



Enhanced proton conductivity and dimensional stability of proton exchange membrane based on sulfonated poly(arylene ether sulfone) and graphene oxide



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ABSTRACT

A series composited membranes of sulfonated poly(arylene ether sulfone) and graphene oxide (SPAES-GO-x) have been exploited as proton exchange membrane. The properties of SPAES-GO-x membranes were evaluated including proton conductivity, water uptake, swelling ratio, oxide and thermal stability. Incorporating GO into SPAES matrix restrained the composite membranes swelling and enhanced their proton conductivity. The SPAES-GO-3% membrane showed a conductivity value of 0.183 S cm^{-1} at 120°C and relative humidity 100%. Compared with the pristine SPAES membrane, the swelling ratio of SPAES-GO-2% membrane was reduced by 55.7% at 90°C . Small-Angle X-ray Scattering (SAXS) revealed GO promoted SPAES molecular chain movement to form bigger ionic clusters in favor of enhancing proton transport. X-Ray Diffraction and Field Emission Scanning Electron Microscope (XRD and FE-SEM) analysis further demonstrated GO was exfoliated and distributed throughout the SPAES matrix. These results indicated GO was an effective filler to trade off proton conductivity and swelling of composite membrane.

1. Introduction

As a kind of promising energy conversion devices, proton exchange membrane fuel cells (PEMFCs) have been attracted more attention owing to zero emission and high efficiency [1,2]. Perfluorosulfonic acid based membranes, particularly Nafion, are considered one of the best performers in PEMFCs due to their excellent proton conductivity and chemical stability. However, the low proton conductivity and severe fuel crossover at elevated temperatures and high cost hinders the Nafion largescale applications [3–5]. These drawbacks have aroused widely research interest on searching for the alternative PEMs based on sulfonated aromatic polymers including sulfonated poly(arylene ether sulfone)(SPAES). SPAES have been considered regarded as one kind of promising attractive material because it has excellent mechanical properties, low fuel crossover, and easy functionalization [6–8].

In general, a high ion exchange capacity (IEC) endows that SPAES PEM gains high proton conductivity, nevertheless it leads to SPAES membrane suffering from excessive swelling. To address above issues, great efforts have been made to trade off the proton conductivity and

the welling of SPAES PEM. Several pathways were employed to constrain the excessive swelling of SPAES PEM including incorporating fillers [9–11], physical blend [12,13], chemical cross-linking [14–16]. It is an effective way to enhance proton conductivity of sulfonated aromatic polymers PEM modified with fillers [17,18]. Among these fillers, graphene oxide (GO) have been an ideal candidate for promoting the proton propagate through hydrogen-bonding networks due to their surface functional groups containing hydroxyl, epoxy and carboxyl groups [19,20]. Intensive researches have been shown that aromatic polymers matrix containing GO or its derivatives exhibited a high proton conductivity and a low permeability to reactant [21,22]. However, it has not been fully realized that the SPAES polymer modified with GO or its derivatives as proton exchange membrane. Ko et al. [23] incorporated poly(2,5-benzimidazole)-grafted GO into the SPAES matrix. The composite membranes had better dimensional stability and proton conductivity than that of pristine SPAES. Zhao et al. [24] reported a series of novel ionic cross-linked sulfonated poly(ether sulfone) comprised with quaternized GO, which enhanced the mechanical property and oxidative stability of composite membrane, but reduced

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its proton conductivity. In addition, the SPAES membranes composited with GO derivatives shown a high proton conductivity, but led to a high swelling ratio [25–27].

Based on above discussion, the relation of proton conductivity and stability of SPAES-GO composite membrane still need to be further addressed. The main goal of this work investigated the GO effecting on the morphology and properties of SPAES-GO-x membranes. The SPAES-GO-x membranes were obtained, which GO exfoliated and dispersed homogeneously in the composite membranes. GO promoted the sulfonic acid groups of SPAES molecular chain aggregation (big ionic clusters) to enhance proton transport. Furthermore, the special two-dimensional structure of GO was helpful to enhancing not only the proton conductivity but also dimensional stability of composite membrane.

2. Experimental

2.1. Materials

Graphite powder (325 mesh) was obtained from Aladdin. Potassium permanganate (KMnO₄), nitric acid (HNO₃), tetrahydrofuran, sulfuric acid (H₂SO₄), *N,N*-dimethylacetamide (DMAc), Hydrochloric acid (HCl) and hydrogen peroxide (H₂O₂) were purchased from Sinopharm Chemical Reagent Co., Ltd. 4,4'-dichlor-odiphenylsulfone(DCDPS), and 3,3'-disulfonate-4,4'-dichlorodiphenylsulfone(SDCDPS) were obtained from shanghai darui finechemical Company. Phenylhydroquinone was prepared by the same method as we have previously reported [28]. All the other chemicals and solvents were used without further purification.

2.2. Measurements

Field emission scanning electron microscope (FE-SEM) (Hitachi U8010) was used to investigate the morphology of membranes. ¹H NMR spectra were measured on A Bruker AV NMR spectrometer (400 MHz) using DMSO-*d*₆ as the solvent and tetramethylsilane as the standard. Fourier Translation Infrared Spectrum (FT-IR) of the membrane was recorded on Nicolet 8700.

The membrane samples were heated under nitrogen at a heating rate of 20 °C min⁻¹ from 50 °C to 350 °C using TA Q20 differential scanning calorimetry (DSC) measurements. The membrane samples were equilibrated to 50 °C and then heated to 800 °C at 20 °C min⁻¹ under nitrogen flow on TA Discovery thermal system (TGA).

Atomic Force Microscope (AFM) images in the tapping mode were obtained by using a Digital Instrument NanoScope in ambient conditions. All data were collected on Small-angle X-ray scattering measurement (SAXS) and corrected for background at room temperature. X-Ray Diffraction (XRD) patterns of dry membranes were recorded in the 2θ range 5–70° at a scan rate of 2° min⁻¹ with X-ray diffractometer (D/MAX-2500, Rigaku) at room temperature. The X-ray photoelectron spectrum (XPS) analysis was performed on PHI-540 with an Al Kα = 1486.6 eV excitation source.

The mechanical properties were measured on an Instron 5969 Tester with a strain rate of 5 mm/min at room temperature. Five individual specimens were used for each sample.

2.3. Preparation of graphite oxide and SPAES-GO-x membrane

Graphene oxide (GO) was prepared by the modified Hummers method [29]. Obtained water dispersion of GO sheets keep in brown reagent bottle for use. The composite membranes were prepared by a solution casting method. SPEAS polymer (0.6 g) was dispersed in the 12 ml DMAc. The desired weight ratios of GO water dispersion was dissolved in the SPEAS polymer solution (V_{DMAc}:V_{water} = 10:3). Then the mixture was sonicated for 30 min. The mixture was filtered and cast onto 90 mm diameter glass dishes, and subsequently dried at 60 °C for

24 h under vacuum.

2.4. Ion exchange capacity, water uptake and swelling ratio

The ion exchange capacity (IEC) of the membrane (10 mm × 30 mm) was determined using a typical titration method. The membranes, completely replaced with sodium ions, titrated with a 0.1 M NaOH solution using phenolphthalein as an indicator. The IEC was calculated via the following formula:

$$\text{IEC (meq g}^{-1}\text{)} = V_{\text{NaOH}} \times C_{\text{NaOH}} / W_{\text{dry}} \quad (1)$$

where V_{NaOH} is the consumed volume of NaOH, C_{NaOH} is the molar concentration of NaOH, and W_{dry} is the weight of dried membrane.

The water uptake (WU) of membrane (10 mm × 30 mm) was estimated from the mass change before and after the membrane was completely dry. A dry membrane was submerged in deionized water in a fully hermetic flask at controlled temperatures for a day, then the surface water was wiped off carefully with filter paper, and the membrane was immediately weighed. Before the testing, the sample was dried in a vacuum oven at 80 °C for 48 h, the WU was calculated using the equation:

$$\text{WU} = (W_{\text{wet}} - W_{\text{dry}}) / W_{\text{dry}} \times 100\% \quad (2)$$

where W_{wet} and W_{dry} are the masses of the fully hydrated membrane and the dry membrane, respectively.

The membrane samples (10 mm × 30 mm) were vacuum dried at 80 °C for 48 h, then were immersed in deionized water at a constant temperature for a day. After the surface water carefully wiped off, the length (L_x) and width (L_y) of the membrane samples were quickly measured. Thus, the swelling ratio (SR) of each membrane was calculated using the expressions:

$$S = L_x \times L_y$$

$$\text{SR} = (S_{\text{wet}} - S_{\text{dry}}) / S_{\text{dry}} \quad (3)$$

where S_{wet} and S_{dry} are the area of the fully hydrated membrane and the dry membrane, respectively.

2.5. Proton conductivity

The membrane sample was immersed in 1M H₂SO₄ at room temperature for 48 h and then washed to a pH of 7 with deionized water. The proton conductivity of the membranes (8 mm × 10 mm) was measured by an AC impedance technique [30]. The proton conductivity was calculated from the following equation:

$$\sigma = L / RA \quad (4)$$

where L and A are the thickness and the contact area of the membrane sample, respectively, and R is the membrane resistance.

2.6. Oxidative stability

The membrane samples (10 mm × 30 mm) were immersed in Fenton's reagent (3% H₂O₂ containing 2 ppm FeSO₄) at 80 °C. The oxidative stability was evaluated by recording the retained weights of the membranes after treatment in Fenton's reagent for 1 h, and the time when the membranes began to break into pieces.

3. Results and discussion

3.1. Synthesis and characterization of sulfonated poly(arylene ether sulfone)

SPAES polymer was synthesized following our previous work [31]. The chemical structures and sulfonation degree (DS) values of SPAES

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