittleness; and these unfavorable properties make the traditional membrane-electrode assembly (MEA) process using hot pressing unable to maximize the interface contact between the electrolyte and electrode [18].

Given their respective merits and demerits of organic and inorganic membranes, it's of great worth to prepare and explore the organic–inorganic hybrid membranes by incorporating inorganic phases into polymer matrix, which probably provides an efficient way to address the challenges faced by organic or inorganic membranes. In this study, SiO_2–Nafion glass powders were prepared via sol–gel process and a low-temperature (150 °C) humid-annealing treatment. Large proportion of the powder was incorporated into a hydrophilic hydrocarbon-based SPEEK matrix by using mechanical ball-milling in order to form a SiO_2–Nafion/SPEEK composite membrane. The composite membrane exhibits high proton conductivity, sufficient mechanical strength and flexibility. The peak power density of a single fuel cell equipped with the composite membrane reaches 589.2 mW cm^{-2} at 70 °C.

2. Experimental procedure

2.1. Materials

$Si(OC_2H_5)_4$ (TEOS, Sinopharm) and Nafion® dispersion (DUPONT DE1020 NAFION® Solution, 10 wt.% Nafion with terms of small aggregates in a mixture of low aliphatic alcohols and water, Ion Power. Inc) were used without further purification. Poly (ether ether ketone) (PEEK) (Grade 450-P, Victrex Inc.) was dried under vacuum condition lower than 10^3 Pa at 110 °C for 24 h in a vacuum box before use.

2.2. Preparation of SiO_2–Nafion/SPEEK composite membrane

The SiO_2–Nafion glass was prepared via sol–gel method. First, TEOS, deionized water and hydrochloric acid were mixed in a molar ratio of 1: 4: 4×10^{-3} (TEOS: H_2O: HCl) and stirred for 1 h at room temperature. Different amounts of Nafion were added to the sol mixtures and then stirred for another 1 h until became transparent. The solutions thus obtained were transferred to polytetrafluoroethylene (PTFE) containers and kept at room temperature until gelation finished. Later, the obtained xerogels were treated by humid-annealing at 150 °C for 24 h under saturated water vapor. The SiO_2–Nafion glass sheets after these treatments were crushed into micron-sized powders by an electric crusher and then the glass powder were screened by using an 800 mesh sieve. The resultant composite SiO_2–Nafion glasses are designated as 9Si–1N, 8Si–2N and 7Si–3N, respectively, to indicate the different weight ratios of SiO_2 and Nafion in the glasses, namely, 9:1, 8:2 and 7:3.

The sulfonation of PEEK followed the method described previously [19]. PEEK powder (20 g) was slowly added to the pre-heated concentrated sulfuric acid (400 mL) and vigorously stirred for 2.5 h at 50 °C at the same time. The sulfonated polymer solution was then quickly poured into to a large ice-water bath to terminate the reaction; and the fibrous SPEEK polymer was precipitated from water. The collected polymer was washed repeatedly with deionized water until the value of pH became neutral and then dried overnight under vacuum condition lower than 10^3 Pa at 80 °C before use.

The inorganic-organic composite membranes were prepared by using mechanical ball-milling and solvent casting. Specifically, SPEEK was first dissolved in dimethylacetamide (DMAc) which was used as the solvent; and then different amounts of SiO_2–Nafion glass powder with different Si/N ratios were added to it, respectively. The resultant mixtures were milled by using a planetary ball-mill apparatus (QM-3SP2, NanDa Instrument Plant) for 36 h at 450 r min^{-1}. The slurries obtained after being milled were cast onto glass plates using a doctor blade and then dried at 90 °C for 3 h under vacuum condition to form SiO_2–Nafion/SPEEK composite membranes. The composite membranes were detached from the glass plates and stored in vacuum-sealed bags. The membranes were designated as x(aSi–bN)/ySPEEK, where x and y were the weight ratio of SiO_2–Nafion glass powder and SPEEK, and a and b denoted the weight ratio of SiO_2 and Nafion in the SiO_2–Nafion glass. The names and compositions of all membranes in this study are listed in Table 1.

2.3. Characterization

The infrared spectra of membranes were recorded on a Fourier transform infrared (FTIR) spectrometer (Nicolet 6700, Thermo Fisher Scientific Inc.). The porous structure of each membrane was analyzed via the nitrogen adsorption–desorption apparatus (TriStar II 3020, Micromeritics Inc.) after degassing under N_2 flow at 120 °C for 6 h. Scanning electron microscopy (SEM) images were obtained from an ultra-high-resolution field-emission SEM (S-4800, Hitachi Co.) using electron-beam deceleration mode. The method of liquid nitrogen brittle fracture was used to acquire the cross-sections of membranes; and Pt was sputtered on the cross-sections. Trace elemental analysis was conducted by an EDAX GENESIS XM2 energy dispersive X-ray spectrometer (EDS).

The mechanical properties of composite membranes were assessed on a dynamic mechanical analyzer (DMA 8000,