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Zwitterion-coated graphene-oxide-doped composite membranes for proton exchange membrane applications



Fuqiang Chu^a, Bencai Lin^{a,b,*}, Tianying Feng^a, Chenyu Wang^a, Shuai Zhang^{a,b},
Ningyi Yuan^{a,b}, Zunfeng Liu^{a,b}, Jianning Ding^{a,b,**}

^a School of Materials Science and Engineering, Jiangsu Collaborative Innovation Center of Photovoltaic Science and Engineering, Changzhou University, Changzhou 213164, Jiangsu, China

^b Jiangsu Province Cultivation base for State Key Laboratory of Photovoltaic Science and Technology, Changzhou University, Changzhou 213164, Jiangsu, China

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ABSTRACT

Zwitterion-coated graphene oxide (ZC-GO) containing ammonium and sulfonic acid groups was synthesized, and various amounts were incorporated into polybenzimidazole (PBI). The effect of the ZC-GO content on the properties of PBI/ZC-GO composite membranes for direct methanol fuel cell (DMFC) applications was investigated. The structure of ZC-GO was confirmed using Fourier-transform infrared spectroscopy, and the purity and structure of PBI were investigated using proton nuclear magnetic resonance spectroscopy. With increasing ZC-GO content, the proton conductivity, methanol permeability, water uptake, and swelling ratio of the composites increased, whereas the thermal stability decreased. Notably, the composite membrane containing 25 wt% ZC-GO exhibited a high proton conductivity ($4.12 \times 10^{-2} \text{ S cm}^{-1}$ at 90 °C and RH 100%) and low methanol permeability ($1.38 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ at 25 °C), which is much lower than that of Nafion 117 under the same conditions. The excellent properties of the composite membranes can be attributed to the homogeneous dispersion of ZC-GO and the formation of proton-transport channels in the membranes. This investigation demonstrates the potential of PBI/ZC-GO composite membranes for DMFC applications.

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1. Introduction

Direct methanol fuel cells (DMFCs), which can directly convert chemical energy into electrical power, are one of the most promising alternative power sources among fuel cells because of their environmentally friendly nature, low operating temperature, and high efficiency [1,2]. The proton exchange membrane (PEM), a core constituent of a DMFC, serves as the proton-conducting medium and separator between the anode and cathode. Today, perfluorosulfonic acid polymers represented by Nafion are widely used as electrolyte membranes because of their high proton conductivity, excellent mechanical behavior, and high chemical durability. However, the applications of Nafion as PEMs are limited by their high cost, low-operating-temperature requirements, and high methanol permeability [3–7]. Therefore, several approaches, including the modification of perfluorosulfonic acid polymers [8–10], synthesis of new types of nonfluorinated polymeric

membranes [11–15], and organic–inorganic hybrid membranes [16–21] have been used to prepare alternative PEMs with low cost, high proton conductivity, low methanol crossover, and good chemical stability.

Among the various PEMs, polybenzimidazole (PBI) has attracted much attention because of its low methanol crossover, excellent thermal stability, and good chemical stability [18,22]. However, PBI itself exhibits quite low proton conductivity; thus, proton carriers, such as phosphoric acid, are generally introduced into PBI-based composite PEMs to enhance their proton conductivities [13,17,23–25]. In phosphoric-acid-doped PBI-based PEMs, part of the phosphoric acid is chemically linked to the polymer matrix while most of it is embedded between the polymer chains [26–28], and the free phosphoric acid could easily release from the membranes. The performance of fuel cells could be seriously affected by the loss of phosphoric acid resulting from the decrease of conductivity of the PEMs. The replacement of water-soluble phosphoric acid with solid proton conductors has been considered an important approach to resolve this problem [29].

Graphene oxide (GO) has received much attention for its various applications because of its good thermal and mechanical properties [30]. Recently, polymer/GO composites have been used in supercapacitors [31], electrodes [32], and biosensors [33]. More

* Corresponding author at: School of Materials Science and Engineering, Jiangsu Collaborative Innovation Center of Photovoltaic Science and Engineering, Changzhou University, Changzhou 213164, Jiangsu, China. Fax: +86 519 86450008.

** Corresponding author.

E-mail addresses: linbencai@cczu.edu.cn (B. Lin), dingjn@cczu.edu.cn (J. Ding).

recently, GO has been used as an inorganic filler in the preparation of PEMs, and the proton conductivity of sulfonated polyimide-based membranes was enhanced by the incorporation of GO [34]. However, the properties of PEMs cannot be greatly improved by the incorporation of GO because of the lack of proton exchangeable groups [35].

Functionalized zwitterionic groups containing ammonium and sulfonic acid groups on the surface of GO may be a novel solution. Zwitterionic materials are well-known superhydrophilic materials [36]. Compared with water-retention materials based on hydrogen-bonding-induced hydration, zwitterionic groups can bind water molecules more strongly via electrostatically induced hydration [37,38]. Moreover, the sulfonic acid group exhibits good proton conduction capacity, and the dissociation of sulfonic acid can be facilitated by the electrostatic attraction of the quaternary ammonium, which results in rapid proton transport via the Grotthuss mechanism [39,40]. To the best of our knowledge, the use of GO with zwitterionic groups has rarely been reported in PEMs.

In the present work, zwitterion-coated GO (ZC-GO) containing ammonium and sulfonic acid groups was synthesized and used as a proton carrier for the preparation of PBI-based proton exchange membranes. The effect of the ZC-GO content on the membrane properties was systematically investigated, and it was expected that the properties of the PBI-based PEMs would be enhanced by the addition of ZC-GO.

2. Experimental

2.1. Materials

Polyetherimide (PEI, M.W. 10000), 1,3-propane sultone, 3,3'-diaminobenzidine, 4,4'-oxybis(benzoic acid), and 1-[3-(dimethylamino)propyl]-3-ethylcarbodiimide were obtained from Aldrich. Graphite powder, potassium permanganate, sulfuric acid (98%), hydrogen peroxide (30%), sodium nitrate, poly (phosphoric acid), dimethyl sulfoxide (DMSO), potassium hydroxide, tetrahydrofuran, dimethyl-aceramide (DMAc), and methanol were purchased from Aladdin (Shanghai). Deionized water was used in all the experiments.

2.2. Preparation of GO

GO was obtained from graphite powder following the procedure used in a previous work [41]. Typically, 1.00 g graphite, 0.50 g NaNO_3 , and 23 mL of H_2SO_4 (98%) was added into a 100-mL flask, and then, the mixture was stirred for 15 min in an ice bath. Next, 3.00 g KMnO_4 was added, and the mixture was stirred at 35 °C for 30 min; then, 46 mL of deionized water was added, and the mixture was stirred at room temperature for 30 min. Finally, 10 mL of 30% H_2O_2 was added into the mixture before cooling it down to room temperature. The obtained precipitate was washed with 5% HCl and H_2O several times before being dried under vacuum.

2.3. Preparation of PEI-g-GO

PEI-g-GO was synthesized as documented in previous literature [42]. Briefly, 100 mg GO was dispersed by sonication and mechanical stirring in 50 mL of deionized water. Then, 125 mL of 0.01 g/mL PEI/deionized water solution and 500 mg 1-[3-(dimethylamino)propyl]-3-ethylcarbodiimide were added into the suspension, and the mixture solution was stirred at 30 °C for 48 h. The product was filtered and washed with deionized water three times to ensure that the excess PEI was completely removed. Finally, the products (PEI-g-GO) were dried at 60 °C overnight in a vacuum.

2.4. Preparation of ZC-GO

The typical synthesis procedure of ZC-GO was as follows: 0.20 g PEI-g-GO was dissolved in 50 mL of dried DMSO under a nitrogen atmosphere; then, 0.50 g 1,3-propanesultone was added into the mixture in a dropwise manner. The reaction mixture was refluxed under stirring at 50 °C for 1 h under a nitrogen atmosphere before the solvent was evaporated. The obtained gray solid was rinsed and centrifuged with H_2O and ethanol several times, filtered, and dried under vacuum. The obtained ZC-GO was dried under vacuum at 40 °C for 24 h.

2.5. Preparation of PBI

PBI was synthesized via the condensation polymerization of 3,3'-diaminobenzidine and 4,4'-oxybis(benzoic acid) in polyphosphoric acid (PPA) at 140 °C, following the synthetic procedure reported in the literature [18].

2.6. Preparation of PBI/ZC-GO composite membranes

PBI/ZC-GO composite PEMs were prepared as follows: a DMAc solution containing 3 wt% PBI and different contents of ZC-GO was vigorously stirred for 0.5 h at room temperature to produce a homogeneous solution. Then, the solution was cast onto a glass plate using a doctor's blade before being dried in a vacuum oven at 80 °C for 24 h to gradually remove the solvent. Finally, a free-standing composite membrane with a thickness of approximately 50 μm was obtained.

2.7. Characterizations

Proton nuclear magnetic resonance spectroscopy (^1H NMR) was performed using a Varian 400 MHz spectrometer. Fourier transform infrared (FT-IR) spectra of the ZC-GO and GO were recorded on a Varian CP-3800 spectrometer in the range of 4000–400 cm^{-1} . Thermal analysis of the PBI/ZC-GO composite membranes was performed using a Universal Analysis 2000 thermogravimetric analyzer (TGA); the samples were heated from 50 to 800 °C with a heating rate of 10 °C min^{-1} under a nitrogen flow. Scanning electron microscopy (SEM) images were obtained using a Hitachi S-4800 microscope with an accelerating voltage of 15 kV. Atomic force microscopy (AFM) images were obtained using an NT-MDT Solver P47 in semicontact mode at room temperature.

2.8. Water uptake, swelling ratio, and ion-exchange capacity

The water uptake (WU) was determined by measuring the weight differences between the wet and dry membranes, and the swelling ratio (SR) of the composite membranes was determined from the dimensional differences between the wet and dry samples. The WU and SR of the membranes were calculated using the following equations:

$$\text{WU}(\%) = \frac{(W_s - W_d)}{W_d} \times 100\% \quad (1)$$

$$\text{SR}(\%) = \frac{(L_s - L_d)}{L_d} \times 100\%, \quad (2)$$

where W_s and W_d and L_s and L_d are the weights and lengths of the wet and dry membranes, respectively.

Ion-exchange capacity (IEC) is defined as the ratio between the number of exchangeable sulfonic acid groups (equivalents) and the weight of the dry membrane. In the present work, the membranes

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