



Quaternized graphene oxide modified ionic cross-linked sulfonated polymer electrolyte composite proton exchange membranes with enhanced properties



Yanxu Zhao ^{a,b}, Yuqin Fu ^{a,*}, Bo Hu ^b, Changli Lü ^{b,*}

^a College of Life Sciences, Jilin Agricultural University, Changchun 130118, PR China

^b Institute of Chemistry, Northeast Normal University, Changchun 130024, PR China

ARTICLE INFO

Article history:

Received 18 February 2016

Received in revised form 8 July 2016

Accepted 11 July 2016

Available online xxxx

Keywords:

Proton exchange membrane
Sulfonated poly(ether sulfone)
Quaternized graphene oxide
Ionic cross-linked
Properties

ABSTRACT

A series of novel ionic cross-linked sulfonated poly(ether sulfone) (SPES)-based proton exchange membranes (PEMs) were successfully constructed by using quaternized graphene oxide (QGO) as the inorganic fillers and cross-linking agents. The ionic cross-linking networks were implemented by the interactions between the sulfonic acid groups of SPES and the quaternary ammonium groups of QGO. The influences of different loading contents of QGO on the properties of the ionic cross-linked composite membranes were studied. The composite membranes showed the enhanced mechanical properties and improved oxidative stabilities. Meanwhile, the swelling ratio, water uptake and methanol permeability of the ionic cross-linked SPES/QGO composite membranes were much lower than that of the pristine SPES membrane. The swelling ratio and water uptake of SPES-10-QGO composite membrane had the minimum values among all the composite membranes. In addition, although the proton conductivity of ionic cross-linked SPES membranes by QGO decreased, SPES-10-QGO still exhibited high proton conductivity of about 0.08 S cm^{-1} at 80°C . All the results indicated that the ionic cross-linked composite membranes with balanced properties were the potential candidate materials for PEMs.

© 2016 Published by Elsevier B.V.

1. Introduction

At present, proton exchange membrane fuel cells (PEMFCs) have been widely studied as one of the next-generation power technologies for automotive, stationary and portable applications [1–3] due to the high conversion rate, low environment pollution and low noise [4,5]. As the vital component of the PEMFCs, the proton exchange membrane (PEM) plays the important role in the performance of the PEMFCs. Nafion is state-of-the-art PEM in the recent times due to its efficient proton conduction, permselectivity, long term thermal and chemical stability. Nevertheless, this type of PEM has the following drawbacks: (I) high cost and the difficulty of fabrication; (II) the requirements of high temperature and water content, the water content decreases rapidly and the conductivity decreases rapidly as the temperature exceeds 80°C ; and (III) high permeability [6]. In the view of these disadvantages, sulfonated aromatic main chain polymers began to receive growing interests and have been widely used in the fuel cells, including sulfonated polyimide (SPI) [7,8], sulfonated poly(ether sulfone) (SPES) [9–12], sulfonated polybenzimidazole (SPBI) [13,14], sulfonated poly(ether ether ketone) (SPEEK) [15,16] and so on. Among the series of the

polymer matrix, SPES containing fluorene chain segments have attracted more attention due to their low cost, good chemical stability and thermal stability. In addition, when the fluorene chain segments were fully sulfonated, there are four sulfonic acid groups on the fluorene segments, in this way, the sulfonated polymer matrix can have high acidity and high water absorption property. Because of this advantage, the prepared sulfonated polymer matrix has higher proton conductivity than other sulfonated polymer matrix [17–19].

For PEMs, the proton conductivity is a vital performance compared with other performances. In order to achieve high proton conductivity, sufficient number of sulfonic acid groups is required. However, as the number of sulfonic acid groups increased, the swelling ratio of the membrane would increase and the mechanical strength of the membrane would be lost [17]. Such drawbacks significantly influenced the comprehensive performance of the PEMs. In recent years, graphene oxide (GO) and functionalized graphene oxide (FGO) are widely used as inorganic fillers in polymer composites due to their large number of surface functional groups, such as hydroxyl, epoxy and carboxyl groups, so it is a promising strategy to introduce GO and FGO into polymer matrix. The comprehensive properties of PEMs could be improved greatly by introducing the inorganic fillers GO and FGO. Wang et al. prepared a new type of graphene oxide (GO)/Nafion composite membranes via layer-by-layer (LbL) procedure [20]. The composite membranes exhibited improved oxidative stability, lower methanol permeability and higher selectivity. Pandey et al. prepared a series of sulfonated imidized

* Corresponding authors.

E-mail addresses: fuyuqin1974@163.com (Y. Fu), luc1055@nenu.edu.cn (C. Lü).

graphene oxide (SIGO) based polymer electrolyte membrane by incorporating SIGO into SPI matrix [21]. The composite membranes exhibited improved thermal stabilities, mechanical stabilities, oxidative stabilities, high water retention and high proton conductivity. Yang et al. prepared a series of composite membranes by incorporating the metal-organic framework-graphene oxide into Nafion matrix [22]. The ZIF-8@GO/Nafion-1 composite membrane exhibited high proton conductivity and low methanol permeability. Therefore, GO and functionalized GO as inorganic fillers can enhance the comprehensive properties of the composite membranes.

It is known to all that cross-linking method can create a three-dimensional network in PEMs, which can reduce the structural flexibility, and so enhance the dimensional stability, mechanical strength and so on. Cross-linking reaction can be realized through the combination of varied interactions, such as hydrogen bonds, ionic or covalent bonds to form the dense three-dimensional networks [23,24]. At present, ionic cross-linking methods are demonstrated to have good prospects for development, as they involve a facile self-combination at the intermolecular level [25,26]. Moreover, compared with covalently cross-linked polymers which have a tendency to become brittle in a dry state [27,28], the ionic cross-linked polymers are more flexible and can exhibit excellent properties useful for PEM applications [29]. Bai et al. prepared the nanohybrid membranes by incorporating phosphorylated graphene oxide (PGO) nanosheets into chitosan (CS) matrix [30]. The PGO-filled membranes achieve higher thermal and mechanical stabilities due to the strong electrostatic interactions between PGO ($-\text{PO}_3\text{H}$) and CS ($-\text{NH}_2$). Wang et al. prepared a series of highly conductive nanofibrous composite membranes by incorporating basic CS matrix into acidic sulfonated poly(ether ether ketone)s nanofiber mat [31]. The obtained composite membranes exhibited high structural and thermal stability. The sample of CS/SP-80-1 could achieve the highest proton conductivity of 0.153 S cm^{-1} . Liang et al. prepared a series of novel ionic cross-linking sulfonated poly(ether ether ketone) (SPEEK) membranes that were realized by the interaction between sulfonic acid groups in SPEEK and pyridyl in diazafluorene [32]. The ionic cross-linked membranes exhibited lower methanol permeability and swelling ratio, better mechanical property and oxidative stability. He et al. incorporated the polydopamine-modified graphene oxide (DGO) sheets into sulfonated poly(ether ether ketone) (SPEEK) matrix to prepare the nanocomposite membranes [33]. The incorporation of DGO enhanced the thermal and mechanical stabilities to SPEEK membrane by tuning its nanophase-separated structure and chain mobility. Zhang et al. reported the preparation of high temperature proton exchange membranes based on the phosphoric acid doped quaternized poly(ether ether ketone) membranes cross-linked with sulfonic groups functionalized graphene oxide [34]. The obtained composite membranes exhibited the improved mechanical strength and oxidative stability. Therefore, ionic cross-linking network can improve the comprehensive properties of the composite membranes.

In this study, we prepared a series of novel ionic cross-linked polymer composite proton exchange membranes through the interactions between sulfonic acid groups of sulfonated poly(ether sulfone) (SPES) and quaternary ammonium groups of quaternized graphene oxide (QGO) to form the ionic cross-linking network structure. This strategy was expected to not only improve the mechanical properties and oxidative stabilities, but also reduce the water uptake, swelling ratio and methanol permeability of the membranes. The structure and properties of the ionic cross-linked composite membranes were studied in details.

2. Experimental

2.1. Materials

Graphite powders (45 μm) were purchased from Shandong Qingdao laixi graphite company in China. Glycidyltrimethylammonium chloride (GDTMAC) and 3-aminopropyltriethoxysilane (APTES) were purchased

from Aladdin. 4, 4'-Dihydroxybenzophenone (DHBP), 9, 9'-bis (4-hydroxyphenyl) fluorene (BHF) and 4, 4'-Sulfonylbis (fluorobenzene) (FPS) were obtained from Aladdin. GO was synthesized according to the modified Hummers method [35]. All other reagents were obtained from Shanghai Chemical Reagent Plant and used as received.

2.2. Synthesis of sulfonated poly(ether sulfone)

The synthesis of the poly(ether sulfone) (PES) is a typical polycondensation reaction (Scheme 1) [19]. 2.066 g BHF, 0.42 g DHBP, 1.998 g FPS and 2.17 g K_2CO_3 were dissolved in the mixture solution of 20 mL toluene and 40 mL *N,N*-dimethylacetamide (DMAc) in three-neck round flask equipped with a magnetic stirrer and a Dean-Stark trap. The reaction was performed at 140 °C under reflux and maintained for 4 h under a nitrogen atmosphere. Then the toluene was removed and the temperature was increased to 165 °C and kept for 24 h. After the reaction was completed, the solution was poured into 300 mL hot ethanol, and the sample was filtered and dried at 70 °C under vacuum for 24 h. GPC results: $M_n = 71,500 \text{ g mol}^{-1}$, PDI = 1.6.

The above obtained PES was sulfonated by the following procedure: PES (1.0 g) was firstly dissolved in 40 mL chloroform. Then a mixed solution of chlorosulfonic acid (0.9 mL) and chloroform (15 mL) was added dropwise to the above solution of PES with a mechanical stirrer. The sulfonation reaction was kept stirring for 24 h at room temperature until all the products had precipitated from the reaction solution. The product was poured into deionized water and filtered, then washed with water. Finally, the product was dried in a vacuum oven at 80 °C for 10 h.

2.3. Preparation of quaternized graphene oxide (QGO)

2.3.1. Synthesis of APTES-functionalized graphene oxide (A-GO)

The synthesis of A-GO was according to the previous work [36,37]. The typical process was as follows: The homogeneous GO dispersion was prepared by dispersing GO (63 mg) into deionized water (80 mL) by ultrasonication, and then APTES (15.6 mL) was added to the above solution under ultrasonication for another 1 h. The mixture solution was stirred for 8 h at 60 °C under N_2 atmosphere. Finally, the suspension was filtered and washed thoroughly with water and ethanol respectively, and dried at 50 °C under vacuum for 10 h.

2.3.2. Preparation of quaternized graphene oxide (QGO)

The quaternized graphene oxide was prepared as follows [38]: The above obtained A-GO (0.5 g) was sonicated into deionized water (500 mL) to form a homogeneous black dispersion, and then GDTMAC (1.0 mL) was added for 30 min under ultrasonication. The black mixture was stirred first at room temperature for 3 h, then at 80 °C for 6 h under a N_2 atmosphere. Finally the black solution was cooled to room temperature, and the product was centrifuged and washed with water and ethanol for three times, respectively.

2.4. Preparation of composite membranes

A solution of SPES was prepared by dissolving SPES (1.2 g) in DMF (16 mL) at 70 °C, and then a homogeneous black dispersion of QGO in DMF (4 mL) was added into the above solution and kept stirring at 70 °C for 6 h. The mixture solution was degassed firstly, then cast onto a glass dish and dried at 60 °C for 6 h, finally heated at 120 °C for 12 h under vacuum to obtain the membranes. The thicknesses of all dry membranes were measured to be 40–60 μm .

2.5. Measurements

2.5.1. Instrumental characterization

Fourier transform infrared (FTIR) spectra were performed on a Magna 560 FTIR spectrometer. The gel permeation chromatographic

Download English Version:

<https://daneshyari.com/en/article/7744926>

Download Persian Version:

<https://daneshyari.com/article/7744926>

[Daneshyari.com](https://daneshyari.com)