



Porous nanofibrous composite membrane for unparalleled proton conduction



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ABSTRACT

Nanostructured porous nanofiber membranes hold a great promise for ultrafast transport of ion and molecule but it remains a technologic challenge to fabricate them with stable nanochannels. We report the use of a new soft template of ionic liquid which has excellent fluidity and molecular-level size to produce porous nanofibers comprising interconnected ~ 4 nm pores/channels. In addition, the topology of the nanopores/channels can be facily tailored by the types and loading amount of ionic liquids. After incorporating polymer matrix, an unique type of porous nanofibrous composite membranes (PNFCMs) was fabricated accordingly. In the PNFCMs, the nanochannels can well function as transfer shortcuts and uptake abundant water/moisture while releasing conducting groups, eventually permitting unparalleled proton conduction. The conductivity of PNFCM can be as high as 1.03 S cm^{-1} in hydrated condition and 0.22 S cm^{-1} in anhydrous condition, which is around 10 times higher than that of the state-of-the-art Nafion. As a further demonstration, the PNFCMs is used for hydrogen fuel cells, exhibiting excellent performance in anhydrous condition, making it great potential for practical application. This soft template approach is also expected to be used for fabrication of other nanostructured porous nanofiber membranes with well-defined porosity and nanostructures.

1. Introduction

Materials with ordered and interconnected nanochannels have efficient and selective mass transport, and are critical in advanced devices with applications in adsorption, separation, catalysis, and energy conversion [1–4]. Particularly, porous membranes that have interconnected nanochannels with size below 10 nm have shown both high throughput and high efficiency in molecular separation and ion conduction [5]. Such a well-known porous membrane is the state-of-the-art polymer electrolyte membrane (PEM), Nafion, which possesses connective ion-rich nanochannels comprising 4 nm clusters connected by 1 nm tubes in hydrated state. This kind of nanochannel is distinguished as it contains optimal arrangement of proton hopping sites and water-bonded networks, enabling a high proton conduction ability with a conductivity of around 0.1 S cm^{-1} . Inspired by the unique structure of Nafion, Guiver et al. constructed membranes with analogous nanochannels via the self-assembly of comb-shaped copolymers, achieving an extraordinary proton conductivity up to 0.6 S cm^{-1} [6]. In another work, Thayumanavan and co-workers prepared a membrane by assembling supramolecules into ~ 4 nm nanochannels, exhibiting two

orders of magnitude enhancement in proton conduction [7]. However, these reported nanochannels are drastically humidity-dependent, which tend to collapse and discontinue after loss of water, resulting in severe performance degradation. Furthermore, these channeled membranes are usually fabricated through self-assembly, which needs both precise molecular-level materials and sophisticated nano-scale fabrication steps [8–10]. This greatly limits membrane functionality, and affects their practical applications. Therefore, a facile strategy is highly required to build stable nanochannels for functional polymer membrane.

Recently, nanofibrous composite membrane (NFCM) with dual-continuous phases has attracted increasing attention in gas separation, water purification, and ionic conduction [11–13]. The high specific surface area and rich functional groups can form long-range transport pathways along fiber surfaces with good selectivity [14]. Moreover, the fiber mat and incorporated matrix can be independently adjusted, offering great opportunities in exploring synergistic effects for desired properties. Particularly, ordered acid-base pairs that can be formed in NFCM can judiciously cooperate to transport protons in an ultralow-energy-barrier manner although it is still a challenge to fabricate such pairs since direct blending of acid and base polymers usually produces

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flocculation. Nevertheless, NFCM suffers from a ubiquitous and pernicious transfer anisotropy, fast in-plane transfer but slow through-plane transfer, because of the impermeable dense nanofibers. When to use as a PEM, its anisotropy degree for proton conduction can be as high as 100, which significantly restrains practical application [15]. Alternatively, porous nanofibrous composite membrane (PNFCM) has shown a great potential to address this anisotropy problem by creating nanoscale pores/channels in the fiber as additional transfer shortcuts. Although considerable efforts have been devoted to fabricating porous microfibers *via* phase separation method or template method [16–20], to the best of our knowledge, there is no relevant study for PNFCM. By precisely manipulating phase separation, the separation procedure is inclined to form dents or shallow holes near fiber surface [16], whereas the template method usually produces uniform pores in the whole fiber [20]. Template method has been used to successfully fabricate high loading and large-sized pores (> 50 nm), which afford superior adsorption, catalysis and energy storage properties [21,22]. Despite these achievements, it remains a challenge to fabricate nanofibers with interconnected and small-sized pores (< 10 nm) because most conventional templates are large-sized and/or inactive in the concentrated polymer electrospinning solution.

Ionic liquids (ILs) have intrinsic advantages including excellent fluidity and dispersibility, chemical stability, low toxicity, and tunable compatibility. They have attracted research interest for applications as solvents or additives [23,24]. Moreover, the molecular-level size (~ 1.0 nm) of ILs makes them great potential as soft template to create nanopores or nanochannels. Nevertheless, ILs have been rarely utilized in porous nanofiber fabrication until now. In this work, we report for the first time, a successful fabrication of nanostructured porous nanofibers using ILs as a new soft template. The good fluidity and small size promote a distinct templating functionality, which enables the formation of ordered and interconnected nanopores/channels (~ 4 nm) in sulfonated poly(ether ether ketone) (SPEEK) nanofiber. The porous nanofibers are further incorporated with fuel resistant and proton conductive chitosan (CS) to fabricate PNFCMs, which render unparalleled proton conduction. As a demonstration, the PNFCMs are further used as membrane for hydrogen fuel cells, exhibiting excellent performance.

2. Experimental

2.1. Materials

Poly(ether ether ketone) (Victrexs® PEEK, grade 381 G) was supplied by Nanjing Yuanbang Engineering Plastics Co., Ltd. CS with a degree of deacetylation of 91% was supplied by Golden-Shell Biochemical Co. (Zhejiang, China) and used as received. Concentrated sulfuric acid (98 wt%), *N,N*-dimethyl formamide (DMF), tetrahydrofuran (THF), acetic acid and methanol were supplied from Adamas-beta®. 1-Octyl-3-methyl imidazolium bis(trifluoromethylsulfonyl)imide ([C₈mim][Tf₂N]) and 1-ethyl-3-methyl imidazolium bis(trifluoromethylsulfonyl)imide ([C₂mim][Tf₂N]) were purchased from Lanzhou Institute of Chemical Physics (Chinese Academy of Sciences) and used as received. De-ionized water was used in all experiments.

2.2. Fabrication of porous nanofiber mats

SPEEK was prepared according to the procedure in literature [25]. During the sulfonation, the degree of sulfonation of SPEEK (69.8%) was controlled by reaction time (9.5 h). Afterwards as illustrated in Scheme 1, certain amount of SPEEK was dissolved in the mixture of DMF and THF (4:1 w/w) at room temperature under stirring for 12 h to give a 17 wt% solution, then a certain amount of ionic liquid was added into the SPEEK solution. The feed amounts of ionic liquid relative to SPEEK were 0 wt%, 15 wt%, 25 wt%, and 35 wt%, respectively. Subsequently, the mixture was under stirring at room temperature for 1 h to obtain homogeneous electrospinning solution. The solution was then loaded in

a 5-mL plastic disposable syringe and pumped through a Teflon tube at a rate of 0.030 mL min⁻¹ with the applied voltage of 23 kV and tip-to-collector distance of 20 cm. The nanofiber mat was peeled off from aluminum foil and immersed in 2% (v/v) methanol ([C₈mim][Tf₂N] as templet) or water ([C₂mim][Tf₂N] as templet) at room temperature for 24 h to release the ionic liquids. Porous nanofiber mats were then obtained after freeze-drying for 24 h and nominated as SP/C₈-X and SP-C₂-X, respectively, where X (X = 15, 25, and 35) referred to the feed amount of ionic liquid. Dense nanofibers were synthesized without incorporating ionic liquid and designated as SP.

2.3. Preparation of porous nanofibrous composite membranes

A certain amount of CS was added in acetic acid aqueous solution (1 wt%) under stirring at 60 °C for 2 h to obtain casting solution. Afterwards, the casting solution was filled into the nanofiber mat on a clean glass bar, which was then thoroughly dried for 72 h at room temperature to obtain a composite membrane. Subsequently, the CS matrix was cross-linked and completely washed with water. The obtained membrane was dried at room temperature under vacuum for 24 h and designated as CS/SP/C₈-X and CS/SP/C₂-X, accordingly.

2.4. Characterization of the nanofiber mats and membranes

The morphologies of the nanofiber mats and membranes were observed by scanning electron microscope (SEM, JSM7500F) after the samples were sputtered with gold. Energy dispersive spectroscopy (EDS) on the same equipment was performed to inspect the deposition of template into the pristine fibers. Transmission electron microscopy (TEM) measurement of the nanofiber mats was conducted on a JEM-2100 F microscope (JEOL, Japan) operated at 200 kV. Fourier transform infrared (FTIR) spectra of the nanofiber mats and membranes were recorded with the wavelength of 400–4000 cm⁻¹ on a Nicolet MAGNA-IR560 instrument. The nanostructures of the porous nanofiber mats and membranes were probed by small-angle X-ray scattering (SAXS) and wide X-ray diffractometer (WXR) using a RigakuD/max2500v/Pc (CuK40 kV, 200 mV), with the rate of 0.1° cm⁻¹ and 2.0° cm⁻¹, respectively. The thermal properties of the nanofiber mats and membranes were detected by thermogravimetric analysis (TGA-50 SHIMADZU) under nitrogen atmosphere, operating from 25 to 800 °C at a heating rate of 10 °C min⁻¹. Differential scanning calorimetry (DSC, 204 F1 NETZSCH) was conducted with nitrogen and the sample was first preheated from room temperature to 130 °C with 10 °C min⁻¹, then cooled to 90 °C and reheated to 260 °C. The Brunauer-Emmett-Teller (BET) surface area, pore size and pore size distribution of the nanofibers were measured at 77 K in the relative pressure (p/p₀) range of 0.05–1.0 according to the BET method using an automated gas sorption analyzer (Quantachrome Ltd., America) [26].

2.5. Water uptake, swelling degree and ion exchange capacities (IEC) of the membranes

Water uptake and area swelling of the membrane were determined as follows. Rectangular membrane sample was dried in an oven at 60 °C for 24 h and then its weight (W_{dry} , g) and area (A_{dry} , cm²) were measured. Afterwards, the sample was immersed in water for 24 h, and its weight (W_{wet} , g) and area (A_{wet} , cm²) were re-measured quickly after removing surface water. The values of water uptake and area swelling were the averages of three measurements with the error within ± 4.0% and calculated as below:

$$\text{Water uptake(\%)} = (W_{wet} - W_{dry})/W_{dry} \times 100\% \quad (1)$$

$$\text{Area swelling(\%)} = (A_{wet} - A_{dry})/A_{dry} \times 100\% \quad (2)$$

IEC value of membrane was determined *via* acid-base titration: the dry and pre-weighted sample was immersed in 2.0 M NaCl solution for

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