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Perfluorosulfonate ionomer membranes with improved through-plane proton conductivity fabricated under magnetic field

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ABSTRACT

Magnetic field treated perfluorosulfonate ionomer (PFSI) membranes (M-PMs) with improved through-plane proton conductivity are facilely fabricated though solvent casting of PFSI/Fe_3O_4 nanocomposite dispersion without any third additive under magnetic field followed by discarding the Fe_3O_4 nanoparticles. In the PFSI/Fe_3O_4 nanocomposite membrane, Fe_3O_4 nanoparticles are clearly uniaxially aligned by magnetic field. Subsequently, M-PMs are obtained by removing Fe_3O_4 from the nanocomposite membranes to eliminate the negative effect of Fe_3O_4 on proton conducting. The effect of magnetic field treatment on M-PMs' performance is investigated by both in- and through-plane proton conductivity. The results demonstrate that the through-plane proton conductivity of the M-PMs prepared from PFSI/Fe_3O_4 nanocomposite membrane with optimized Fe_3O_4 content is enhanced, while the in-plane proton conductivity is reduced compared to the pristine PFSI membrane, which indicate through-plane anisotropic phenomenon of proton conducting in the membranes. Such magnetic field treated PFSI membranes exhibit good appropriateness for using in electrochemical applications, for example fuel cells.

1. Introduction

Polymer electrolyte membranes (PEMs) have been widely used as core parts in Fuel cells[1,2], water electrolyzers[3], chlor-alkali cells[4], soft actuators/sensors[5] and so on. Perfluorosulfonate ionomers (PFSIs) [6] have drawn most attention for their high conductivity, fine chemical stability and good mechanical strength, which are the basic requirements for the above electrochemical mechanical devices.

In PFSI membranes, many randomly dispersed local parallel cylindrical channels[7] play the role as ionic paths for ions to transport between two electrodes by means of the side chains' sulfonic acid groups and bulk water in the pores [8]. The randomly dispersed channels might result in isotropic phenomenon in ion conducting which means the ion conductivities along in- and through-plane direction may be identical[9,10]. Besides, even the results that the in-plane conductivity is higher than through-plane were frequently obtained in literatures [11–14]. However, when the membranes are applied in electrochemical devices, it is the through-plane direction that the current flows along, so the through-plane conductivity may play a leading role in practical applications.

Therefore, the fabrication of anisotropic membranes orientated along the normal direction is quite an attractive idea to enhance through-plane conductivity for electrochemical applications. In recent years, many researchers began to focus their attention on the orientation of proton conducting membranes in the through-plane direction. Two methods, including fabricating membranes under electric and magnetic field, were applied [15–17]. Yates and their coworkers [15] have fabricated Nafion®/polystyrene-b-poly(ethylene-ran-butylene)-b-polystyrene composite membranes under electric field. The through-plane proton conductivity of composite membrane prepared in electric field was improved compared to the one without electric field. They attributed this enhancement to the aligning of the Nafion® domains across the membrane by the field. A similar result was gained when using poly (vinylidene fluoride) composite in another article from them [16]. Gopinadhan et al. [18] have created well-aligned arrays of amorphous poly(ethylene oxide) microdomains in a liquid crystalline block copolymer in magnetic field. γ-Fe_2O_3 nanoparticles were introduced to membrane preparation in magnetic field by Brijmohan et al. [19] and Hasanabadi et al. [20]. The matrixes they have used were sulfonated poly (ether ketone ketone) and sulfonated poly (ether sulfone) respectively. Owing to the orientation of γ-Fe_2O_3 nanoparticles along the

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through-plane direction, the magnetic field treated composite membranes had higher through-plane conductivity than the composite membranes without magnetic field treatment.

In the magnetic field treatment, since magnetic nanoparticles cannot be directly mixed with polymers to form composition with sufficient stability, researchers turned to introduce a third additive, for example polystyrene, to stabilize the nanoparticles in polymer matrix [19,20]. However, this is not an ideal solution because the third additive itself may bring some negative effects on the final performance of the membranes, such as blocking proton conducting, reducing the membrane stability and so on. In addition, the magnetic nanoparticles stabilized by a third additive are not easy to be removed, which might result in a decrease of conductivity due to the extremely low ion exchange capacity (IEC) of the magnetic nanoparticles.

In this work, we have synthesized Fe_3O_4 nanoparticles in-situ in PFSI solution similar to Kim et al. [21] reported. This pre-stabilization procedure could solve the above mentioned problems successfully, although the interaction mechanism between Fe_3O_4 and PFSI is unclear and need further investigation. The PFSI-stabilized Fe_3O_4 (P-Fe_3O_4) nanoparticles were stably composited into PFSI solution, and the obtained PFSI/Fe_3O_4 dispersions were cast under magnetic field to form aligned membranes. Afterwards, the low-IEC Fe_3O_4 in the membrane matrix can be easily removed through dissolving in sulfuric acid solution, and the treated membranes with only the PFSI matrix left were obtained. The effect of the magnetic field treatment on the membranes was systematically investigated by in- and through-plane proton conductivity measurements.

2. Experimental

2.1. Materials

The H^+ type PFSI resin with equivalent weight (EW) of 990 g mol^{-1} was kindly supplied from Dongyue Shenzhou New Materials Company Ltd., China, and the structure formula is displayed in Fig. 1. Hydrogen peroxide (30%), concentrated sulfuric acid and anhydrous $FeCl_3$ were purchased from Sinopharm Chemical Reagent Co., Ltd, $FeCl_2 \cdot 4H_2O$ from Aladdin Chemistry Co., Ltd, anhydrous ethanol from Changshu Yangyuan Chemical Co., Ltd, and N, N-dimethylformamide (DMF) from Shanghai Lingfeng Chemical Co., Ltd. All the reagents were directly used without any purification.

2.2. Sample preparation

The sample preparation processes are shown in Fig. 2.

2.2.1. Preparation of PFSI solution

The H^+ type PFSI resin was dissolved into 1:1(*w/w*) ethanol/water mixture in an autoclave at 230 °C for 2.5 h to gain a 5% (*w/w*) solution. Then the solution was filtrated and heated at 40 °C in an electrical blast oven for 20 h and some yellowish-white powders formed. These powders were vacuum dried at 40 °C for 12 h to further remove the residue solvent. To prepare 33% (*w/w*) PFSI DMF solution, PFSI powders were dissolved into DMF at 40 °C in a constant temperature oscillator for 12 h. The newly prepared solution was filtrated to remove some impurity and gel before use.

Fig. 1. The structure formula of perfluorosulfonate ionomer, *m* is about 5.5 for EW 990 g mol^{-1}.

2.2.2. Synthesis of PFSI-stabilized Fe_3O_4 nanoparticles (P-Fe_3O_4)

PFSI-stabilized Magnetic nanoparticles were prepared in-situ in PFSI solution modified from the traditional co-precipitation method [22]. 2% PFSI ethanol/water solution was fabricated by directly diluting of 5% PFSI ethanol/water solution. Afterwards, 0.7 g anhydrous $FeCl_3$ and 0.43 g $FeCl_2 \cdot 4H_2O$ were dissolved into 50 ml of 2% PFSI solution, which had been previously heated to 80 °C in a hot water bath and purged with N_2 for about 5 min. The mixture was kept for 80 °C under mechanical stirring with N_2 still flowing for 5 min, after the dissolution of the two chlorides. Then 3.75 ml of 25% $NH_3 \cdot H_2O$ was dropwise added into the solution, which turned black gradually from the initial yellow with increasing the formed magnetic nanoparticles. After that the mixture was kept at 80 °C under stirring for 10 min. Next the suspension was washed for at least five times by distilled water with the aid of magnetite to speed up precipitation of the black mud. The black precipitates were dried at 80 °C in vacuum oven for 12 h, which were then grinded to black fine power (P-Fe_3O_4) in an agate mortar. Finally, 2% (*w/w*) P-Fe_3O_4 DMF dispersion was prepared by adding P-Fe_3O_4 into DMF through 30-min ultrasonic processing. In addition, Fe_3O_4 magnetic nanoparticles were also fabricated for comparison in water using the traditional co-precipitation method[22].

2.2.3. Preparation of magnetic field treated PFSI membranes (M-PMs)

Firstly, the 2% P-Fe_3O_4 DMF dispersion was mixed with 33% PFSI DMF solution to form a series of PFSI/Fe_3O_4 DMF dispersions. The dispersions were dispersed through ultrasonic treatment for 30 min, constant temperature oscillating at 40 °C for 12 h and another 30 min of ultrasonic processing. Next we cast the dispersion onto a glass plate with a stainless steel scraper, and applied a magnetic field perpendicular to the plate with the strength of 0.185 T. In the first hour after casting, no heating was supplied to the system to align the nanoparticles along the magnetic field direction. Then the system was heated to 180 °C and maintained for 3 h, during which the DMF slowly evaporated and a light brown membrane was generated. After that, the heating oven was turned off and the whole system was gradually cooled to room temperature. These PFSI/Fe_3O_4 composite membranes (CMs) with magnetic field treatment were recorded as M-CMs. For comparison, we fabricated the same composite membranes using the same procedure but without magnetic field, which were noted as NM-CMs accordingly. Among them, we named each membrane according to its P-Fe_3O_4 weight percentage. For example, 1-M-CM was the M-CM with 1% (wt %) of P-Fe_3O_4. Pristine PFSI membranes without adding P-Fe_3O_4 were also prepared by casting method with the same heating program.

All the membranes were purified and activated with the widely used procedure. They were immersed in 3% H_2O_2 solution, de-ionized water and 1 M H_2SO_4 solution at 80 °C in sequence, each of which lasted for 1 h. The Fe_3O_4 nanoparticles in the PFSI/Fe_3O_4 composite membranes (M-CMs or NM-CMs) can be easily dissolved in the one-hour H_2SO_4 step for H_2SO_4 was likely to react with Fe_3O_4. Finally, the membranes were washed for three times in de-ionized water at 80 °C each for 1 h. All the treated membranes were stored in de-ionized water at room temperature for further use. The obtained magnetic field treated PFSI membranes purified from M-CMs were recorded as M-PMs, for example 1-M-PM, and for comparison the purified NM-CMs were named as NM-PMs. The P-Fe_3O_4 weight percentage was also added in the sample name