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Enhanced proton conductivities of nanofibrous composite membranes enabled by acid–base pairs under hydrated and anhydrous conditions



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ABSTRACT

Herein, a series of nanofibrous composite membranes (NFCMs) are designed and prepared by incorporating chitosan (CS) matrix into electrospun sulfonated poly(ether ether ketone) (SPEEK) nanofiber mats with controllable structures. Fourier transform infrared results suggest that the $-\text{SO}_3\text{H}$ groups of SPEEK and the $-\text{NH}_2$ groups of CS assemble into acid–base pairs along the nanofiber surface. The electrostatic attractions within the pairs inhibit the chain mobility of CS and SPEEK, endowing NFCMs with reinforced thermal and structural stabilities. Besides, the attractions drive the enrichment of acid/base groups near the nanofiber surface, thus providing more proton-hopping sites in the perpendicular direction of NFCMs. Together with the conducting groups in the amorphous CS phase, these sites donate significant enhancement in proton conduction *via* a low-energy-barrier manner. Particularly, a hydrated conductivity of 0.153 S cm^{-1} is achieved by the NFCM, much higher than those of CS (0.024 S cm^{-1}) and SPEEK (0.037 S cm^{-1}) casting membranes. Meanwhile, the formed acid–base pairs display unique anhydrous transfer ability, affording the NFCM a high anhydrous conductivity (59.6 mS cm^{-1}) at 120°C . Moreover, the influence of sulfonation degree and diameter of SPEEK nanofiber on proton conductivity is systematically investigated.

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1. Introduction

Proton conducting materials play a vital role in diverse chemical/biological processes and technological devices, such as proton exchange membrane fuel cell (PEMFC) [1–3]. As the key component of PEMFC, proton exchange membrane (PEM) should efficiently transport protons to fulfill the energy conversion and output [4–6]. Nafion is the dominant PEM material, which consists of a hydrophobic polytetrafluoroethylene backbone and hydrophilic side-chains terminated with $-\text{SO}_3\text{H}$ groups [4,7,8]. This amphiphilic structure affords a distinct nanophase separation to Nafion membrane, in which the $-\text{SO}_3\text{H}$ groups assemble into ionic clusters, working as facile proton transfer pathways [9–14]. Accordingly, Nafion membrane acquires the conductivity as high as 0.1 S cm^{-1} [4]. However, the intrinsic “dead ends” and discontinuity of the ionic clusters restrict the conduction ability of Nafion membrane. Besides, the low conductivity at anhydrous condition seriously limits the commercial application of Nafion-based PEM in the fuel cell.

Recently, one promising approach is developed by turning Nafion casting membrane into nanofiber *via* the facile electrospinning method. Driven by the shear force and hydrophobic interaction, the $-\text{SO}_3\text{H}$ groups preferentially converge along the axial direction of the nanofiber, forming a wide and continuous ionic channel. This channel serves as the long-range pathway for ultrafast proton migration, providing an extraordinary proton conductivity of 1.5 S cm^{-1} at 30°C and 90% RH, over 10 times higher than that of Nafion casting membrane [8]. Triggered by this, conducting nanofiber mats are employed to prepare conducting nanofibrous composite membranes (NFCMs) by filling the void space among nanofibers with polymer matrix. Choi et al. fabricated sulfonated poly(arylene ether sulfone) (SPAES) nanofiber mats and then filled them with an inert polymer. The resulting NFCM achieved an in-plane conductivity of 0.086 S cm^{-1} , slightly lower than that of pure SPAES nanofibers (0.135 S cm^{-1}) [15]. By comparison, Yao et al. incorporated the sulfated zirconia nanofiber mat with conducting polymer matrix (Nafion), and the authors found that the hydrogen-bonding interactions drove $-\text{SO}_3\text{H}$ groups to aggregate onto the nanofiber surface, giving an enhanced in-plane conductivity of 0.31 S cm^{-1} to the NFCM when compared with those of the pure nanofiber mat and Nafion

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membrane [16]. Accordingly, for NFCMs, the interfacial interactions play a key role in the proton transfer ability by regulating the arrangement of conducting groups near the nanofiber surface. Despite of these advantages, the conduction anisotropy between the perpendicular and parallel directions of NFCMs seriously limit their application as PEM at present [17,18]. Particularly, the deficiency of transfer pathways and conducting groups cause the proton conductivity in perpendicular direction to be one to two magnitudes lower than that in parallel direction. However, the former is the determiner on fuel cell performances. To overcome this intrinsic shortcoming, one facile and effective approach is to provide sufficient proton-hopping sites and thereby establish efficient conducting pathways in the perpendicular direction.

The carrier site (conducting groups) is another crucial determiner on proton transfer. The earliest developed proton carrier is acid groups (e.g., $-\text{SO}_3\text{H}$, $-\text{PO}_3\text{H}_2$, etc.), which dissociate H^+ to supply additional protons and work as proton donors. This kind of carrier possesses high proton conductivity ranging of 10^{-2} – $10^{-1} \text{ S cm}^{-1}$, and the acid group loading governs the proton conductivity. High acid group loading could result in high conductivity but excessive membrane swelling, which is detrimental to structural stability. In contrast to acidic carrier, basic carrier (e.g., $-\text{NH}_2$, $-\text{NH}-$) serves as proton acceptor, which first accepts the H^+ and then releases it to accomplish the proton transfer. The electrostatic force between basic group and H^+ makes the H^+ dissociation difficult, giving a weaker conducting ability ($< 10^{-2} \text{ S cm}^{-1}$) when compared with acidic carrier. To overcome the inherent shortcomings of acidic and basic carriers, a novel carrier (acid–base pair) is developed, in which the acid group and base group assemble into acid–base pair driven by the electrostatic interaction. Within the pair, protons could transport directly between the linked donor (acid group) and acceptor (base group) *via* Grotthuss mechanism. Meanwhile, the electrostatic interaction (i.e., Coulomb force) among the pair would promote the protonation/deprotonation and the subsequent proton-hopping. In such a way, the enthalpy change for proton conduction is reduced and the acid–base pair could transport protons *via* a low-energy-barrier manner [19–21]. Besides, the electrostatic attractions would inhibit the motion of polymer chains, conferring improved structural stability on the resultant membrane. For instance, Ji et al. developed an acid–base paired nanofiber through the assembly of trimesic acid and basic melamine, which obtained extraordinarily high proton conductivity of 5.5 S cm^{-1} at room temperature [22]. Coincidentally, acid–base pairs were also found in biological cells to form proton transfer pathways, and for example, bacteriorhodopsin proton pump is composed of carboxylic acid–Schiff base pair, through which ultrafast proton transfer is acquired [23]. However, the design and fabrication of NFCMs based on establishing acid–base pairs along the nanofiber/matrix interface has seldom been reported.

In this study, novel NFCMs were designed and fabricated by incorporating basic polymeric matrix into acidic nanofiber mat based on the following factors: (i) the acid groups within the nanofibers would be induced and gathered onto the nanofiber surface by the interfacial attractions, thus increasing the transfer sites on nanofiber surface; (ii) the conducting groups would form ordered acid–base pairs at nanofiber surface and then construct continuous conducting pathways in perpendicular direction supported by the inter-lapped nanofibers; and (iii) the bicontinuous-phase structure and strong interfacial interactions would endow NFCMs with improved structural stability [24]. Sulfonated poly(ether ether ketone) (SPEEK), a representative of aromatic sulfonated polymers, was chosen as the acidic material in virtue of its controllable $-\text{SO}_3\text{H}$ group loading and then electrospun into nanofiber mat [25–29]. Chitosan (CS) was chosen as the basic polymer on account of its excellent film-forming ability and low fuel crossover as well as low cost [30]. NFCMs were facilely prepared by directly immersing the SPEEK nanofiber mats into CS solution. The microstructures and physicochemical properties

of NFCMs were investigated in detail. The proton conduction properties and transfer mechanism of the 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. CS (see Scheme 2) with the 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), and acetic acid were purchased from Kewei Chemistry Co., Ltd. and used without further purification.

2.2. Fabrication of SPEEK nanofiber mats

SPEEK was fabricated according to the procedure in literature [31], and its chemical structure was presented in Scheme 2. During the sulfonation, the degree of sulfonation (DS) of SPEEK was controlled by tuning the sulfonation time. Four kinds of SPEEK with the DS of 52.5%, 60.2%, 74.0%, and 80.0% were obtained when the sulfonation time was 7, 8.5, 9.5, and 10 h, respectively. Afterwards, certain amount of SPEEK was dissolved in the mixture of DMF and THF (4:1 w-w) at 25 °C under stirring for 12 h. Four kinds of homogeneous SPEEK electrospinning solutions with the concentrations of 16, 17, 18 and 20 wt% were obtained by varying the amount of SPEEK. Then, the solution was held inside a 5-mL plastic disposable syringe for electrospinning. The needle-to-collector distance was fixed at 20 cm and the potential between the needle and the collector was kept at 25 kV. The rotating speed of the collector was set at 10 rpm. During the electrospinning, the diameter of SPEEK nanofiber was controlled by adjusting the solution concentration. The fabricated nanofiber mats were designated as SP-X-Y (Table 1), where X indicated the DS of SPEEK and Y (Y = 1, 2, 3, or 4) referred to the nanofiber diameter (94, 101, 131, or 142 nm). The nanofiber mats were peeled off from the aluminum foil and used for the preparation of NFCMs after being fully dried.

2.3. Preparation of the NFCMs

A certain amount of CS (1 wt%) was dissolved in acetic acid aqueous solution (1 wt%) under stirring at 60 °C for 2 h and then deaerated by ultrasonic treatment to prepare the casting solution. Afterwards, the CS solution was incorporated into the nanofiber mat on a clean glass bar, which was then dried for 72 h at room temperature to obtain a NFCM. Then, the NFCM was immersed in H_2SO_4 (1 M) for 24 h to completely cross-link the CS matrix, followed by thoroughly washing with de-ionized water until pH 7.0. The resultant NFCM was dried at room temperature under

Table 1
The entitling of the nanofiber mats and membranes.

Entry	Sulfonation degree (%)	Nanofiber diameter (nm)	Nanofiber mat	Membrane
1	52.5	94	SP-52-1	CS/SP-52-1
2	60.2	94	SP-60-1	CS/SP-60-1
3	74.0	94	SP-74-1	CS/SP-74-1
4	80.0	94	SP-80-1	CS/SP-80-1
5	60.2	101	SP-60-2	CS/SP-60-2
6	60.2	131	SP-60-3	CS/SP-60-3
7	60.2	142	SP-60-4	CS/SP-60-4

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