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High performance sulfonated poly(phthalazinone ether phosphine oxide)s for proton exchange membranes

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ABSTRACT

A series of sulfonated poly(phthalazinone ether phosphine oxide)s with disulfonated moieties (dsPPEPO) were synthesized. Sulfonated poly(phthalazinone ether phosphine oxide)s with mono-sulfonated moieties (msPPEPO) were also prepared for comparative study. These two series of polymers represented two kinds of distribution modes of sulfonic acid side groups. The distribution mode of the sulfonic acid side groups within membranes could remarkably change their microstructure. As a result, dsPPEPO exhibited better dimensional and oxidative stability as compared to msPPEPO on condition of equal sulfonation degree. Moreover, the as-synthesized dsPPEPO showed enhanced proton conductivity further by increasing sulfonation degree while remaining excellent dimensional and oxidative stability. Therefore, the resulting membranes displayed excellent overall properties. For example, the dsPPEPO membrane with a sulfonation degree of 110% presented a lower swelling and much higher proton conductivity than those of Nafion 117. Its oxidative stability was also comparable to the highly durable aromatic PEMs.

1. Introduction

Proton exchange membranes (PEMs) greatly affect the efficiency, durability and other properties of proton exchange membrane fuel cells, which have attracted extensive attention as green power sources [1,2]. The perfluorosulfonic acid membranes such as Nafion have been widely used as proton exchange membranes, showing high proton conductivity and chemical stability [3]. However, their drawbacks including high methanol permeability, low operation temperature and expensive cost hinder the widespread applications [2,3]. Therefore, a large number of sulfonated aromatic polymers and their derivatives have been developed as alternative PEMs [2–6].

The derivatives of aromatic polymers are the focus of PEMs because of high mechanical properties, excellent thermal properties, wide variety of chemical compositions and anticipated stability [4,5]. Generally, sulfonated aromatic polymers with high proton conductivity required high ion exchange capacity (IEC) [2]. However, high IEC often results in excessive swelling and thus deteriorates the mechanical properties [2,7,8]. Therefore, many approaches such as physical blend and chemical cross-linking were employed to reduce the swelling while remaining considerable proton conductivity [7,9–22]. In addition, the incorporation of intermolecular hydrogen bonds to aromatic polymer membranes by direct polycondensation could effectively depress the swelling without sacrificing proton conductivity [23–28]. For example, sulfonated poly(phthalazinone ether phosphine oxide)s exhibited low swelling and high proton conductivity because the intermolecular hydrogen bonds between the phthalazinone and sulfonic acid groups restricted the swelling [25]. Very recently, the microscopic structure of aromatic proton exchange membranes was well controlled by tuning the distribution and content of pendant sulfonic acid groups through direct polycondensation, thus the overall properties such as dimensional stability, proton conductivity and oxidation resistance were remarkably improved [29].

In this work, the properties of the above sulfonated poly(phthalazinone ether phosphine oxide)s membranes were expected to be further improved by adjusting the distribution and content of sulfonic acid side groups. At first, bis(4-fluorophenyl)phenyl phosphine oxide (BFPPO) was sulfonated under the designed conditions to obtain the mono-sulfonated and disulfonated monomers, *i.e.* bis(4-fluorophenyl)-3′-sulfonate phenyl phosphine oxide (MSPPO) and (3-sulfonate-4-fluorophenyl-3′-sulfonate phenyl)-4′′-fluorophenyl phosphine oxide (DSPPO). Thereafter, sulfonated poly(phthalazinone ether phosphine oxide)s with disulfonated moieties (dsPPEPO) were synthesized by polycondensation of DSPPO, BFPPO and 4-(4-hydroxyphenyl) phthalazinone (HPPT), the sulfonation degree of which was controlled by the molar ratio of DSPPO in the feed, as

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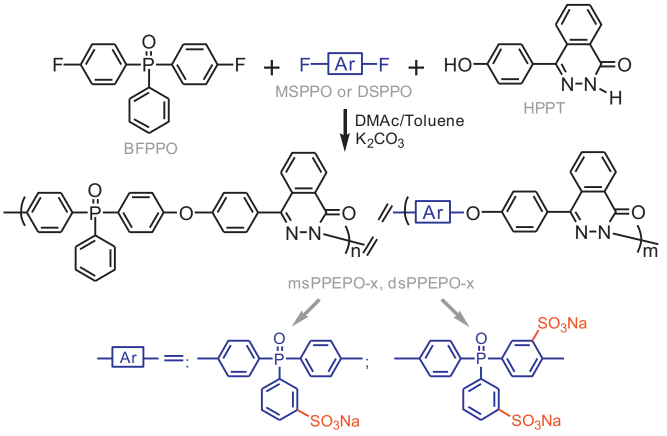

Scheme 1. Synthesis of polymer.

shown in Scheme 1. For comparative study, the above-mentioned sulfonated poly(phthalazinone ether phosphine oxide)s were also synthesized by polycondensation of MSPPO and HPPT. This kind of sulfonated polymer is exactly the sulfonated poly(phthalazinone ether phosphine oxide)s with mono-sulfonated moieties (msPPEPO, Scheme 1). From the viewpoint of chemical structure, these two series of sulfonated polymers represented two different distribution modes of sulfonic acid side groups, which possessed identical polymer backbone. The effect of the distribution mode and content of –SO_3H side groups on the properties of the resulting membranes was investigated in detail.

2. Experimental section

2.1. Materials

Phenylphosphonic dichloride and 4-bromofluorobenzene were purchased from Aldrich and used as received. Magnesium, fuming sulfonic acid and other reagents were obtained from commercial sources and used without further purification. 4-(4-hydrolphenyl) phthalazinone (HPPT) was prepared following the earlier procedure [30]. Bis(4-fluorophenyl)phenyl phosphine oxide (BFPPO), bis (4-fluorophenyl)-3′-sulfonate phenyl phosphine oxide (MSPPO) and (3-sulfonate-4-fluorophenyl-3′-sulfonate phenyl)-4′′-fluorophenyl phosphine oxide (DSPPO) were synthesized according to our earlier reports [25,29]. *N*,*N*-dimethylacetamide (DMAc) was distilled at reduced pressure and stored over 4 Å molecular sieves. Toluene was distilled prior to use. Tetrahydrofuran (THF) was dried by refluxing over sodium filament for 6 h and then distilled just before use.

2.2. Synthesis of polymers

Taking dsPPEPO-100 as an example, the polycondensation reaction was described as follows. 0.7147 g (3.0 mmol) of HPPT, 0.4714 g (1.5 mmol) of BFPPO, 0.7775 g (1.5 mmol) of DSPPO, 0.4561 g (3.3 mmol) of K_2CO_3, 8 mL DMAc and 8 mL toluene were charged to a 100 mL three-necked flask, equipped with a mechanical stirrer, a Dean-Stark trap and a nitrogen gas inlet/outlet. The reaction mixtures were refluxed at 150 °C for 4 h. The resultant of water was removed by azeotropic distillation through the Dean-Stark trap. Then, the reaction temperature was increased to 160 °C. After removal of toluene, the reaction mixtures were kept at 165 °C for several days until the solution became very viscous. The resulting mixtures were cooled to 120 °C, diluted with 2 mL of DMAc, and then poured into 300 mL of deionized water with vigorous stirring to precipitate the pale-yellow fibrous polymer. The product of polymer was immersed in boiling deionized water to remove inorganic salts. The final product was obtained by drying under vacuum at 120 °C for 48 h.

2.3. Preparation of membranes

A polymer solution in DMSO was cast on a clean glass plate, followed by drying at 65 °C for 36 h. The glass plate was cooled to room temperature and then immersed in deionized water, thus the transparent and ductile membrane peeled off. The membrane was acidified by immersing in 0.5 M sulfuric acid at room temperature for 24 h and 90 °C for 2 h. Subsequently, it was soaked in de-ionized water at 90 °C for 2 h and then at room temperature for 24 h to remove inorganic acid. The acid-form membrane was dried *in vacuo* at 120 °C for 24 h.

2.4. Characterization

NMR spectra were recorded on a Varian MERCURYplus 400 MHz spectrometer using deuterated dimethyl sulfoxide (DMSO-d_6) as solvent and H_3PO_4 as external standard. The samples for NMR measurement are in the salt form. Fourier transformation infrared (FT-IR) spectra were performed on a Bruker Equinox-55 Fourier transform spectrometer. Intrinsic viscosity was measured in 0.5 g/dL DMSO solution (containing 0.05 mol/L LiBr) at 25 °C using an Ubbelohde viscometer. The thermal stability was conducted on a Q5000IR thermogravimetric analyzer (TGA) under nitrogen from 150 to 800 °C at 20 °C/min. The acid-form samples were held at 150 °C for 30 min to remove the moisture. Differential thermal analysis was carried out on a TA Q2000 differential scanning calorimeter (DSC) under nitrogen. The acid-form samples for DSC were also kept at 150 °C for 30 min and then cooled to 80 °C at 5 °C/min. The DSC curves were recorded in a range of 100–350 °C at 10 °C/min. Small-angle X-ray scattering (SAXS) was measured on a SAXSess mc2 instrument with Cu Kα radiation (Anton Paar, Austria). The lead-stained membrane samples were prepared by immersing the acid-form membranes in 0.5 M lead acetate for 24 h, rinsing with deionized water and then drying *in vacuo* for 12 h [31]. The characteristic periodicity (d) between the hydrophilic and hydrophobic domains was calculated by the equation of $d = 2\pi/q$, in which q is the scattering vector [31]. Scanning transmission electron microscopy (STEM) was observed on a JEOL JEM-2100 at an accelerating voltage of 200 kV. The samples for STEM were made of the lead-stained membranes [31]. The preparation process of samples was as follows. A strip ($1 \times 3\ \mathrm{mm}^2$) was cut from the lead-stained membrane, then embedded into an epoxy resin and sectioned to ~120 nm thickness films by an ultramicrotome. The ion exchange capacity (IEC) of membranes was measured by titration according to the typical procedure [22].

The water uptake and swelling of membranes were determined by the change of the weight and length between the dry and wet state, respectively. The acid-form membranes (6 cm × 6 cm × ~40 μm) were dried *in vacuo* at 120 °C for 24 h. The weight (W_{dry}) and length (l_{dry}) of dry membranes were measured. Thereafter, the membranes were soaked in deionized water at desired temperatures for 24 h, then taken out and wiped off the water on the surface. The weight (W_{wet}) and length (l_{wet}) of wet membranes were measured. The values of water uptake and swelling were calculated by the following formulae:

$$\text{Water uptake} = (W_{wet} - W_{dry})/W_{dry} \times 100\%$$

$$\text{Swelling} = (l_{wet} - l_{dry})/l_{dry} \times 100\%$$

The oxidative stability of membranes was investigated according to a typical procedure [32,33]. The membrane samples (0.5 cm × 1 cm × ~40 μm) were tested in Fenton's reagent (3% H_2O_2 containing