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Phosphoric acid-doped ionic liquid-functionalized graphene oxide/sulfonated polyimide composites as proton exchange membrane

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ABSTRACT

A series of sulfonated polyimide (SPI) composite proton exchange membranes with different contents of an ionic liquid-functionalized graphene oxide (FGO) were prepared in order to study the effects of FGO fillers on the membranes properties. Graphene oxide (GO) was synthesized by the modified Hummers method and then was functionalized with 1-methylimidazole. The phosphoric acid-doped FGO nanosheets were incorporated into the sulfonated polyimide for preparation of composite proton exchange membranes. The sulfonated polyimide (SPI) was synthesized via a solution imidization method. A series of techniques such as FT-IR, ^{1}H-NMR, XRD and XPS were used for the characterization of synthesized materials. The membranes properties such as thermal and mechanical stability, morphology, water uptake, phosphoric acid uptake and proton conductivity were investigated. The proton conductivities of the membranes were measured as a function of temperature in ambient humidity and also 80% relative humidity (RH) conditions. The pure SPI showed its maximum proton conductivities of 0.0282 and 0.0864 S cm^{-1} at ambient and 80% RH, respectively, while SPI/FGO 5% showed the maximum proton conductivity values of 0.0772 S cm^{-1} (at 160 °C and ambient humidity) and 0.1243 S cm^{-1} (at 120 °C and 80% RH) among all of the samples.

Introduction

The human beings ever-growing demands for power and the Exhaustible resources of fossil fuel have motivated our interest for developing renewable energy resources and highly efficient energy conversion systems. Fuel cells as an alternative energy devices which convert chemical energy directly into electrical energy without releasing toxic substances are widely regarded for transport sector, portable and mobile electric vehicles [1,2]. Recently, great spectra of researches have been devoted to the development of proton exchange membrane fuel cells (PEMFCs) because of their advantages such as high efficiency, lower operation temperature, quick start-up, lower pollutant emission and feasibility of mobile and transport applications and several types of the membranes have been used as PEM in order to improve the fuel cell properties [3–5].

Recent studies revealed that the incorporation of graphene oxide (GO) nanosheets could be a promising attitude for the

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modification of proton exchange membranes (PEMs). GO is an amphiphilic soft material with large surface area and excellent physical and chemical properties possessing much interfacial oxygen containing groups such as hydroxyl, epoxy and carboxylic acid. The presence of hydrophilic sites and acidic groups in GO, such as carboxylic acid and epoxy oxygen could facilitate the hydration of GO and also help the hopping of protons [6–8]. Furthermore, the intermolecular hydrogen bond interactions between the membrane structures, GO and water molecules can lead to the higher proton conductivities in GO-composite membranes [8,9].

Newly, the functionalized GO (FGO) nanosheets have been developed as attractive fillers for PEM modifications. The functional groups of FGO could ease the dispersion of FGO in organic solvents; so the composite membranes with improved distribution of nanofillers in polymer matrix could be expected [10], while the GO particles can hardly be dispersed in some organic solvents and the aggregation problems may occur [11]. Additionally, the functional groups on the FGO structure can enhance the water retention and proton conductivity of the membranes [12,13]. The works of Jiang et al. also showed that synthesized sulfoated organosilane functionalized graphene oxide can enhance the ion exchange capacity, water uptake and proton conductivity of poly(ether ether ketone) membranes [14]. Feng et al. synthesized sulfonated graphene oxide −silica (SGO-SiO₂) nanohybride particles which were used for the preparation of composite membranes via Nafion. The SGO-SiO₂/Nafion composite membranes exhibited significant increment in proton conductivity and they also reduced the methanol permeability [15]. The studies of Zarrin et al. showed that the introduction of sulfonic acid functionalized GO can increase the water uptake and also the proton conductivity of the FGO embedded membranes by the increment of the FGO ratios in the samples [16]. Additionally, some recent works provided acid doped membranes using FGO particles. Xue and co-workers reported the synthesis of a tert-butyl isocyanate functionalized GO (iGO) which improved the acid doping level and proton conductivity of iGO-Polybenzimidazole (iGO-PBI) composite membranes compared to the GO-PBI and pristine synthesized Polybenzimidazole membranes [8]. Moreover, Xu et al. prepared ionic-liquid-GO/PBI composite membranes loaded with phosphoric acid which showed higher proton conductivities and fuel cell performances compared to the pristine acid-doped PBI membranes [17]. Therefore, it is expected that utilization of prudently designed FGO particles can lead us for achieving proton exchange membranes with improved properties. Phosphoric acid, as a triprotic amphoteric acid with excellent proton conductivity, high thermal stability and low vapor pressure at elevated temperatures, is a good proton solvent for doping the thermally stable polymers such as polybenzimidazole, poly ether sulphone, sulfonated polyimide etc. which can operate in medium−high temperature [18–23]. Sulfonated polyimides (SPI) owing to their high thermal stability, proper mechanical and chemical properties, good film-forming property and also low cost, have been considered as one of the promising candidates for proton conductive membranes [24–29]. It is expected that SPIs as a high thermally stable polymer can be utilized as the matrix polymer for holding FGO nanosheets and phosphoric acid

molecules to form a composite PEM which can show good performances at medium−high temperature conditions.

Here we report the synthesis and characterization of functionalized GO particles with 1-methylimidazole groups and $H_2PO_4^-$ as the counter anion and then the preparation of phosphoric acid doped composite membranes by the combination of FGO nanosheets with a synthesized six-membered ring sulfonated polyimide. The SEM, XRD, XPS, TGA, tensile strength, water uptake, acid uptake and proton conductivity of the membranes are studied.

Experimental

Materials

1,4,5,8-Naphthalenetetracarboxylic dianhydride (NTDA), 4,4-diaminostilbene-2,2-disulfonic acid (DSDSA) and 4,4′-(1,4-Phenylenediisopropylidene) bisaniline(PDBA) were purchased from Sigma−Aldrich. Natural Graphite, sodium nitrate (NaNO₃), hydrogen peroxide (H₂O₂), potassium permanganate (KMnO₄), Sulfuric acid (H₂SO₄), 1-methylimidazole, Thionyl chloride (SOCl₂), meta-cresol, triethylamine (TEA), benzoic acid (BA) and phosphoric acid (PA) (85%) were purchased from Merck. All other materials were used as received.

Preparation of GO and functionalized GO (FGO)

Firstly, GO was synthesized according to the modified hummers method from oxidation of natural graphite [30]. Then, 4.0 g of dry GO and 40 mL of thionyl chloride were placed into a 100 mL round-bottomed flask equipped with a condenser and magnetic stirrer. The mixture was then refluxed at 70 °C for 48 h. After that, the extra thionyl chloride was extracted from the mixture using rotary and vacuum pump. The product was washed by dichloromethane several times and dried in vacuum oven at 60 °C overnight. Afterwards, 2.0 g of the resulting acylated graphene oxide (GO−Cl) with 40 mL of 1-methylimidazole were put into a 100 mL round-bottomed flask topped with a condenser and stirred at 50 °C for 48 h. The resulting FGO was filtered and washed with dichloromethane and deionized water several times and dried in vacuum oven at 60 °C overnight. FGO nanosheets with chloride counter ions were added to 30 mL of phosphoric acid 85% and stirred in room temperature for 6 h in order to exchange the chloride ions with $H_2PO_4^-$. The schematic procedures for synthesis of FGO with $H_2PO_4^-$ counter anions are sketched in Scheme 1.

Synthesis of sulfonated polyimide (SPI)

Scheme 2 shows the synthesis of sulfonated polyimide via a solution imidization method using the same procedure described in our previous work [19].

At the first, 1.825 g (5 mmol) of DSDSA as a sulfonated diamine and 50 mL of m-cresol were placed into a 250 mL double-necked round-bottomed flask equipped with a dean-stark trap, condenser and magnetic stirrer with nitrogen flow. After adding 1.7 g of triethylamine (TEA), the mixture was stirred at 80 °C until DSDSA was completely dissolved. Then 1.725 g