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A morphology and property study of composite membranes based on sulfonated polyarylene ether sulfone and adequately sulfonated graphene oxide

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ABSTRACT

In this study, the sulfonic acid groups' adequately functionalized graphene oxide (FGO) was prepared using a temperate and controllable method. The morphological changes of the FGO and sulfonated polyarylene ether sulfone (SPES) composite membranes were investigated in detail by using X-ray scattering (SAXS), atom force microscopy (AFM), transmission electron microscopy (TEM), scanning with an electron microscope (SEM), and so on. The SAXS showed an increscent d-spacing, and reflected the enlargement of the ionic clusters, which was caused by the addition of sulfonated groups into the composite membranes. The AFM and TEM showed phase separation phenomenon. The phase separations led to the formation of more continuous and larger channels for proton conducting. Also, the SEM pictures intuitively showed the inner-structures of the membranes. When a small amount of the FGO was blended, the structure of the composite membrane was compact. The compact structures resulted in the improvement of the mechanical properties and methanol resistance. However, when more of the FGO was blended, the structures became loose and caused damage to the mechanical properties. The FGO can effectively hinder the methanol passing through and enhance the water retention by its special sheeted structure. The properties of the composite membrane with a 5% blended FGO was found to be superior to that of Nafion117[®] and other samples. It was determined that the changed properties of the composite membranes must have been derived from the different microstructures. The relationships between the properties and the morphologies of the samples were established in detail. Therefore, this study provides helpful information regarding the design of excellent proton exchange membranes.

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Introduction

In recent years, proton exchange membrane fuel cells (PEMFCs) have been considered as the most promising clean energy technology for converting chemical energy into electrical energy. The technologies currently under development are due to their high energy efficiency, high power density, compact cell design, rapid start-up, and so on [1–3]. The direct methanol fuel cell (DMFC) is one type of PEMFC. The direct methanol fuel cell can be operated at a relatively low operating temperature, high energy density of methanol, and direct oxidation of fuel on an anode catalyst. The DMFC is a promising fuel cell for small-scale portable applications. As the core in PEMFC fabrication, the proton exchange membrane (PEM) transfers protons from the anode to the cathode, and acts as the barrier to the fuel. The most common commercially used PEMs are perfluorinated sulfonic acid ionomers, such as Nafion, which was developed by Dupont. This is due to their high proton conductivity, and excellent stability. However, the high cost and gas crossover, as well as the loss of the preferable properties at high temperature, have restricted the applications and stimulated the development of new alternatives for PEM materials [4–6]. It has been determined that sulfonated poly (ether sulfone) (SPES) is an attractive application material, due to its super mechanical properties, excellent thermal stabilities, and fuel resistance [7,8].

The proton conductivity of SPES increases with the degree of sulfonation (DS). However, the mechanical properties, permeability, and so on become damaged by the increase of DS [9–11]. Therefore, methods are needed to improve this type of membrane material. The first such method is to blend the alkaline polymer materials, such as polybenzimidazole, polyimide, polyaniline, polypyrrole, and so on, into the acidic polymer types of SPES. The acid-based composite membranes maintain or improve the mechanical property, thermal stability, and fuel permeability. However, the proton conductivity decreases with the increasing of alkaline material content [12–15]. The second method is to prepare the composite membranes by using heteropolyacids, such as phosphotungstic acid, silicotungstic acid (STA), phosphomolybdic acid (PMA), and silicomolybdic acid (SMA). However, heteropolyacid molecules easily agglomerate, and form large particles, which then cause a phase separation between the heteropolyacid and the polymer matrix. This in turn results in a lower conductivity. In addition, the heteropolyacid may leach out during the operation, and lead to the instability of the composite membranes [16,17]. The third method includes the use of super acids, such as types of $\text{TiO}_2\text{-SO}_4^{2-}$ and $\text{ZrO}_2\text{-SO}_4^{2-}$ solid super acid, which have been assumed to improve the proton conductivity, and would be stable in the membranes without leaching out. On the contrary, the results of the proton conductivity showed a slight decrease when compared with the pure polymer [18].

Graphene oxide (GO) has a two-dimensional laminated structure and possesses epoxy and hydroxyl groups on the basal plane, and carboxylic acid groups along the sheet edge [19], which can be differentially functionalized. Yuseon Heo [20] et al. synthesized partial sulfonated graphene oxide by using NaH as a reducing agent, and the sulfonated graphene

oxide was then blended into a sulfonated poly (ether ketone). The sulfonated degree of the functionalized graphene oxide was difficult to control with NaH, due to the fact that the groups of hydroxyl were difficult to calculate. An excess quantity of NaH would lead to the graphene oxide reducing to graphene. However, a small quantity of NaH would result in incomplete sulfonation, which would not improve the proton conductivity in the composite system.

In this study, the completely sulfonated graphene oxide was prepared, and the hydroxyl groups on the basal plane of graphene were almost absolutely replaced by the sulfonic acid group. The sulfonated groups functionalized graphene oxide blended with the sulfonated polyarylene ether sulfone (SPES). It was then assumed that there was improvement of the proton conductivity by the addition of the sulfonated graphene oxide, and the enhancements of the mechanical properties were caused by the special two-dimensional sheets of graphene oxide. Furthermore, the special two-dimensional structures would be helpful to hinder the access of the methanol.

Experimental

Materials

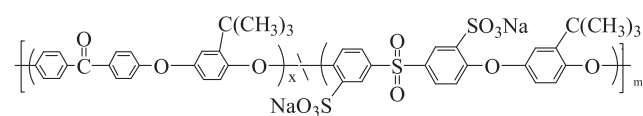
The dimethyl sulfoxide (DMSO), K_2CO_3 , NaNO_3 , KMnO_4 , HCl, and H_2SO_4 were purchased from the Tianjin Kermel Chemical Reagent Co., Ltd. All of the other chemicals were obtained commercially, and used without further purification. The SPES was prepared according to Reference [11]. The sulfonated degree and the ion-exchange capacity (IEC) of the SPES were 0.6 and 1.31 mmol/g, respectively. The sulfonated polyarylene ether sulfone was immersed in a 2 M HCl solution for 6 days, and then transformed to an acid form (Scheme 1).

Synthesis of sulfonated GO

The GO was synthesized from expandable graphite, in accordance with a modified Hummers method [21]. The GO was dispersed into DMSO, and an ultrasonic treatment was carried out for two hours. After the GO was entirely dispersed, the excess K_2CO_3 was mixed thoroughly with the exfoliated GO by stirring at 80 °C. Then, the excess 1, 4-butyldisulfone was dropped into the former mixture, and stirring continued for 24 h. The sample was filtered, centrifuged, and washed with HCl and ethanol four times. It was then dried at 60 °C for 12 h in a vacuum desiccator. The synthesis process (Scheme 2) is similar to those in Refs. [22,23].

Preparation of composite membrane

The SPES and FGO were separately dissolved into the DMSO in order to afford a mass fraction of 6 to 10%. Then, the two



Scheme 1 – Structure of sulfonated polyarylene ether sulfone.

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