



High level of solid superacid coated poly(vinylidene fluoride) electrospun nanofiber composite polymer electrolyte membranes



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ABSTRACT

Electrospun fiber-based composite polymer electrolyte membranes (PEMs) with artificially constructed long-range proton conductive channels have been drawn considerable attention due to their promising applications in fuel cells. Herein, high level of superacidic phosphotungstic acid (PWA) coated poly(vinylidene fluoride) (PVDF/PWA) electrospun mat as a new three-dimensional proton conducting network was prepared using a polydopamine-assisted coating method. Polydopamine can homogeneously adhere PWA on the PVDF nanofibers' surface. This new mat was then used to fabricate PEMs after filled with polycation chitosan. With the introduction of the PVDF/PWA network, the obtained chitosan filled composite membrane showed significantly improved proton conductivity, which was about one order of magnitude higher than that of the chitosan filled pure PVDF membrane. Moreover, the chitosan can not only effectively inhibit the leaching out of PWA through the strong static interaction between chitosan and PWA, but also act as an ionomer matrix to further increase the proton transport. The direct methanol fuel cell of the PVDF/PWA composite membrane exhibits a peak power density of 85.0 mW cm^{-2} , whereas it is only 47.5 mW cm^{-2} for the membrane without PWA coating. Consequently, this study provides a new strategy to design high-performance PEMs by utilization of solid superacid coated electrospun nanofibers.

1. Introduction

Polymer electrolyte membrane based fuel cells, including proton exchange membrane fuel cells (PEMFCs) and direct methanol fuel cells (DMFCs), have attracted more and more attention because of their potential application in transportation and in portable and stationary electronics [1]. As one of the crucial parts in PEMFCs and DMFCs, polymer electrolyte membranes (PEMs, also known as proton exchange membranes) should possess the essential functions of conducting protons as well as separating fuels and oxidants. Up to now, Dupont's Nafion[®] perfluorinated sulfonic acid membranes are still the most commonly used PEMs due to their relatively high proton conductivity and good chemical and electrochemical stabilities. However, their very high cost, poor methanol barrier ability and limited operation temperature in fuel cells are difficult to meet the requirement of widespread applications. Consequently, numerous researches have been performed on seeking alternatives of Nafion[®] [2,3]. Although sulfonated aromatic polymers have been extensively investigated among

these replacements [4–7], the connected sulfonic acid-aggregated ionic clusters can not be easily formed when compared with Nafion[®] because of the electron-withdrawing characteristics of fluorine atoms around the terminal sulfonic acid groups on Nafion's side chains. Thus, with consideration of the mechanism of proton conduction in PEMs, constructing connective pathways for proton transport is an effective way to significantly increase the proton conduction ability of PEMs [8].

Two main strategies have been utilized to generate proton conductive channels in PEMs. One is self-organization of proton transport pathways through microphase separation in some statistical and segmented polyelectrolyte copolymers with specially tailored polymer structures [8–12]. For these ion-containing copolymers, the structure morphology of PEMs plays an important role in constructing continuous proton conductive channels which are closely associated with the domain size and connectivity level of ionic clusters. Unfortunately, in these cases, it is difficult to guarantee the high-level (or long-range) organization of the phase-separated ionic domains because the complicated interactions between solvents and polymers often affect the final

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morphology during the solution casting process [13]. Therefore, compared with the first method, long-range proton conductive channels artificially fabricated by electrospinning technique, which is able to produce fibers in submicrometer to nanometer scale, is more attractive in improving proton conductivity of PEMs. Since the first report by Pintauro's group [13] in 2008 successfully prepared three-dimensional composite nanofiber PEM composed of electrospun polyelectrolyte and inert polymer, many studies have focused on electrospinning of polyelectrolyte nanofibers [14–20]. It was reported that, due to the induced long-range ionic channels, rapid proton transport could be available in these polyelectrolyte-based electrospun nanofibers. Nevertheless, polyelectrolyte-based electrospun nanofibers usually suffer from their less mechanical strength and relative difficulty of electrospinning when compared with other polymer nanofibers.

Considering the induction effect of formation of long-range ionic channels majorly performs at the surfaces of the nanofibers [21], apart from direct electrospinning of polyelectrolytes, surface modification of some non-ionic polymer nanofibers but with highly spinnable ability might be another effective way to artificially construct ionic-conducting nanofibers. Zhang's group [22] introduced sulfonic acid groups to the surfaces of polystyrene electrospun fibers and then impregnated Nafion into the voids. With the assistance of the sulfonic acid groups on the continuous fiber surfaces, long-range pathways for facile proton transport were formed and the resulting composite membrane showed a proton conductivity as high as $1.8 \times 10^{-1} \text{ S cm}^{-1}$ at 80 °C and 100% RH. Subsequently, they further used superacidic sulfated zirconia (S-ZrO₂) electrospun fibers as the highly-conductive mat, which was prepared firstly by electrospinning polyvinylpyrrolidone and the precursors of S-ZrO₂ and then by sulfation and calcination [23,24]. The obtained S-ZrO₂-based conductive inorganic fiber/polymer hybrid PEMs demonstrated higher proton conductivities than that of recast Nafion. Lee et al. [25,26] developed a hygroscopic silica nanoparticle-coated polyimide (PI) electrospinning nanofibers as a reinforced porous substrated for Nafion-impregnated composite membranes. The SiO₂ nanoparticles in the PI fiber substrate not only improved the dimensional change and mechanic strength, but also increased the adsorbed water content in the composite membranes, which effectively suppressed the decline of proton conductivity at a low humidity condition of 10% RH. Liu and co-workers [21,27] used poly(vinylidene fluoride) (PVDF), which has high mechanical strength, chemical resistance and spinnability, as the nanofiber mat. To further increase the interfacial compatibility between the PVDF nanofibers and Nafion filler, and provide an ionic channels along the nanofibers, poly(styrenesulfonic acid, PSSA)-[21] and Nafion-functionalized [27] PVDF nanofibers were prepared using surface-initiated atom transfer radical polymerization and ozone-assisted 4-step chemical reaction, respectively. The results showed that the performances of the single cells employing the Nafion impregnated the Nafion- and PSSA-functionalized PVDF fiber composite membranes were superior to that of the commercial Nafion 212 membrane. However, the synthesis procedures are complicated and thus lead to a high processing cost.

Recently, phosphotungstic acid (PWA), which possesses a very strong Brønsted acidity, was immobilized onto the Nylon-66 electrospun nonwoven to obtain a highly selective methanol barrier interlayer [28]. And then, mechanically stable membranes also with high proton conductivity and methanol barrier ability were assembled by sandwiching the PWA/Nylon-66 nonwoven between two outer layers of recast Nafion membrane. Nevertheless, no obvious PWA coating layer on Nylon-66 fibers could be found even if the PWA content was as high as 54 wt%. Moreover, the long-time stability of this sandwich structured membrane during the fuel cell operation still remains doubts. Therefore, in this work, high level of PWA was uniformly coated on the surfaces of PVDF electrospun nanofibers using a facile polydopamine (PDA)-assisted coating method, which is an effective secondary surface modification way [29,30] and has also been verified in our previous work [31]. In order to inhibit the leaching out of PWA with high water

solubility, chitosan, a natural alkaline polycation, was chosen to fill the void space in the nanofibers because positively charged chitosan can tightly anchor negatively charged PWA [32,33] and it is also a typical PEM matrix [34,35]. The preparation, microstructure and properties of the chitosan filled PWA coated PVDF nanofiber composite membranes were investigated and discussed.

2. Experimental

2.1. Materials

PVDF (Kynar HSV 900, Arkema, France), H₃PW₁₂O₄₀·xH₂O (PWA, Sinopharm Chemical Reagent Corp., China), and chitosan ([η] = 100 mPa s, Shanghai Kayon biological Co. Ltd., China.) were used after dried. Dopamine hydrochloride (A.R.) was purchased from Acros Organics Inc., Belgium. Trihydroxymethyl aminomethane (tris, A.R.) was purchased from Shanghai Ruji Biotech Co. Ltd., China. *N,N*-dimethylacetamide (DMAc, A.R.), acetone (A.R.), and sulfuric acid (98%) were purchased from Sinopharm Chemical Reagent Corp. and used directly without any purification.

2.2. Preparation of chitosan filled PVDF/PWA composite membranes

Electrospun PVDF nanofibers were prepared using a 16 wt% polymer solution in a 7:3 weight ratio of DMAc and acetone. The electrospinning process was carried out at a voltage of 15 kV and a solution feeding rate of 0.5 mL h⁻¹. The distance between the spinneret and an aluminum collector was fixed as 15 cm.

PWA coated PVDF (PVDF/PWA) nanofiber mats were prepared via a polydopamine-assisted surface coating method. Typically, PVDF electrospun nanofiber mat was evenly soaked in a dopamine solution (2.0 mg mL⁻¹) containing a tris-buffer solution (2 mM, pH = 8.5) as a solvent. Subsequently, the soaking solution was stirred at room temperature for 24 h to obtain polydopamine modified PVDF. Then, a series of PVDF/PWA-*x* (*x* refers to the concentration of PWA soaking solution) mats were prepared by further immersion of PDA modified PVDF in PWA solutions with different concentrations (5, 10, 15 and 20 wt%) at room temperature for 24 h. After removal of unloaded PWA by washing with water, the PVDF/PWA mats were repeatedly impregnated by a 2 wt% chitosan solution, which was prepared by dissolving chitosan in a 1% (v/v) acetic acid aqueous solution. Finally, the resultant membranes were soaked in a 0.5 M H₂SO₄ solution for crosslinking chitosan to obtain chitosan filled PVDF/PWA composite membrane. The preparation process of the chitosan filled PVDF/PWA composite membrane is illustrated in Fig. 1.

2.3. Characterization

Raman spectra and X-ray diffraction (XRD) measurements were performed on a LabRAM HR Evolution Raman Spectrometer (HORIBA Scientific Co., Japan) and a D8 Advance X-ray diffractometer (Bruker Co., Germany), respectively, to confirm the chemical and phase structure of the PVDF/PWA mats. Attenuated total reflection-Fourier transform infrared spectroscopy (ATR-FTIR) analysis was carried out with a Nicolet 8700 FTIR Spectrometer (Thermo Electron Co., USA). The morphology of samples was observed by scanning electron microscope (SEM, FEI Co., Netherlands). Thermo-gravimetric analysis (TGA) was conducted on an STA 6000 instrument (PerkinElmer Co., USA) at a heating rate of 10 °C min⁻¹ in a N₂ flow to determine the thermal stabilities of the PVDF/PWA mats. The crystallization and melting behavior was investigated by a STA 449 F5 differential scanning calorimeter (DSC, Netzsch Co., Germany).

PWA leaching test was carried out using a TU1901 UV-vis spectrometer (Beijing Persee Co., China). The CPVDF/PWA membrane was immersed in 100 mL of water and the concentration of PWA in the leaching solution was determined every 24 h [36]. A standard curve of

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