Solid State Ionics 289 (2016) 199–206

Contents lists available at ScienceDirect

Solid State Ionics

journal homepage: www.elsevier.com/locate/ssi

Sulfonated poly(ether ether) ketone/polyurethane composites doped with phosphoric acids for proton exchange membranes

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ARTICLE INFO

Article history:
Received 18 December 2015
Received in revised form 25 February 2016
Accepted 12 March 2016
Available online 2 April 2016

Keywords:
Polyurethane
Sulfonated poly(ether ether) ketone
Phosphoric acid
Proton exchange membrane
Proton conductivity

ABSTRACT

The performance of proton exchange membrane (PEM) is critically dependent on the selection of materials and the optimization of individual components. Polyurethane (PU) as a common polymer has the superior mechanical properties. However, the poor oxidation and thermal stability after doping phosphoric acids (PAs) prevented its application as PEM electrolytes. Here, we introduced the negatively charged sulfonated poly(ether ether) ketone (SPEEK) into the positively charged PU matrix, expecting to improve its performance after doping PA molecules. The strong electrostatic interaction enables the formation of homogenous and compact SPEEK/PU membranes. The decomposition temperature of SPEEK/PU/PA membrane could reach 180 °C, which was higher than 110 °C for PA doped PU membrane. Importantly, these prepared PA doped membranes presented the satisfactory proton conductivity and acceptable mechanical property. SPEEK/PU/PA(1/1/100) membrane possessed a maximum proton conductivity of 3.0×10^{-2} S cm^{-1} at 160 °C under anhydrous conditions.

1. Introduction

Owing to the merits of high energy conversion efficiency, high power density and low greenhouse gas emissions, fuel cell technology has been regarded as an attractive energy source to replace fossil fuels [1,2]. Among the various fuel cells, proton exchange membrane fuel cell (PEMFC) is suitable for the applications including the stationary, automotive and mobile devices [3–6]. Proton exchange membrane (PEM) as one of the vital components of PEMFC acted as a proton conductor as well as a separator between the anode and cathode compartments [7]. At present, perfluorosulphonic acid (PFSA) membranes such as Nafion® series membranes have been widely used as PEMs due to their high proton conductivity, excellent chemical and oxidative resistance [8,9]. However, the drawbacks such as the high price, low operation temperature, hydrogen storage, low mechanical strength and high methanol permeability restrict their further [10,11].

Recently, PEMFC working at high temperature above 110 °C under reduced humidity even anhydrous conditions gained more wide attention [12–14]. With temperature rising, the accelerating kinetics of chemical reactions could improve the proton conductivity and reduce the catalyst poisoning by carbon monoxide [15,16]. Novel PEM materials with the superior performance and low cost were needed to accelerate the process of commercialization. In this context, the modified PFSA membranes, acid–base polymer membranes, alternative sulfonated aromatic polymer membranes, blend polymer membranes and ionic liquid/polymer membranes have been extensively researched in the past decade [17–20]. Specifically, the membranes of PA doped polymers such as polybenzimidazole (PBI) [21], poly(2,5-benzimidazole) (abPBI) [22], sulfonated polybenzothiazoles (sPBT) [7,23], Nafion® [24], sulfonated poly(ether ether ketone) (SPEEK) [20,25], polyvinylidene fluoride (PVDF) [26], Polyethersulfone (PES) [27], polysulfone (PSF) [28], poly(ethylene-*co*-tetrafluoroethylene) (ETFE) [29] and polyvinyl chloride (PVC) [1,30] have been reported frequently and gained the inspired results. Notwithstanding, some new functional membranes are still needed to cater for the development of high temperature PEMFC.

Aqueous polyurethane (PU) dispersions are of three types, nonionic, cationic and anionic depending upon the type of hydrophilic segments in backbone. The researches on cationic or anionic PU ionomers have developed rapidly owing to their unique morphology and properties [31]. PU ionomers have been thus extensively used in different fields, even providing an alternative to PVDF and its copolymers for the preparation of gel electrolytes [32,33]. Moreover, the blend membranes based on PU ionomers also have been prepared to improve performance of polymer materials [34,35]. However, the interaction between each component was usually neglected in these blend membranes. Although some conductive membranes based on PU could function as PEMs [10], there was no report about the application as high temperature PEMs due to suffer from the degenerating thermal stability.

In this paper, we designed the composite membranes by incorporating SPEEK into PU to improve the chemical and thermal stability against the temperature effect. SPEEK is a reasonably good choice as PEM for its adequate tensile strength, thermal stability and high chemical resistance [6,36,37]. Importantly, its strong negative charge is complementary to the positive charge of PU matrix. We could prepare the SPEEK/PU membranes via the electrostatic interaction. As a model system, SPEEK/

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http://dx.doi.org/10.1016/j.ssi.2016.03.009
0167-2738/

PU membranes were subsequently doped with PAs to improve the proton conductivity. In SPEEK/PU/PA membrane, PA molecules were firstly bounded through the hydrogen bonds. Then the free PA molecular chains formed owing to the hydrogen bonds between the neighboring PA molecules. Although high proton conductivity was obtained in SPEEK/PU/PA membranes, the tensile strength at break was still needed to enhance through optimizing the constituents. We expected to exploit some functional membranes based on PU matrix with the balanced properties for high temperature PEMFC.

2. Experimental

2.1. Materials and instruments

We used as-received cationic PU aqueous dispersion (30 wt.%, molecular mass approximately 92,000, from Hepce Chem, South Korea) to prepare 3 wt.% aqueous solution. Poly(ether ether) ketone (PEEK) powder was purchased from Jida High Performance Materials Co., Ltd. China. Chemical structures of cationic PU, SPEEK and the electrostatic interactions were shown in Fig. 1. 85 wt.% PA solution was dissolved into de-ionized water to prepare 20 wt.%, 40 wt.% 60 wt.% and 80 wt.% PA solution respectively. Moreover, 100 wt.% PA was obtained by dissolving polyphosphoric acid (62.6 g) in de-ionized water (10 mL).

2.2. Methods

2.2.1. Membrane preparation

Sulfonation of PEEK polymer SPEEK was synthesized by a mature sulfonation process of PEEK polymer by electrophilic substitution reaction. 5 g PEEK powder was firstly dissolved in 100 mL 98 wt.% sulphuric acid at 65 °C and continued heating for 7 h. The tan-colored and viscous solution was then poured into ice cold de-ionized water with manual stirring. Resulting white-colored SPEEK precipitate was finally rinsed with a large amount of de-ionized water, filtered, and dried in oven for 2 days at 60 °C. SPEEK polymer was characterized using the acid–base titration method to obtain the sulfonation degree (SD) of 73.5% [12].

Preparation of SPEEK/PU membranes and PA doped membranes 3 wt.% SPEEK solution was obtained by dissolving SPEEK polymer into de-ionized water under magnetic stirring at room temperature. SPEEK/PU homogeneous solution was prepared by blending SPEEK solution with PU solution under magnetic stirring for 6–8 h and then it was spread onto a leveled glass plate. SPEEK/PU membranes were finally prepared after evaporating de-ionized water in an oven at 50 °C for 12 h, followed by further drying at 80 °C overnight. Moreover, SPEEK/PU/PA membranes were prepared through immersing the SPEEK/PU membranes into 20 wt.%, 40 wt.%, 60 wt.%, 80 wt.% PA solution and 100 wt.% PA in a conical flask with cover at room temperature. The period of immersion into PA solution lasted 48 h.

2.2.2. Weight gain and volume swelling

The weight gain and volume swelling values of SPEEK/PU/PA membranes were calculated from the weight and volume variations with PAs loading. The weight and dimension of membrane samples were measured rapidly after wiping the surface-attached PAs with a tissue paper. Each membrane was tested for at least three specimens and average values were used as the results. The values were calculated according to Eqs. (1) and (2).

$$\text{Weight gain}(\%) = \frac{W - W_0}{W_0} \times 100 \quad (1)$$

$$\text{Volumeswelling}(\%) = \frac{V - V_0}{V_0} \times 100 \quad (2)$$

Herein, W_0 and W represent the weight of original membrane and PA doped membrane; Similarly, V_0 and V are the volume (length × width × thickness) for these membranes.

2.2.3. Fourier transform infrared spectra

Fourier transform infrared spectra (FTIR) of PU, SPEEK, SPEEK/PU and SPEEK/PU/PA membrane samples were recorded using a Vertex 70 Spectrometer (Bruker optics Company, Germany). Infrared rays pierced the membrane samples with air as blank.

2.2.4. Thermal and chemical stability

Thermal stabilities of PU, SPEEK/PU and SPEEK/PU/PA membrane were measured with a thermogravimetric analyzer TGA 290C (Netzsch Company, Germany). Approximately 5 mg of each sample was analyzed under a temperature range of 25–800 °C at a heating rate of 10 °C/min with an air flow rate of 30 mL/min. All samples were heated at 100 °C for overnight beforehand. Chemical stabilities were tested by soaking the membrane samples into Fenton reagent (H_2O_2, 3 wt.%; Fe^{2+}, 4 ppm) at 68 °C. We recorded the time of break-up and dissolution for membrane samples in Fenton reagent, evaluating the chemical stabilities and degradation behaviors. Fenton reagent was renewed with every interval of about 24 h.

2.2.5. Fine surface structure

The surface morphologies of PU, PU/PA, SPEEK/PU and SPEEK/PU/PA membrane were investigated on a SSX-550 (Shimadzu Company, Japan) scanning electron microscope (SEM). Membranes were sputtered with a thin layer of gold nanoparticles prior to SEM examination.

2.2.6. X-ray diffraction

X-ray diffraction (XRD) test was performed using a Part Pro-MPD X-ray diffractometer (Panalytical B.V., the Netherlands) with a Cu Kα radiation source. The test angle was at a range of 5–80° with a scanning speed of 5 min^{-1}.

2.2.7. Proton conductivity

Proton conductivities (σ) of SPEEK/PU and SPEEK/PU/PA membrane were measured with four electrode method. Specifically, a pair of platinum probes supplying about 2 kHz frequency alternative current were placed on the both sides of membranes. The voltage drop between another pair of probes was recorded manually and the resistance (R)

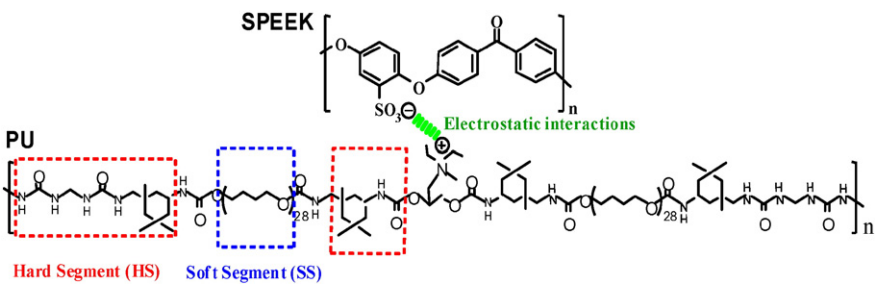

Fig. 1. Chemical structures of cationic PU, anionic SPEEK and the electrostatic interactions.