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Carbonaceous nanofiber-supported sulfonated poly (ether ether ketone) membranes for fuel cell applications

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ABSTRACT

A facile spinning-based strategy was developed to fabricate continuous carbon nanofiber (CNF)- and activated carbon nanofiber (ACNF)-supported sulfonated poly(ether ether ketone) (SPEEK) membranes as proton exchange membranes (PEMs) for fuel cells. Polyacrylonitrile nanofibers were solution blown as precursor to obtain CNF and ACNF mats. These mats were then impregnated into a SPEEK solution to fabricate pore-filled composite membranes. The morphologies as well as thermal and mechanical properties were examined. Moreover, the performance of the mats as PEMs was investigated. Results showed that carbonaceous nanofibers were dispersed incompactly in the SPEEK matrix and thus made dense membranes. The introduction of CNFs and ACNFs to composite membranes significantly improved mechanical properties and proton conductivity, which indicated that carbonaceous nanofiber-supported membranes are promising materials for PEM fuel cells.

1. Introduction

Proton exchange membrane fuel cells (PEMFCs) have attracted considerable attention as a clean energy source for their high energy density and efficiency with low emission of pollutants. Proton exchange membranes (PEMs) are one of the most important components of PEMFCs. Perfluorosulfonated polyelectrolytes, such as Nafion, are widely used as PEMs for fuel cells. However, this type of ionomer has limited application because of critical drawbacks, such as high cost, high methanol crossover, and relatively low operation temperature [1]. Sulfonated aromatic hydrocarbon polymers have been investigated extensively as promising alternative PEM materials [2]. Among these polymers, sulfonated poly(ether ether ketone) (SPEEK) exhibits most of the required properties, thereby making it a promising alternative material for fuel cell applications [3]. However, some drawbacks remain to be overcome before practical use.

The fabrication of organic–inorganic composite membranes is an important strategy for high-performance PEMs. Inorganic functional fillers, such as zeolites, heteropolyacids, titania, and tungstophosphoric acid, have been added to enhance mechanical strength and reduce methanol crossover in direct methanol fuel cells [4,5]. Carbonaceous nanomaterials, especially carbon nanotubes (CNTs), are a new class of advanced filler with interesting properties that have the capacity to improve the properties of polymer matrices for membrane fuel cells or electrolyzer applications [6]. However, CNTs tend to hold together as ropes and bundles because of strong intrinsic van der Waals forces, thus resulting in poor dispersion when mixed into the polymer matrix [7]. Meanwhile, carbon nanofibers (CNFs) are continuous fibers that accumulate as fiber mats, which easily disperse in a polymer matrix. In addition, this kind of fiber-supported composite membrane is expected to possess excellent physical properties and performances. Continuous CNFs can be easily fabricated by spinning their precursor polymers. The solution blowing process has been reported as a novel method for making nanofibers using high-speed gas flow. Moreover, a disassembly containing a series of orifices can be easily used without considering the electric field interference, as in electrospinning [8]. The process is expected to be developed as an important method for the mass production of nanofibers.

In this work, we adopted this process as a new strategy to obtain carbonaceous nanofiber-supported SPEEK composite membranes for fuel cell applications. A polyacrylonitrile (PAN) nanofiber mat was first fabricated using the solution blowing process. CNFs and activated CNFs (ACNFs) were then obtained through the subsequent stabilization, carbonization, and activation treatment. CNF and ACNF mats were impregnated into a SPEEK solution to form pore-filled membranes.

2. Experimental

Preparation of carbonaceous nanofiber-supported SPEEK membrane: As reported in our previous work, the schematic of the solution

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blowing apparatus is illustrated in Fig. S1 [8,9]. Detailed synthetic methods of CNFs, ANCFs, and SPEEK are shown in Supporting information (SI). ACNF-supported SPEEK (CNF/SPEEK) membrane was prepared by impregnating a CNF mat with a defined amount of SPEEK solution (15 wt%) through a multi-step process. Briefly, SPEEK solution was casted onto a glass plate, and a CNF mat was then mounted on the plate and filled with SPEEK solution. The membrane was dried at 60 °C for 6 h to remove the solvents and annealed at 100 °C for 12 h to form a good pore-filled CNF/SPEEK membrane. An ACNF-supported SPEEK membrane (ACNF/SPEEK) was prepared following the same procedure. The contents of CNFs and ACNFs were 0.51% and 0.48% by weight, respectively. The thicknesses of SPEEK, CNF/SPEEK, and ACNF/SPEEK were 63, 71, and 74 μm, and the mats of CNF and ACNF impregnated into the matrix were 40 and 36 μm, respectively.

Characterization: The morphologies of the nanofibers and membranes were characterized using a scanning electron microscope (SEM, Hitachi S-4800). X-ray diffraction (XRD) measurements and thermogravimetric analyses (TGAs) were performed by XRD spectroscopy (D8 Discover with GADDS) and TGA instruments (STA409PC), respectively. Tensile strength of the composite membranes was measured using an Instron universal testing machine (3369, USA). The water uptake (*WU*) and swelling ration (*SR*) were calculated using the following equation: $WU\ (\text{wt\%})=(W_w-W_d)/W_d$, $SR\ (\text{wt\%})=(V_w-V_d)/V_d$, where W_w and W_d were the water swollen membrane weight and dry membrane weight and V_w and V_d were the water swollen membrane volume and dry membrane volume, respectively.

The proton conductivity of samples was measured using two electrodes [1]. The proton conductivity, σ, was calculated from the impedance data using the relationship, $\sigma = l/twR$, where l, t, and w are the length, thickness, and width of the membrane, respectively. R was derived from the low intercept of the high-frequency semicircle on a complex impedance plane with the real axis.

3. Results and discussions

Morphology of CNFs and ACNFs: SEM images of the precursor, carbonized, and activated nanofibers are shown in Fig. 1. The corresponding diameter distribution maps are given in SI (Fig. S2). PAN nanofibers with diameter of 240–500 nm were arranged in a disorderly manner. The diameters were observed to decrease from 200 nm to 350 nm for CNFs and from 100 nm to 300 nm for ACNFs. Furthermore, nanofibers have shown a high orientation degree under constant drafting force during the stabilization process.

Structure and properties of CNF/SPEEK and ACNF/SPEEK: Fig. 2a and b shows the surface images of membranes. The pores among nanofibers were completely filled with SPEEK, and dense membranes were formed. Nanofibers that were well encased in the polymer matrix were clearly observed in the cross section images (Fig. 2c and d). No significant crack indicated good compatibility between carbonaceous nanofibers and the SPEEK phase. As expected, the nanofibers were well dispersed in the polymer matrix, but not agglomerated.

The XRD curves of CNFs and ACNFs are shown in Fig. 3a. The two nanofibers showed similar crystallization curves with two peaks at 26.0°and 43.5°. The peak for SPEEK occurred at 2θ of 17° [10]. The composite membranes occurred at peak 21°, which may indicate that the movement of SPEEK and CNF peaks toward each other was caused by the CNF redistribution in SPEEK, thus revealing the good compatibility of the materials.

The TGA of the membranes, as shown in Fig. 3b, indicates that all the membranes exhibited two distinct weight-loss steps [10]. In addition, the char yield of composite membranes was higher than that of pure SPEEK, which mainly originated from the addition of CNFs and ACNFs.

The mechanical properties of the pure SPEEK membrane and the composite membranes are summarized in Fig. 4a. Compared with the pure SPEEK film, the tensile strength of composite membranes evidently increased. All membranes had acceptable mechanical properties for PEM application with their tensile strength ranging from 55 MPa to 60 MPa. Furthermore, the elongation at break of the composite membranes decreased slightly from 19.88% to 17.23%. This observation was mainly attributed to the reinforcing effect of CNFs and ACNFs, which delayed crack propagation.

The measured *WU* at varying membrane temperatures are shown in Fig. 4b. The *WU* of the composite membranes increased with the addition of CNFs and ACNFs into SPEEK matrices. A similar conclusion was reported by Ghasemi, who synthesized CNF/Nafion nanocomposites membranes [11]. ACNF/SPEEK exhibited higher *WU*, possibly because of the presence of a cellular structure attributed to ACNFs; this cellular structure became available to accommodate water [12]. However, it is interesting that the continuous and intertwined CNF and ACNF mats effectively suppressed the swelling of composite membranes, and led to slight increase of *SR* value with temperature increasing and lower *SR* value than SPEEK above 60 °C (see Fig. S3).

Proton conductivity behavior was investigated at temperatures ranging from 20 °C to 80 °C. All membrane samples were in their protonated state and measured in water (100% humidified). Overall, conductivity was measured in the range from 2.1×10^{-2} to 4.5×10^{-2} S cm^{-1} with CNFs added into SPEEK at room temperature, as shown in Fig. 4c. The plots of conductivity also showed that the conductivity of all membranes exhibited positive dependency with temperature, which reveals that proton conduction is a thermally activated process. Carbonaceous nanomaterials are known to be good electronic conductors. However, the effect of such materials on proton conductivity has not been thoroughly investigated. Based on semi-empirical quantum mechanical calculations, Zaporotskova et al.

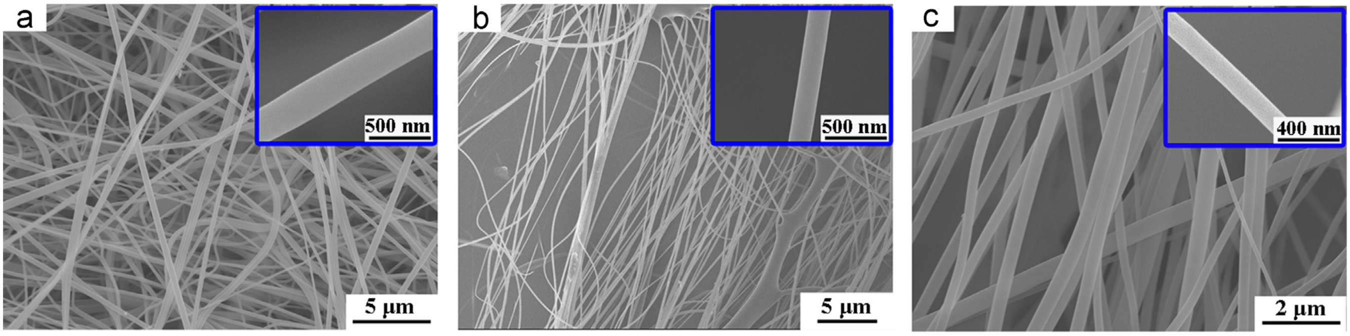

Fig. 1. SEM images of (a) as-spun PAN nanofibers, (b) CNFs, and (c) ACNFs.