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Enhanced properties of quaternized graphenes reinforced polysulfone based composite anion exchange membranes for alkaline fuel cell

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ABSTRACT

A series of novel composite anion exchange membranes for alkaline fuel cell were prepared by incorporating quaternized graphenes (QGs) into the chloromethylated polysulfone (CMPSU), and followed by quaternization and alkalization. The highly exfoliated quaternized graphenes (QGs) were obtained by epoxide ring opening reaction of APTES-functionalized graphenes (A-FGs) with glycidyltrimethylammonium chloride (GDTMAC). The influence of the content of QGs on the properties of the obtained composite membranes was studied. The results indicated that the QPSU – 0.5%-QGs showed a 4-fold improvement in the bicarbonate conductivity than that of pristine QPSU membrane at 80 °C, and the QPSU – 0.25%-QGs showed a 3-fold increase in Young's modules and tensile strength. The performance improvement of the membranes could be attributed to the formation of the interconnected transfer channels provided by the QGs and the excellent compatibility between QPSU and QGs. In addition, the good morphologies without phase separation, acceptable thermal properties, alkaline resistances and oxide stabilities, low water uptakes and swelling ratios were also presented in the composite membranes. Our study demonstrated that the incorporation of proper content of QGs into the polymer matrix to fabricate the composite membranes is a facile way to improve the properties of the anion fuel cell membranes, especially in the anion conductivity and mechanical property.

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1. Introduction

Fuel cells are being considered for the renewable energy conversion devices that can convert chemical energy of fuel to electrical energy by electrochemical reaction, thus have a great competitive advantage in the mobile phone, laptop and other small household energies, becoming a research hotspot of the international fuel cell. As one important type of fuel cells, alkaline membrane fuel cell (AMFC) is more attractive than the current acid proton exchange membrane fuel cell (PEMFC) recently due to its advantages in alkaline conditions, including more options to non-precious metal catalysts and enhanced electrode reaction kinetics [1,2].

As a crucial component of AMFC, anion exchange membrane (AEM) plays an important role in anion transportation, fuel and oxidant separation, and catalyst-supporting [3,4]. Therefore, many efforts have been devoted to the preparation of AEMs with good conductivity, mechanical properties for AMFC application. In PEMFC, a series of perfluorosulfonated polymers such as Nafions, have been regarded as the benchmark polymer all the time. Thus, some fluorinated polymers as AEMs were prepared to evaluate the properties in basic circumstance. For instance, a kind of perfluorinated AEM based on Nafion and PSF precursor was prepared and the results demonstrated good fuel cell performances [5]. In addition, many efforts have been devoted to the development of the AEM materials without fluorine. As a result, a variety of AEMs based on poly(arylene ether) [6–10], poly(ether ketone)s [11–14], SEBS [15,16], poly(aryl ether oxadiazole) [17], poly(phthalazinon ether sulfone ketone) [18], poly(ether imide)s [19,20], poly(vinyl alcohol) [21,22], polyethylene [23] and PPO [24,25] etc. have been widely studied in recent years. With the deepening of the research, more and more AEMs based on new structures of polymers arose [26,27]. However, there are still some disadvantages in the single polymer AEM materials, such as the relatively low thermal stabilities and bad mechanical properties. So it is necessary to further improve their properties. Despite the efforts devoted on the synthesis of new structured polymers with better properties, several methods like organic – inorganic hybrid [28,29], cross-linking [30–32], PTFE-reinforcement [33,34] were used to prepare the AEMs mainly to improve the thermal stability and mechanical property. As to the methods for improving conductivity of the AEMs, the most usual strategy is to improve the IEC value by increasing the degree of functionalization, but the high degree of functionalization may lead to cross-linking and consequent dissolution. Another effective approach is to regulate

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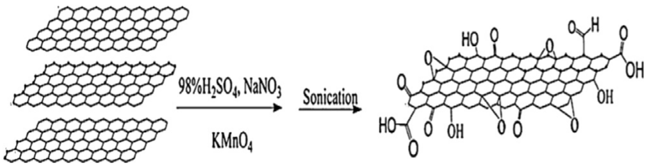
the polymer micro-phase structure via the preparation of block copolymers [6,35–38] or comb-shaped copolymers [39,40] to form the hydrophobic/hydrophilic phase separation morphology, which can build the ion transport channels in the membranes. In addition, there is a widely used strategy to improve conductivity of AEMs by introducing the inorganic fillers into the matrix. The incorporation of the inorganic fillers such as ZrO_2 [28,29], SiO_2 [21,22,41,42], Al_2O_3 [43], and CNTs [44,45] could also improve the thermal stability and mechanical property, making up the drawbacks of the single polymer matrix. Pan et al. [44] had introduced the PVA-functionalized MWCNT into the PVA matrix to prepare composite AEMs and found that the DMAFC performance of composite membranes was higher than that of the membrane without CNT. Li et al. [45] prepared the imidazolium-type ionic liquid polymer functionalized multiwalled carbon nanotubes and then blended them with imidazolium group-functionalized poly (2,6-dimethyl-1,4-phenylene oxide). The result demonstrated that the incorporation of functionalized CNTs greatly improved both ionic conductivity and mechanical property of AEMs.

In recent years, as a precursor of reduced graphene oxide, graphene oxide (GO) is attracting more and more attention because of its oxygen-containing functional groups, which ensures chemical tunable properties via covalent or noncovalent approaches, and thus the functionalized GO/polymer composites had been widely used in many fields [46–50]. Moreover, many attentions have been focused on the preparation of the composite proton exchange membranes (PEMs) using GO or functionalized GO as carbon nanofillers which led to the remarkable improvement in the performance of composite PEMs, for instance in proton conductivity, thermal stability and many other properties [51–56]. However, there is few report on the preparation of GO or reduced GO/polymer composite anion exchange membranes. Ye et al. [57] reported the preparation of composite AEMs based on fully exfoliated graphene nanosheets and PVA. The composite membrane with 0.7% graphene exhibited 126% improvement in ionic conductivity and 148% in maximum power density, and the graphene used above was without any functionalization. However, the PVA and graphene have no ionic conductive groups and some conductive materials (such as KOH) are needed to promote the ionic conductivity. In particular, the hydrolysis resistance and thermal stability of PVA matrix are relatively poor when compared with aryl polymers. As so far, the functionalized graphene has not been reported to be incorporated into the polymers to prepare composite AEMs.

Herein, we reported a series of composite AEMs based on quaternized graphene (QGs) and quaternized polysulfone (QPSU). The highly dispersible QGs were prepared by the following steps: firstly the preparation of graphite oxide by the modified Hummers' method (see Scheme 1), then APTES-functionalized graphenes were prepared by hydrothermal approach, leaving free amino groups on them, and at last the QGs were obtained by epoxide ring opening reaction between the free amino groups of APTES and glycidyltrimethylammonium chloride (GDTMAC) (see Scheme 2). We chose the polysulfone (PSU) with proper degree of chloromethylation as the matrix of the composite membranes since the PSU possess several advantages such as relatively good properties and low price. The composite AEMs were prepared via a simple solution casting method after blending the chloromethylated PSU and QGs, followed by quaternization, alkalization, and exposing to air to obtain the bicarbonate form. The incorporation of the QGs could improve the density of quaternary ammonium ions within the composite membranes compared with the pristine membrane without QGs and form ion-conducting channels on the surface of the QGs. In addition, the composite membranes with a certain content of QGs could also enhance other properties especially in the mechanical property.



Scheme 1. Synthetic reaction of the GO from 40 nm natural graphite.

2. Experimental

2.1. Materials

Polysulfone (PSU, M_w =58000) was purchased from Sigma-Aldrich, graphite powders (40 μm) were purchased from Shandong Qingdao laixi graphite company and chloromethyl methyl ether (CMME) was purchased from Linyi Fude Fine Chemical. Glycidyltrimethylammonium chloride (GDTMAC) and 3-aminopropyltriethoxysilane (APTES) were purchased from Aladdin. All other reagents were obtained from Shanghai Chemical Reagent Plant and used as received.

2.2. Chloromethylation of polysulfone

For the preparation of chloromethylated polysulfone (CMPSU), 20 g PSU was dissolved in 180 mL chloroform at 45 °C. When PSU was completely dissolved, 3.41 g $ZnCl_2$ and 25 mL chloromethyl methyl ether were slowly added. The reaction was allowed for 7 h at 45 °C to get dark viscous mixture, then the chloromethylated polymer was precipitated in methanol to remove the unreacted reagents and solvent. The product was further washed with abundant water and methanol several times until the pH is neutral. The final product was dried at 50 °C in vacuum for 12 h.

2.3. Preparation of highly dispersible QGs

2.3.1. Preparation of graphene oxide

Graphite oxide (GO) was prepared according to the modified Hummers' method [58]. Briefly, 2.0 g graphite powders, 1.67 g $K_2S_2O_8$, 1.67 g P_2O_5 and 8.0 mL concentrated H_2SO_4 (98%) were added into a three-necked flask and kept stirring for 4.5 h at 80 °C, then the dark mixture was cooled to room temperature and diluted with 200 mL distilled water. The dark mixture was filtered and washed thoroughly with abundant water, after drying in vacuum at room temperature for 24 h, the pre-oxidation graphite was prepared. The pre-oxidation graphite was added into a three-necked flask with 100 mL concentrated H_2SO_4 in an ice bath, then 10 g $KMnO_4$ was slowly added under vigorous mechanical stirring and kept 4 h at 35 °C, afterwards 60 mL H_2O was added below 50 °C under ice bath and the resulting mixture was further stirred at 98 °C for 15 min. The resulting mixture was diluted with 600 mL H_2O, and then 12 mL of 30 wt% H_2O_2 was added. The resulting mixture was cooled to room temperature, centrifuged and washed with 10 wt% HCl solution for several times. The yellow product was dialyzed in distilled water for 7 d to remove residual metal ions and acids. Finally, the graphite oxide dispersion (0.1 mg/mL) was exfoliated by water-bath ultrasonication (300 W) for 1 h. GO dispersion was obtained by high speed centrifugation and the GO was collected by freeze-drying.

2.3.2. Synthesis of highly dispersible APTES-functionalized graphenes (A-FGs)

A-FGs was synthesized according to the previous report [59]. The detailed process is as follows: 42 mg GO was dispersed into

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