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Enhanced performance of the sulfonated polyimide proton exchange membranes by graphene oxide: Size effect of graphene oxide

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ABSTRACT

Different sizes (statistical mean radius of 60 nm–1 μm) of graphene oxide (GO) were synthesized from various sizes of graphite by the modified Hummers method. The GO obtained from the smallest size graphite had the smallest size and maximum oxidation degree under the same reaction condition. Different sizes of GO were incorporated into the sulfonated polyimide (SPI) to investigate the size effect on the structure and performance of composite proton exchange membrane (PEM) for direct methanol fuel cells (DMFCs). As the size of GO increased, the properties of SPI–GO composite membranes, such as proton conductivity, methanol permeability and mechanical property, presented a regular variation. Noteworthy, the SPI–0.5%–GO₁ composite membrane with the smallest size GO showed the best result, such as high conductivity (1.2 S cm⁻¹ at 80 °C and RH 100%), low methanol permeability (1.07 × 10⁻⁷ cm² S⁻¹ at 25 °C) and outstanding fuel cell performance compared to that of pure SPI and other SPI–GO composite membranes. These excellent properties can be attributed to the formation of the well-defined microstructure and well-connected proton transport channels due to the strong hydrogen bonding interaction between the smallest size GO and SPI. Furthermore, the direct methanol fuel cell with SPI–0.5%–GO₁ membrane possessed a 1.4 times higher power density than pure SPI at 25 °C.

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1. Introduction

Direct methanol fuel cells (DMFCs), which utilize methanol as fuel to generate electricity without the use of any reforming unit, have made a vigorous evolution among the fuel cells because they combine high efficiency with low operating temperatures. The proton exchange membrane (PEM), a core material of proton exchange membrane fuel cells (PEMFCs), serves as the conducting medium of the proton and the separator of anode and cathode, and determines the efficiency and durability of PEMFCs. To date, the perfluorosulfonated ionomers represented by Nafion are still most widely used as electrolyte membranes, although they have high cost, serious methanol crossover and conductivity loss at the temperature higher than 80 °C. The phase separation between the hydrophilic proton conducting sites and the hydrophobic domain in the perfluorinated polymers provides the ionic channels for proton, resulting in high proton conductivity at moderate condition. However, the proton conductivity deteriorates and the methanol crossover aggravates rapidly at elevated temperatures because of dehydration [1,2]. Therefore, many effectual modifications for Nafion and different sulfonated aromatic hydrocarbon polymers were developed to meet

the requirements of cost-effectiveness, high proton conductivity, and low methanol crossover [3,4].

Sulfonated aromatic hydrocarbon polymers have attracted considerable attention because of their excellent thermal and mechanical stabilities. High degree of sulfonation (DS) can provide the sulfonated aromatic hydrocarbon polymers with high proton conductivity and offers great potential as PEMs for DMFC applications [5–7]. However, the high DS might also make them highly swellable in water or even soluble in aqueous methanol solution, which limits their direct use as PEMs in DMFCs [8,9]. For practical use, the properties of the membranes obtained from the plain sulfonated polymer electrolytes have to be improved. An effective and common strategy to improve proton conductivity and reduce methanol permeability is to integrate inorganic fillers [10,11], such as silicon oxides [12,13], titania [14], zirconia [15], or carbon nanotubes [16]. Wu and Choi [12,14] have introduced the sulfonated titania and sulfonated carbon nanotubes into the sulfonated polymer matrix. The introduction of those fillers not only enhanced the mechanical and thermal properties, but also improved the proton conductivities, restricted the swelling and the methanol permeabilities of composite membranes.

In recent years, GO is one of the most important derivatives of graphene, which is produced from graphite using various chemical oxidation routes. GO is characterized by a layered structure with hydroxyl, carboxyl, and epoxide groups bearing on the basal plane and edge, which entrusts it with a large specific surface area and

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tunability through covalent or noncovalent approaches, leading to a good compatibility between GO and the host materials [17–19]. GO or functionalized GO/polymer composites had been investigated in supercapacitors, water treatment materials, biomedical engineering, photovoltaic devices, conductive polymer composite materials and other fields [20–24]. Several recent studies based on the fabrication of organic–inorganic nanocomposite materials had already demonstrated that the incorporation of GO was a promising approach for the modification of PEMs. Poly (ethylene oxide)/GO composite membrane with a GO content of 0.5 wt% was prepared by Cao's group [25]. The carboxyl groups on the surface of GO afforded the proton exchange groups, which provided the possibility of GO being used as a filler to improve the performance of PEMs. Choi et al. have introduced GO into Nafion membrane and discovered that the microstructure of Nafion membrane was altered [26]. The composite membrane showed outstanding mechanical properties and DMFC performance. In order to enhance the proton exchange capability and water retention, the GO were functionalized by the small molecules containing sulfonic acid groups, and then introduced into Nafion [27]. It was found that the proton conductivity of composite membrane with 10 wt% sulfonic acid group-functionalized GO was almost 4-fold higher than that of the unmodified one at 120 °C and 30% humidity, and the value was enhanced with the increasing content of sulfonic acid group-functionalized GO. Similar results were obtained from the sulfonated GO/Nafion composite membranes [28]. The interaction between the sulfonated GO and Nafion matrix could reduce the size of ionic clusters, resulting in the decrease of methanol crossover or enhancement block for methanol in the composite membrane. Composite PEMs with high proton conductivity and device performances were achieved. Moreover, the performances of the composite membranes based on the sulfonated polyelectrolyte can also be tuned by controlling the content of GO.

However, the influences of the size and characteristics of fillers on the performance of composite membranes are crucial, because the structure and the size of fillers play an important role in determining the properties and applications of the composite PEMs. For example, a composite membrane based on sulfonated poly (arylene ether sulfone) and hydrophilic SiO₂ nanoparticles with the small size and high surface area exhibited excellent proton conductivity, methanol barrier property and high oxidation resistance [29]. In surface-functionalized mesoporous silica/sulfonated polyethersulfone (SPES) composite membrane, the smaller-sized silica particles exhibited better interfacial adhesion with the SPES matrix, resulting in optimal permselectivity [30]. It can be predicted that the size of GO should also affect the microstructure and properties of the sulfonated polyelectrolyte membranes. Although there were a few reports on the fabrication of GO/polymer electrolyte nanocomposites [26,28], the relationships between the size and structure of GO and the performances of composite membranes were not studied in previous reports. In particular, the proton transport properties and microstructures of the resultant composite membranes were not controlled by the incorporation of different sizes and structures of GO as practical application into fuel cells. For example, several GO/Nafion composite membranes have been reported, but from these results, it could be found that the change trend of the proton conductivities of composite membranes was entirely different after the incorporation of GO [26,28,31], which might be caused by the different sizes and structures of GO.

Three main methods have been used to prepare different sizes of GO by tuning the oxidation condition, controlling the process of centrifugation and ultrasonic time, which could produce different structures of GO with varying degrees of oxidation [32–34]. One way is successive centrifugation. After ultrasonic treatment the different sizes of GO sheets can be obtained from GO aqueous

solution by different speed centrifugation. The size of GO is decreased as the speed increases [32]. The second strategy for controlling the average size of GO sheets is carried out by modifying the oxidation and exfoliation procedure. With the increase in reaction time and oxidants, the mean size of GO sheets is decreased [33]. The third is to control the ultrasonic time to tune the size and structure of GO [34]. So far, however, there is no report about the synthetic method of controlling the size of GO from different sizes of graphite. Herein, we described a novel approach to synthesize different sizes of GO from three kinds of graphite with a statistical mean radius of 400 nm, 4 μm and 40 μm, respectively. Compared to previous methods, our strategy can obtain the different sized GO at the same condition. The method not only saves the reaction time in the preparation process of different sized GO, but also avoids the trouble of long-playing high speed centrifugation. And then the different sizes of GO were incorporated into SPI membranes to prepare a series of GO/SPI composite proton exchange membranes. The effect of the size and content of GO with various oxidation degrees on the structure and properties of the resulting SPI/GO composite membranes was extensively investigated. This study enables us to better understand the relationships among size, oxidation degree and properties in composite membranes, and provides a simple way to control the properties of SPI/GO composite membranes. In this work, we have studied in detail the size effect of GO on membrane properties, including membrane morphology, swelling behavior, thermal stability, mechanical strength, methanol permeability, proton conductivity and fuel cell performance.

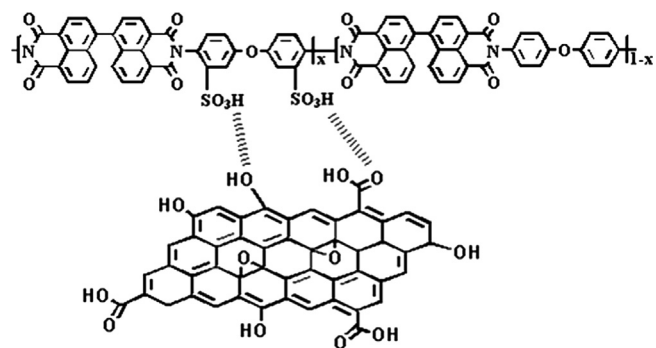
2. Experimental

2.1. Materials

Graphite powders (statistical mean radius size: 400 nm, 4 μm and 40 μm) were purchased from Shandong Qingdao laixi graphite company in China. 4,4'-Binaphthyl-1,1',8,8'-tetracarboxylic dianhydride (BNTDA) [35] and 4,4'-diaminodiphenyl-ether-2,2'-disulfonic-acid (ODADS) [36] were prepared according to the reported procedures. The other reagents used in this study were purchased from Shanghai Chemical Reagent Plant. 4,4'-Diamino-diphenyl ether (ODA) was purified by sublimation in vacuum. Other reagents were analytical grade and used as received.

2.2. Synthesis of sulfonated polyimide

Sulfonated polyimide (SPI) was synthesized according to the method reported in the literature [35]. The chemical structure of SPI is given in Scheme 1, and the molar ratio of BNTDA, ODADS and ODA is 1:0.6:0.4. The synthetic procedure was as follows: 1.62 g (4.5 mmol) of ODADS, 45 mL of m-cresol, and



Scheme 1. Scheme diagram of the interaction between SPI and GOs.

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