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Electrospun Nanofiber-Based Cardo Poly(aryl ether sulfone) Containing Zwitterionic Side Groups as Novel Proton Exchange Membranes

The sulfonated cardo poly(aryl ether sulfone) with zwitterionic side groups (PES-DS-70) was electrospun to bead-free nanofibers. The PES-DS-70 nanoporous mat was successfully filled with Nafion solution. Scanning electron microscopy observed that the PES-DS-70/Nafion composite membrane has bilayer morphology and good interfacial compatibility. Compared with the neat PES-DS-70, the PES-DS-70/Nafion bilayer membranes showed improved swelling resistance and proton conductivity. Moreover, methanol crossover of the composite film was suppressed due to incorporation of the PES-DS-70 nanofibers. The tensile strength and Young's modulus for the PES-DS-70/Nafion composite membranes were higher than Nafion117. Therefore, the composite membrane with superior combined properties has potential applications for polymer electrolyte membrane fuel cells.

1 Introduction

Direct methanol fuel cells (DMFC) are of particular interest and importance as a clean and efficient energy for mobile power sources (Yamaguchi et al., 2007). Proton exchange membranes (PEMs) are key materials for DMFC which have been most intensively explored for the past decades (Chen et al., 2012). Due to high proton conductivity and good chemical stability, Nafion can be used as PEMs (Fu et al., 2016). However, Nafion membranes also have some drawbacks, such as excessive fuel crossover, high cost, and poor mechanical properties (Hickner et al., 2004). Therefore, new strategies have been developed to overcome the limitations of Nafion, which is very necessary and urgent.

A strategy consists in incorporating inorganic fillers into the Nafion matrix (Sultan et al., 2017; Vittadello et al., 2008; He et al., 2016). Even so, it is still not satisfactory for development of PEMs. Recently, the introduction nanofibers through electrostatic spinning to fabricate composite proton exchange membranes become a focus of research (Choi et al., 2008; Liu et al., 2013). Electrospinning technique (EST), as a novel method of preparing nanofibers, has been successfully applied in proton exchange membranes, owing to the mats with high surface area and porosity, to greatly enhance the electrochemical performance of the DMFC (Chigome et al., 2011).

Non-ionic nanofibers have been utilized for the preparation of Nafion-based composite membranes, for example for poly(vinyl alcohol) (Lin et al., 2010), poly(vinylidene fluoride) (Choi et al., 2008), poly(lactic-co-glycolic acid)PLGA (Wang et al., 2013), and so on. It was noted that the nanofibers increased the mechanical strength, but reduced the conductivity for composite membranes due to the decrease in the ion exchange capacity. In contrast, polyelectrolyte nanofibers also have been introduced in the Nafion matrix. For instance, Li et al. (2014) reported Nafion-functionalized poly(vinylidene fluoride) (PVDF) nanofibers (PVDFNF-Nafion) to improve the interfacial compatibility between the nanofibers and Nafion matrix. Nevertheless, the manufacture of PVDFNF-Nafion nanofibers is very difficult. Shabania et al. (2011) fabricated bilayer membranes based on incorporation of nanofibers web. The results showed that the bilayer films have preferable electrochemical performance. On the other hand, Yao et al. (2011) reported a novel type of hybrid membranes which consist of electrospun inorganic sulfated zirconia (S-ZrO_2) fibers and Nafion matrix. Unfortunately, the interfacial compatibility of the hybrid membrane is weak due to lack of chain entanglements.

Zwitterionic polymers have both anion and cation groups in one molecular chain. Because of their special structure in the side-chain, Zwitterionic polymers possess outstanding chemical properties and better thermal stability (Xuan et al., 2009; Lowe et al., 2002). Zhang et al. (2011) reported a novel amphoteric polyelectrolyte, which carries zwitterionic groups [-$CH_2CH_2CH_2N^+CH_3(CH_2CH_2SO_3^-)_2$] in the side chain. The proton exchange membranes with zwitterionic side groups present low swelling ratio and high oxidative resistance, due to strong intermolecular interaction.

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In this paper, the zwitterionic sulfonated poly(aryl ether sulfone) (PES-DS-70) nanoporous mats were primarily electrospun. Subsequently, the PES-DS-70 nanofibers mat was incorporated in the Nafion matrix. The performance of the composite membrane will be comprehensively evaluated in terms of conductivity, swelling, methanol permeability and so on. We look forward to improve the properties via embedded of three-dimensionally interconnected network.

2 Experimental

2.1 Materials

The 3,3-bis(4-hydroxyphenyl)-2-(3-(methylamino)propyl)isoindolin-1-one (PPH-MPDA) was supplied by Changchun Institute of Applied Chemistry, Changchun, PRC. 4,4-Difluorodiphenylsulfone (DFDPS), N,N′-dimethyl-1,3-propanediamine (DMPA) and sodium 2-bromoethanesulfonate were purchased from Aldrich, Shanghai, PRC. All other chemicals were reagent grade and used as received.

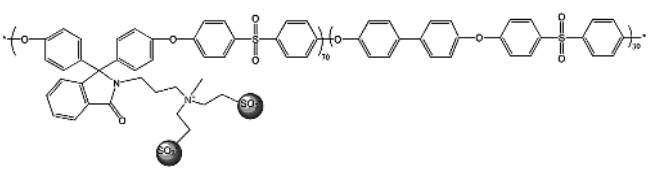
According to the previous reports by Zhang et al. (2011), the zwitterionic sulfonated poly(aryl ether sulfone) was synthesized, the chemical structure being displayed in Scheme 1. The polyelectrolyte was marked as PES-DS-70, where 70 represents the mole percentage of zwitterionic side chain.

2.2 Electrospinning of PES-DS-70 Nanofibers Mat

The nanofibers mat (NFM) was systematically fabricated by electrospinning. The PES-DS-70 was dissolved in DMF at a concentration of 35 wt%. The electrospinning processes were conducted at 15 kV of applied voltage with a flow rate of 0.05 ml/h. The needle-to-collector distance was 15 cm. Afterwards the nanofibers mat was dried under vacuum at 80 °C for 12 h to remove the residual solvent.

2.3 Preparation of the Composite Membrane

A certain amount of 5 % Nafion solution was poured on PES-DS-70 nanoporous mat. Then, the above solution was naturally dried for 3 days, thereby a flexible composite membrane (PES-DS-70/Nafion) having been obtained. Subsequently, the PES-DS-70/Nafion films were treated at 80 °C for 12 h under vacuum. Finally, all the membranes were analyzed after treatment with 1 mol/l H_2SO_4 solution for 48 h.



Scheme 1. Chemical structure of PES-DS-70

2.4 Measurements

Morphological observations were made with a Hitachi XE-100 scanning electron microscope (SEM). The sample was coated with gold before examination. The membrane was cut into strip-shaped specimens (5 mm × 20 mm) and measured by Instron-1211 instrument (Instron Co., Boston, USA) at the speed of 1 mm/min.

The dry membrane was weighted and immersed in deionized water for 24 h at 20 °C. Then the wet weight of the membrane was quickly determined. The percentage of weight gain with respect to the original weight was taken as the water uptake. The swelling ratio in water, a useful parameter for the numerical evaluation of dimensional stability, was calculated according to: swelling ratio (%) = $[l_{wet} - l_{dry}]/l_{dry}$, where l_{dry} and l_{wet} are the length of the dry and wet samples, respectively.

The proton conductivity (σ, S/cm) of full hydrated membranes was measured by a Solartron 1260 impedance/gain-phase analyzer (Solartron 1287, Farnborough, Hempshire, ONR, UK) over the frequency range of 10 to 10^6 Hz. The proton conductivity was calculated using: $\sigma = d/L_s \times W_s \times R$, where R is the determined membrane resistance, d is the distance between the reference-sensing electrodes, and L_s and W_s are the thickness and width of the membrane, respectively.

Methanol diffusion coefficients were measured using a diffusion cell consisting of two compartments at 20 °C. The increase of methanol concentration with time in the water compartment was monitored by GC-1020A chromatography (Shimadzu, Kyoto, Japan). The methanol diffusion coefficients were calculated by:

$$C_B(t) = \frac{A}{V_A}\frac{DK}{L}C_A(t - t_0), \quad (1)$$

where A, L and V_A are the effective area, the thickness of membrane and the volume of permeated compartment, respectively. C_A and C_B (mol/l) are the methanol concentration in the feed and in the diffusion compartment, respectively. DK is defined as the methanol permeability.

The oxidative stability of membranes (the size of each sheet: 0.5 cm × 1.0 cm) were evaluated from the membrane weight retention after immersion in Fenton's reagent (3 % H_2O_2 containing 2 ppm $FeSO_4$) at 80 °C for 1 h.

3 Results and Discussion

3.1 Electrospun Fibers and Membrane Morphology

The polymer concentration is an important parameter that influences the quality of electrospun fibers. DMF was chosen over other possible solvents because of its higher dielectric constant. At relatively low solution concentration, e. g., 25 wt%, the solution electrosprayed and hollow pellets were formed (Fig. 1A) as a consequence of Rayleigh instability in the jet due to high surface tension and low elasticity of the solution. For a higher concentration, 30 wt%, finer fibers with beads morphology was produced, as shown in Fig. 1B. Bead morphology has also been associated with capillary instability. The hypothesis is that at lower concentrations, the chains are insufficiently entangled to provide the high extensional viscos-

ity and strain-hardening behavior required to resist capillary break up of the threadline, leading to bead morphology. Above a solution concentration of 35 wt% (Fig. 1C), continuous, bead-free fibers were produced. As shown in Fig. 1C, the diameter distribution of the fibers is uniform with 200 to 500 nm range.

As shown in Fig. 1D, electrospun fibers have liquid drops and beads which occur at 8 kV voltage, and result in a brittle structure. The formation of defects is initiated by the jet stream not stretching sufficiently due to the low voltage. When the voltage rises to 15 kV (Fig. 1C), a few beads appear as a flat long spindle shape that can be seen uniform and no with tangles. Increasing to a higher voltage 20 kV (Fig. 1E), we can get a non-bead nanometer fiber mat, however, inevitably followed with tangles. Considering safety, the optimal voltage choosen is 15 kV.

The cross-sectional morphology of the samples is shown in Fig. 2. As shown in Fig. 2A, the electrospun PES-DS-70 mat exhibits a three-dimensional, porous and interconnective network of nonwoven fibers, which is helpful for enhanced proton conductivity and mechanical force of the resultant membrane (Tamura et al., 2010). The cross-sectional SEM photograph of the composite film is depicted in Fig. 2B, where a layered mor-

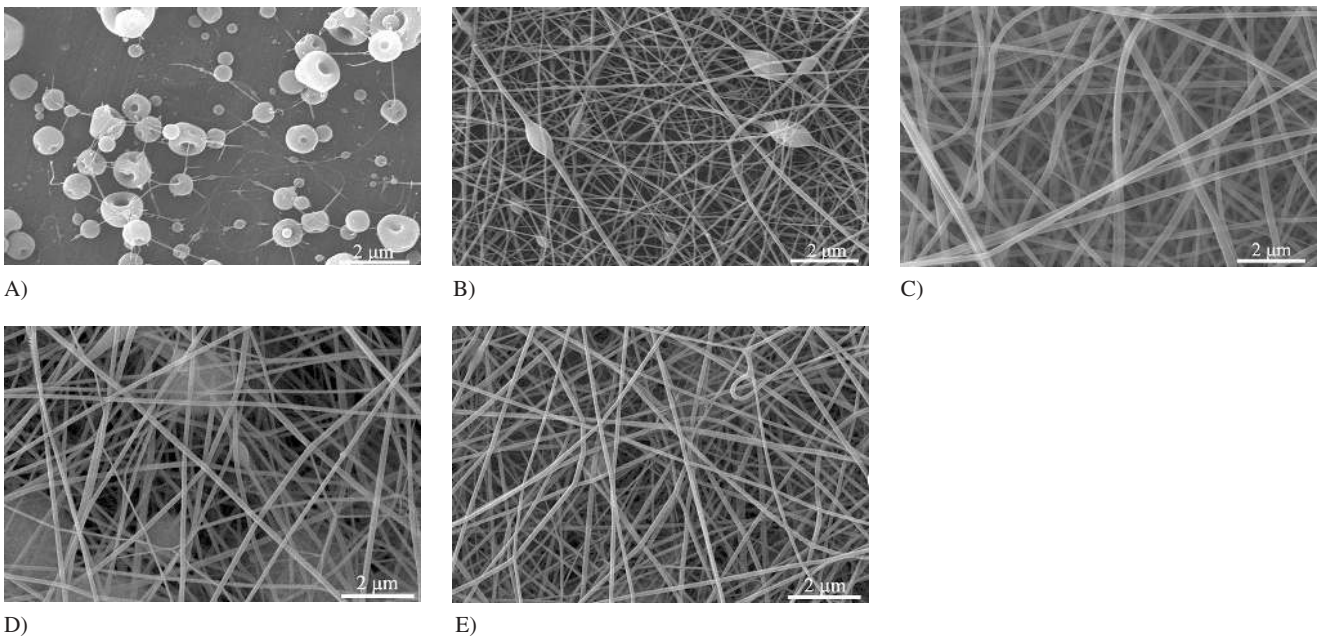


Fig. 1. SEM image of PES-DS-70 nanofibers electrospun from DMF with different mass fraction: A) 25%), B) 30%, C) 35%, V = 15 kV, D = 15 cm, T = 27°C and at different voltages: D) 8 kV, E) 20 kV, D = 15 cm, 35%, T = 27°C

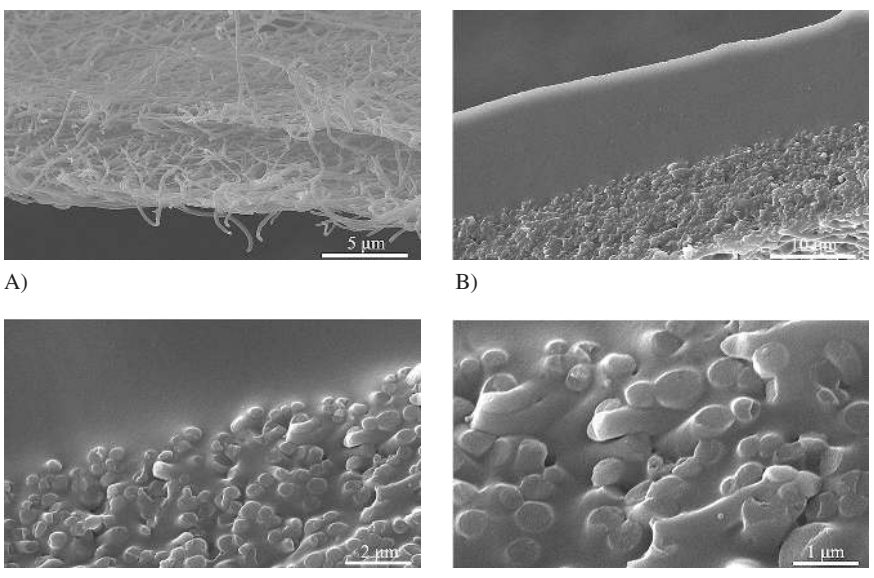


Fig. 2. Cross-sections of SEM images of the prepared samples for A) PES-DS-70 nanofiber mat, B, C) PES-DS-70/Nafion composite membrane, D) higher magnification micrographs

phology was observed including a Nafion layer and a composite layer with nanofibers. From the magnification image in Fig. 2C, no markedly crack or small holes along the interface bilayer were observed. This indicated good interfacial compatibility between Nafion layer and composite layer. Higher magnification micrographs can clearly show desirable composite structures (in Fig. 2D). All the pores within the nanofibers mat were successfully filled with Nafion matrix upon evaporation of the solvent. Fortunately, the nanofiber structure was integrallty preserved during the composite process, without noticeable decreasing in the fiber diameter.

3.2 Water Uptake and Swelling Ratio

The water uptake and swelling ratio of the membranes were determined at 20 °C. As shown in Fig. 3, the water uptake of NR212, Nafion117, PES-DS-70, and PES-DS-70/Nafion composite were 29.2, 19.6, 12.6, and 10.8 wt%, respectively. The water uptake has a direct influence on the proton transport, meanwhile the swelling ratio also must be considered for proton exchange membranes.

Good dimension stability has to be provided primarily in order to obtain excellent mechanical strength for PEMs. As expected, the swelling ratio of the PES-DS-70/Nafion composite was lower compared with NR212, Nafion117 and neat PES-DS-70 film. The three-dimensional network structures formed by PES-DS-70 nanofibers within the composite membrane eventually restrict the swelling ratio (Yun et al., 2011). These results imply that the Nafion matrix was efficiently reinforced by nanofibers, and the electrospun nanoporous mat was suitable for use as a supporting material in a pore-filling membrane.

3.3 Proton Conductivity

The proton conductivity is considered the most crucial property for PEMs. As show in Fig. 4, the conductivity of all membranes steadily increases with temperature because the free volume, which favors ion transport and the mobility of cations, is increased as the temperature rises. Among the PES-DS-70/Nafion bilayer membranes, the conductivity goes up to 0.13 S/cm at 80 °C, which is higher than the for neat PES-DS-70 film in whole temperature range (20 to 80 °C). This result is satisfactory, which perhaps is the contribution of the Nafion with greater conductivity. Moreover, this conductivity increase is also due to the PES-DS-70 nanofibers. The proton channel structure due to the network of the sulfonic acid groups formed within the nanofiber may lead to the rapid proton transport (Tamura et al., 2010).

3.4 Methanol Permeability

Excess methanol crossover for proton exchange membrane, which not only leads to the significant decrease of the fuel efficiency, but also reduces the output voltage of the battery, will poison cathode catalyst, declining the battery performance dramatically (Ge et al., 2005). Therefore, it is expected for low methanol diffusion coefficient. The methanol permeability of the films is listed in Table 1. Under the same test conditions, the PES-DS-70/Nafion composite membranes exhibited methanol permeability of 9.3×10^{-7} cm^2 s^{-1}, which was much lower than Nafion117 (2.4×10^{-6} cm^2 s^{-1}). The methanol crossover got inhibited in the composite, owing to the formation of a long and tortuous path within the nanofibers network (Hasani-Sadrabadi et al., 2011). Meanwhile, the methanol permeability of PES-DS-70/Nafion composite film was slightly higher than the PES-DS-70 membrane.

It is desirable to have high proton conductivity together with low methanol crossover for DMFC. The selectivity represents the ratio of proton conductivity to methanol permeability. It is often used to evaluate the prospect of the membrane for the DMFC. The relative selectivity of the PES-DS-70/Nafion composite membrane was about 7.1×10^4 S s cm^{-3}, which is higher than 2.5×10^4 and 3.7×10^4 S s cm^{-3} for PES-DS-70 and Nafion117, respectively. Combining nanofibers maybe increased the selectivity of the composite film. The oxidative stability of membranes was evaluated at 80 °C Fenton's reagent for 1 h as

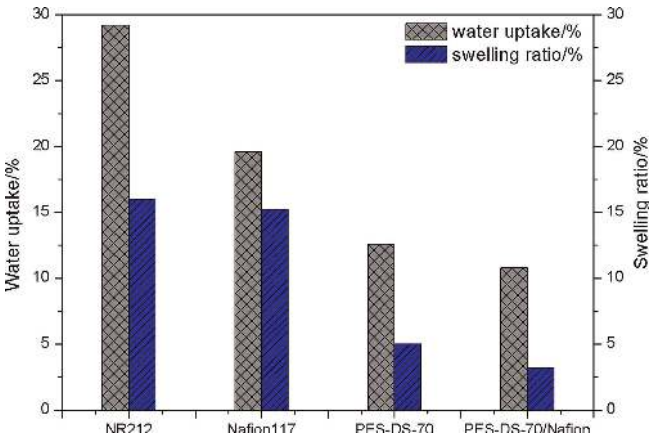


Fig. 3. Water uptake and swelling ratio of the membranes

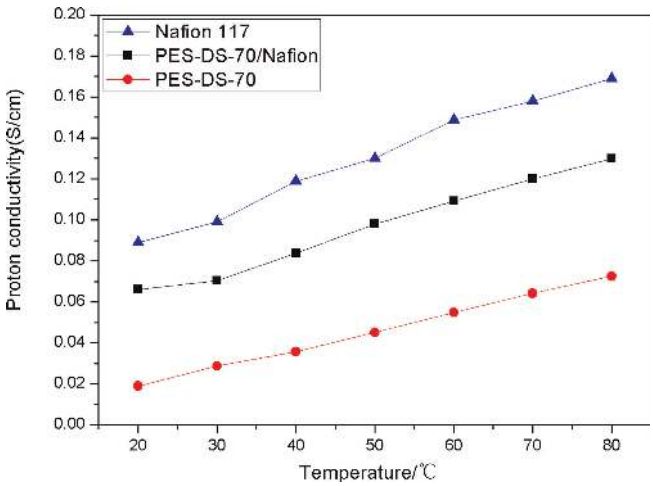


Fig. 4. Influence of temperature on proton conductivity

Membrane	σ S cm^{-1}	P_M $\times 10^{-6}$ cm^2 s^{-1}	Φ 10^5 S s cm^{-3}	Oxidative stability wt%
PES-DS-70	0.019	0.75	0.25	95.2
PES-DS-70/Nafion	0.066	0.93	0.71	97.4
Nafion117	0.089	2.4	0.37	99.0

Table 1. Methanol permeability and oxidative stability of membranes

an accelerated test. As presented in Table 1, the residue of all the membranes is above 95 %, which shows excellent oxidative stability.

3.5 Mechanical Properties

The mechanical properties were summarized in Table 2 at room temperature in 50 % relative humidity (RH). The tensile strength and Young's modulus for the PES-DS-70/Nafion composite membranes were 20.2 MPa and 665 MPa, respectively, which is higher compared to Nafion117. The PES-DS-70 nanofibers formed better connectivity nonwoven network, acting as reinforcement of the Nafion matrix. Although the PES-DS-70/Nafion mechanical properties are slightly lower than those of PES-DS-70 film, the resulting membrane still would meet the requirements for DMFC application.

4 Conclusions

The bilayer composite membrane composed of zwitterionic sulfonated cardo poly(aryl ether sulfone) (PES-DS-70) nanofibers and Nafion matrix was produced using a pour out method. The morphology reveals that the inter voids were successfully filled with Nafion. The swelling ratio of the PES-DS-70/Nafion composite film was appreciably reduced compared to the neat PES-DS-70 membrane. The conductivity of the bilayer composite is much higher relative to a homogeneous PES-DS-70 film. Moreover, the PES-DS-70/Nafion bilayer membrane exhibited lower methanol permeability and higher selectivity than Nafion117. Undoubtedly, this work has provided an effective approach for the development of proton exchange membranes.

Polymer	Tensile strength MPa	Young's modulus MPa	Elongation at break %
PES-DS-70	31.5	860	4.4
PES-DS-70/Nafion	20.2	665	20
Nafion117	18.3	164	190

Table 2. Mechanical properties of membranes

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