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Constructing dual-interfacial proton-conducting pathways in nanofibrous composite membrane for efficient proton transfer

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ABSTRACT

To achieve high proton conduction ability, we report here a novel and facile strategy to construct dual-interfacial proton-conducting pathways in the platform of nanofibrous composite membranes (NFCMs) by mixing sulfonated halloysite nanotubes (SHNTs) with chitosan (CS) matrix and then incorporating them into the pores of sulfonated poly (ether ether ketone) (SPEEK) nanofiber mat. In such a way, two distinct interfacial pathways are created at SPEEK/CS and CS/SHNTs interfaces, on which ordered acid–base pairs ($-SO_3^-\ldots{}^+H_3N-$) are formed. And the strong electrostatic attractions endow NFCMs with enhanced structural stabilities by regulating polymer chain mobility and stacking. The dual-interfacial proton-conducting pathways confer ultrafast proton conduction on NFCM under both hydrated and anhydrous conductions via Grotthuss mechanism. Especially, CS/SPNF/SHNTs-5 achieves remarkable conductivities of 117.7 mS cm^{-1} under 90 °C and 100% RH, and 19.95 mS cm^{-1} at 100 °C and 0% RH. Benefiting from the structural stability, the as-prepared NFCMs display excellent conduction stability for promising long-term operation. Moreover, to verify the universality of this nanostructured-transfer pathway, another kind of NFCM is fabricated using polydopamine modified nanofiber mat bearing numerous polydopamine nanoparticles. SPEEK is chosen as polymer matrix and incorporated into the mat to prepare the NFCMs, which also display expected efficient proton transfer behaviors.

1. Introduction

Nanofibrous composite membranes (NFCMs), which are prepared by incorporating polymer matrix into the pores of nanofiber mat, possess unique merits such as: (i) inter-connected networks with high specific area, (ii) facilely controllable bi-continuous phase structure, and (iii) superior mechanical properties and diversified composition, and so forth [1–3]. They have been considered as promising candidates in filtration, textiles, medical and pharmacological products, energy storage and conversion (e.g., proton exchange membranes, PEMs). PEM, the core part of hydrogen fuel cell, should exhibit high proton conduction ability and thus endow fuel cell with high energy conversion efficiency [4–7].

There are three parts in NFCM for proton transfer, i.e., nanofiber phase, polymer matrix phase, and the interfacial regions among the two phases. Nanofibers are consecutive at in-plane direction but discontinuous at vertical direction, which would be detrimental for the perpendicular proton transfer [8,9]. For interfacial regions, the functional groups from nanofiber and/or incorporated polymer matrix could transport protons along the inter-lapped fibers, creating continuous conduction pathways. The type and amount of conducting groups can be facilely tuned by changing the materials of nanofiber mat and polymer matrix; also through different matching, the physical structure and chemical environment of this pathway could be controlled [10–12]. For instance, acidic and basic groups are the main conducting groups for proton conductor. When existing in nanofibers and polymer matrix respectively, these two kinds of groups would be induced to enrich in the interfacial regions, forming ordered acid–base pairs. These pairs would work as facile hopping sites for ultrafast proton conduction along the interfacial pathways [13,14]. This is quite different from the blending membrane, which is prepared by directly blending acidic and basic polymers. Along with the dis-ordered distribution, the block aggregation of acidic and basic polymer chains makes it difficult to obtain dense and uniform PEM [15].

For polymer matrix in NFCM, it is interconnected throughout the entire membrane and usually occupies above 70% in volume, thus serving as one important transfer pathway [16]. However,

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when located in the confined sub-micrometer pores in nanofiber mat, the chain segment of polymer is difficult to fully stretch, and the group configuration, molecule assembly and ionic cluster formation would be interfered with and even disappear [9]. Therefore, continuous ionic channels could not be formed for most of the conducting polymers in NFCMs, especially for perfluorinated sulfonic acid polymers and sulfonated aromatic polymers. This situation is difficult to be improved by thermal treatment or induced rearrangement. The proton conduction ability of polymer matrix in NFCM would be limited to a great extent. The proton transfer pathway at interfacial region between nanofiber and polymer matrix of NFCM is relatively easy to be tuned and there have been lots of attempts to construct efficient pathways at these regions [17,18]. For the incorporated polymer matrix of NFCM, however, the adjustment of its transfer ability is rare to our best knowledge at present.

Apart from nanofiber framework, the filled polymer matrix is actually similar to the casting membrane. For casting membrane, a facile and effective approach to tune the nanostructure and transfer property is to incorporate inorganic nanofillers [19–21]. The addition of inorganic nanofillers would adjust the polymer chain mobility and assembly through various interfacial interactions, driven by which the functional groups could be arranged near nanofiller/polymer interfaces. The large surface area and high aspect ratio of nanofillers would allow the arranged groups forming long-range pathways for proton transport. Nanofillers, including nanoparticles, nanotubes and nanosheets bearing conductive groups, have been incorporated in casting membrane to obviously improve its proton conduction ability [18,19,22]. It should be noted that the pores among nanofibers are mainly in the sub-micrometer scale and nanosheets (e.g., graphene oxide, usually in sub-micrometer size) may cover the pore mouths of fiber mat and thus fail to be used for preparing dense and homogeneous NFCM [23,24]. Accordingly, nanotubes and nanoparticles were adopted to tune the proton conduction abilities for polymers filled in the NFCMs. Recently, dopamine, a low-molecular-weight catecholamine, was found to be able to self-polymerize under mild conditions. The formed polydopamine (PDA) bearing numerous amino and imino groups can adhere tightly to the surface of virtually all inorganic and organic materials by means of strong physical or chemical interactions [25,26]. In such a way, dopamine provides a facile and universal method to modify the material surface.

In this study, acid–base paired NFCMs containing dual-interfacial proton-conducting pathways were prepared and their proton conduction properties were studied in two relative works. In the first one, sulfonated polyelectrolyte brushes modified halloysite nanotubes (SHNTs) were mixed with basic CS matrix and then incorporated into sulfonated poly (ether ether ketone) (SPEEK) nanofiber mat to prepare NFCM. In the second one, the poly (vinyl alcohol)/tetraethyl orthosilicate (PVA/TEOS) nanofibers were modified by dopamine to form a basic PDA layer and extra PDA nanoparticles, followed by incorporating acidic SPEEK matrix to obtain NFCMs. By doing so, dual-interfacial proton-conducting pathways were expected to emerge on the nanofiber/matrix and nanofiller/matrix interfaces, along which acid–base pairs would act as efficient proton hopping sites. The microstructures and physicochemical properties of NFCMs were investigated in detail. The proton conduction properties and transfer mechanism of NFCMs under both hydrated and anhydrous conditions were evaluated systematically.

2. Experimental

2.1. Materials and chemicals

Poly(ether ether ketone) (Victrex® PEEK, grade 381G) was supplied by Nanjing Yuanbang Engineering Plastics Co., Ltd, which was completely dried under vacuum prior to the sulfonation. Tetraethyl orthosilicate (99.9%, Fw 208.33), Poly (vinyl alcohol) (Mw 22,000–26,000, 86–89% hydrolyzed) and Sodium-pstyrenesulfonate (SS) were obtained from Alfa Aesar. Dopamine hydrochloride was obtained from Yuancheng Technology Development Co., Ltd., China. Tris(hydroxymethyl) aminomethane (Tris) was supplied by Sigma-Aldrich and used without further purification. 3-(Methacryloxy) propyltrimethoxysilan (MPS) and Styrene (St) were obtained from Aldrich and distilled under vacuum. HNTs were refined from clay minerals in Henan province, China. 2, 2′-Azobisisobutyronitrile (AIBN), acetic acid, hydrochloride acetonitrile, ethanol, hydrochloric acid (HCl, 37 wt%), concentrated sulfuric acid (98 wt%), and *N,N*-dimethyl formamide (DMF) were purchased from Kewei Chemistry Co., Ltd. (Tianjin, China) and used without further purification. CS with a degree of deacetylation of 91% was supplied by Golden-Shell Biochemical Co. (Zhejiang, China) and used as received. De-ionized water was used throughout the experiment.

2.2. Fabrication of the first kind of NFCMs

2.2.1. Synthesis of SPEEK nanofibers and SHNTs

SPEEK was fabricated according to the procedure in literature [27]. During the sulfonation, the degree of sulfonation (DS) of SPEEK was controlled by tuning the sulfonation time. Four kinds of SPEEK with the DSs of 58.2%, 66.1%, 74.4%, and 82.0% were obtained when the sulfonation time was 7.5, 9.0, 10.0, and 10.5 h, respectively. SPEEK with the DS of 66.1% was chosen to be electrospun into nanofibers. The detailed electrospinning process was the same with that in the previous study [9].

SHNTs were synthesized via distillation-precipitation polymerization method [20]: HNTs (5.0 g) were dispersed into the mixture of ethanol (150 mL), water (15 mL) and aqueous solution of ammonium (12 mL) under stirring at room temperature for 24 h. Then, MPS (1.0 mL) was added into the resultant mixture and stirred for another 24 h. Afterwards, the MPS-modified HNTs were purified by three cycles of centrifugation and followed by drying in a vacuum oven at 50 °C. MPS-modified HNTs (0.30 g), St (0.40 mL), SS (0.40 mL), and AIBN (0.016 g) were dispersed into acetonitrile (80 mL) in a dried three-necked flask. The above mixture was heated and kept under boiling state until half acetonitrile was distilled out. Afterwards, the hybrid HNTs were purified by centrifugation and washing with acetonitrile. The resultant hybrid HNTs were treated with 0.1 M HCl to exchange the Na^+ in $–SO_3Na$ with H^+. Then halloysite nanotubes bearing sulfonated polyelectrolyte brushes were obtained after being dried in a vacuum oven at 50 °C till constant weight.

2.2.2. Preparation of membranes

CS (1.5 g) was dissolved in acetic acid aqueous solution (2%, 40 mL) under stirring at 80 °C. Simultaneously, certain amount of nanotubes (HNTs or SHNTs) were dispersed into acetic acid aqueous solution (2%, 35 mL) with ultrasonic treatment for 30 min. These two parts of solution were then mixed and stirred vigorously at 80 °C for another 2 h. After degasification, the above homogenous solution was cast onto a clean glass plate with a piece of SPEEK nanofiber mat placed in advance, and dried at room temperature to obtain a membrane. The membrane was then immersed in 1.0 M H_2SO_4 for 24 h for complete cross-linking and then extensively rinsed with water to remove the residual H_2SO_4.