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Synthesis and characterization of high temperature proton exchange membrane from isocyanatopropyltriethoxysilane and hydroxyethane diphosphonic acid

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ABSTRACT

High temperature proton exchange membranes with phosphonic acid functionalization were prepared from 3-Isocyanatopropyltriethoxysilane (IPTES), 1-hydroxyethane-1,1-diphosphonic acid (HEDPA) and Tetraethoxysilane (TEOS) by sol–gel process. These hybrid membranes with different amount of phosphonic acid were investigated with respect to structure, thermal property, proton conductivity and hydrogen bond network. The results of FT-IR and ^{13}C NMR reveal that HEDPA is chemically bound to siloxane network as a result of reaction between the OH group of HEDPA and the isocyanate group of IPTES. XRD patterns of the hybrid membranes show the membranes are amorphous. Thermal analysis including TG and DSC confirm that the hybrid membranes are thermally stability up to at least 225 °C. The proton conductivity of hybrid membrane with the molar ratio of IPTES/TEOS/HEDPA = 1/0.5/0.8 is $4.6 \times 10^{-2} \text{ S cm}^{-1}$ and $2.36 \times 10^{-2} \text{ S cm}^{-1}$ at 100 % relative humidity and under anhydrous condition, respectively, at 160 °C. ^1H NMR and Variable-temperature FT-IR analysis demonstrate that there is complex hydrogen bond network within hybrid membranes among P–OH, C=O, P=O and N–H.

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Introduction

Proton exchange membrane fuel cells (PEMFC) show many advantages as a promising energy source, such as high energy conversion efficiency, low pollution levels and high energy density per volume and weight [1]. The proton exchange membrane (PEM) is one of the core components in PEMFC, which directly determines the performance of PEMFC.

Currently, the perfluorosulfonic polymer membranes, such as Nafion, have many attractive properties including good mechanical strength, excellent chemical stability and relatively high proton conductivity at temperature below 100 °C under high humidity condition [2–4]. The perfluorosulfonic polymer membranes are operated at low temperature (typical temperature around 80 °C) due to dependence on water for proton conduction. As we all know, the low operating temperature would bring PEMFC several defects such as contamination of

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Pt anode catalyst by trace amounts of CO, complex water management and relatively low energy conversion efficiency [5,6]. Therefore, new proton conducting membranes which can operate at high temperature (100–200 °C) are highly desirable.

The limitations of perfluorosulfonic polymer membranes have stimulated the development of other proton conducting membranes, such as composites of perfluorosulfonic polymer membranes [7–11], sulfonated poly (ether ether ketone) (SPEEK) [12–15], aromatic polyimide ionomers [16], poly(ether sulfone) [17,18], organosiloxane-based inorganic–organic hybrids with various acid species [19–24]. Inorganic–organic hybrid membrane based on organosiloxane is one of promising membrane for the proton-conducting material because they combine the attractive properties of both organic and inorganic components. The inorganic component of siloxane backbone endows good thermal stability and mechanical property of hybrid membrane. The organic functional groups increase the flexibility and proton conductivity of hybrid membrane. In addition, these hybrid membranes can be prepared by sol–gel route which is an easy synthetic process with low cost and less impact on the environment.

Recently, phosphoric acid and phosphonic acid have attracted much attention for the development of high temperature PEM due to the high charge carrier concentration, good thermal stability, oxidation resistance and high proton conductivity [25]. More importantly, organosiloxane hybrid membranes with phosphoric/phosphonic acid functionalization show higher proton conductivity under anhydrous condition because proton conduction mainly results from proton hopping among hydroxy groups of phosphonic acid through Grotthuss mechanism [26]. Moreover, the dynamical hydrogen bond networks will also be constructed in the membranes to facilitate proton conduction [27]. However, organosiloxane-based inorganic–organic hybrid membrane by doping phosphoric/phosphonic acid is not stable, which results in leach out phosphoric/phosphonic acid due to weak interaction with organosiloxane network. Therefore, chemically bound phosphoric/phosphonic acid with siloxane network is an efficient approach to solve this problem.

We have reported that the preparation of inorganic/organic hybrid proton exchange membranes with chemically bound hydroxyethane diphosphonic acid [28]. The membranes showed high thermal stability because of a presence of siloxane backbone and relatively high proton conductivity at anhydrous condition. But C–O–P bonds are not stable towards hydrolysis [29,30], and the mechanical strength of the membranes is hoped to be more improved. This paper synthesizes an inorganic–organic hybrid membranes from (3-Isocyanatopropyl)triethoxysilane (IPTES) and 1-hydroxyethane-1,1-diphosphonic acid (HEDPA) via sol–gel process. The siloxane of IPTES can form the Si–O–Si network structure through hydrolysis and condensation, which increase the thermal, chemical stabilities and mechanical strength of the membranes. 1-hydroxyethane-1,1-diphosphonic acid (HEDPA) was used as the proton conductor which was chemically bound to organosiloxane network between the hydroxyl group of HEDPA and the isocyanato groups of IPTES. The structure, thermal stability, proton conductivity and hydrogen bond network of the hybrid membranes were investigated.

Experimental

Materials

3-Isocyanatopropyltriethoxysilane (IPTES, Aladdin), 1-hydroxyethane-1,1-diphosphonic acid (HEDPA, Aladdin) and Tetraethoxysilane (TEOS, Aladdin) were used as received. Ethanol and tetrahydrofuran (THF) were obtained from Sino-pharm Chemical Reagent Co., Ltd. Ethanol and THF were dried by molecular sieve, and then distilled before use. Fig. 1 shows the chemical structures of IPTES, HEDPA and TEOS.

Preparation of the membranes

The proton exchange hybrid membranes were prepared by the sol–gel method through hydrolysis and condensation reactions of IPTES and HEDPA. Under an argon atmosphere, HEDPA was dissolved in THF with stirring at room temperature for 30 min. Then IPTES was added dropwise to the mixed solution, followed by stirring for 24 h at 45 °C. The solvent THF was evaporated and the precursor (white solid) was obtained through the above process. The precursor and TEOS were dissolved in ethanol. After stirring, deionized water was added dropwise to the mixture solution to hydrolyze silicon alkoxide. The molar ratio of precursor/TEOS/ethanol was 1:0.5:10 and the amount of deionized water added is four times of the total Si in mole. Then the clear and transparent precursor sol was obtained. The sol was poured to Teflon dishes and stood without sealing until gelation at room temperature. The obtained gel was dried at 60 °C for 3 days, and then heat-treated at 80 °C for 24 h, 100 °C for 6 h and 120 °C for 1 h. Through this synthesis process, three membrane samples with IPTES/TEOS/HEDPA ratios of 1/0.5/0.4, 1/0.5/0.6 and 1/0.5/0.8 were prepared, which were named as IHM-1, IHM-2, and IHM-3, respectively.

Characterization of membranes

Fourier-transform infrared (FT-IR) spectra was collected between 4000 cm^{-1} and 400 cm^{-1} on a Nicolet 170SX using the hybrid membranes sample with the same thickness and weight. Variable-temperature FT-IR spectra was also recorded at a resolution of 2 cm^{-1} using a Nicolet 170SX FT-IR spectrometer equipped with a variable-temperature cell. A minimum of 32 scans were signal-averaged. Data was obtained from room temperature to 160 °C with a heating rate of 5 °C min^{-1} . Before data collection, the sample was equilibrated for at least 10 min at each temperature.

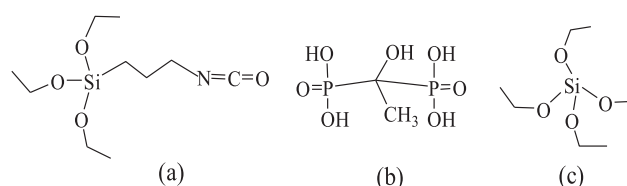


Fig. 1 – Molecule schemes of starting monomers: (a) IPTES, (b) HEDPA, (c) TEOS.

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