



Sulfonated poly(ether ether ketone)-based hybrid membranes containing graphene oxide with acid-base pairs for direct methanol fuel cells



Yongheng Yin^{a,b}, Haiyan Wang^{a,b}, Li Cao^{a,b}, Zhen Li^{a,b}, Zongyu Li^{a,b}, Mingyue Gang^{a,b}, Chongbin Wang^{a,b}, Hong Wu^{a,b,c,*}, Zhongyi Jiang^{a,b}, Peng Zhang^d

^a Key Laboratory for Green Chemical Technology of Ministry of Education, School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, China

^b Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Tianjin 300072, China

^c State Key Laboratory of Separation Membranes and Membrane Processes, School of Materials Science and Engineering, Tianjin Polytechnic University, Tianjin 300387, China

^d Key Laboratory of Nuclear Analysis Techniques, Institute of High Energy Physics, Chinese Academy of Sciences, Beijing 100049, China

ARTICLE INFO

Article history:

Received 17 December 2015

Received in revised form 8 March 2016

Accepted 9 April 2016

Available online 11 April 2016

Keywords:

Graphene oxide
Hybrid membrane
Acid-base pair
Proton conductivity
Methanol permeability

ABSTRACT

The graphene oxide (GO) sheets are functionalized by histidine molecules and incorporated into sulfonated poly(ether ether ketone) (SPEEK) matrix to fabricate hybrid polymer electrolyte membranes for direct methanol fuel cells (DMFCs). The loading of functionalized GO is varied to investigate its influence on cross-sectional morphology, crystalline structure, polymer chain stiffness, thermal stability and fractional free volume of membrane, etc. The acidic $-\text{SO}_3\text{H}$ groups (proton donors) in SPEEK and basic imidazole groups (proton acceptors) in histidine molecules form acid-base pairs and transport protons synergistically, thus yielding efficient proton channels inside the hybrid membranes. The maximum proton conductivity (at 100% RH) of hybrid membranes is elevated by 30.2% compared with the plain SPEEK membrane at room temperature. The functionalized GO flakes also confer the hybrid membranes low methanol permeability in the range of $1.32\text{--}3.91 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$. At the filler content of 4 wt%, the hybrid membrane shows a superior selectivity of $5.14 \times 10^5 \text{ S s cm}^{-3}$ and its maximum power density of single DMFC cell (43.0 mW cm^{-2}) is 80.7% higher than that of plain SPEEK membrane.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

Direct methanol fuel cell (DMFC) has received tremendous attention in recent years as methanol is one of the most promising fuels besides hydrogen due to its abundant source, high energy content, easy storage and transportation, etc. [1]. As the performance-limiting component of DMFC, polymer electrolyte membrane (PEM) needs to meet two basic requirements, high proton conductivity and low/zero methanol permeability [2,3]. Unfortunately, like the commonly found trade-off effect between separation factor and permeability for polymeric membranes used in separation processes [4,5], a similar trade-off limit has also

been found in DMFC membranes, i.e. increasing the methanol resistance property (reducing methanol permeability) usually compromises the proton conductivity and vice versa [6]. This is because that the water molecules in membrane will promote the proton conduction via Vehicular mechanism (mainly in the form of H_3O^+) and the diffusion of methanol molecules simultaneously.

Developing organic-inorganic hybrid membranes seems to be an effective approach to overcome the trade-off effect between proton conductivity and methanol permeability [7,8]. The recent discoveries and researches of 2D carbonaceous materials represented by graphene oxide (GO) have aroused particular interest in the area of new and high-performance materials [9–11]. It has been demonstrated that the protons can be transferred by the carboxylic acid groups along edges of GO and epoxy groups on the surface of GO [12,13], consequently, the proton conductivity of single-layer GO can reach as high as $10^{-2} \text{ S cm}^{-1}$ [11]. Additionally, the GO nanosheets also possess an outstanding blocking effect on methanol molecules [14]. These unique characteristics make GO

* Corresponding author at: School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, PR China. Tel.: +86 22 23500086; fax: +86 22 23500086.

E-mail addresses: wuhong@tju.edu.cn, 1015471149@qq.com (H. Wu).

a promising candidate as inorganic component in the fabrication of hybrid proton conductive membranes. Currently, graphene oxide sheets are usually sulfonated by either direct oxidation [15,16], physical adsorption [17] or chemical grafting [18], and then blended with polymer to make hybrid PEMs.

Nature offers various inspirations for fabricating new membrane materials [19–21]. Ion channels, which are ubiquitous in cell membrane, play an important role in intercellular mass transport such as proton transfer [22,23]. Usually, the proton transfer occurs along the amino acid-lined channels with high efficiency, for example, 10^5 protons could be conducted per second through one channel in adenosine triphosphate (ATP) synthase systems [24]. It has been demonstrated that for acid-base pairs, the acidic groups act as proton donors and the basic groups act as proton acceptors, resulting in efficient proton conduction [25]. Based on these findings, acid-base pairs have been introduced into polymer to fabricate PEMs [26–28]. Tributsch et al. incorporated silica nanoparticles attached with lysine into the pores of polyethylene terephthalate [24], the power output of the obtained membrane with acid-base pairs approached the commercial Nafion[®] membrane. Wang et al. used dopamine-modified silica nanoparticles to prepare sulfonated poly (ether ether ketone)-based hybrid membranes [29], the hybrid membrane achieved a high conductivity of $4.52 \times 10^{-3} \text{ S cm}^{-1}$ at 120°C under anhydrous condition. We have previously introduced acid-base pair functionalized titania-silica into chitosan membrane and found that the highest selectivity of the as-prepared hybrid membrane was $4.85 \times 10^4 \text{ S cm}^{-3}$, which was ~ 3 times higher than that of pure chitosan membrane [30].

The aim of this study is developing hybrid membranes using functionalized GO as additives in order to pursue both high proton conductivity and strong methanol resistance for DMFC application. Herein, GO is functionalized by histidine molecules and then incorporated into sulfonated poly (ether ether ketone) (SPEEK) to prepare organic-inorganic hybrid membranes with acid-base pairs. The fabricated hybrid membranes are characterized by SEM, FTIR, DSC, PALS, etc, and the membrane is made into membrane electrode assembly for single DMFC performance test. The reason why as-prepared hybrid membranes could solve the trade-off effect between proton conductivity and methanol permeability is discussed.

2. Experimental

2.1. Materials and chemicals

Poly (ether ether ketone) (PEEK) was purchased from Victrex High-performance Materials Co., Ltd (Shanghai, China). Histidine (purity 98%), oxalic acid dihydrate (analytical grade), calcium hydride (analytical grade) and thionyl chloride (analytical grade) were obtained from Aladdin. Sulfuric acid (H_2SO_4), *N,N*-dimethylformamide (DMF), tetrahydrofuran (THF), methanol and other reagents were purchased from Guangfu Fine Chemical Research Institute (Tianjin, China). DMF was dehydrated by stirring with calcium hydride and distilling under reduced pressure before use. Deionized water was used in all the experiments.

2.2. Preparation and functionalization of graphene oxide

Pristine graphene oxide (GO) was synthesized using a modified Hummers method [31], then pristine GO was esterified to produce more carboxylic acid groups [32]. Typically, the prepared GO was suspended in 100 mL of H_2O (5 mg mL^{-1}), 6 g of oxalic acid dihydrate was added into the mixture and stirred for 24 h. Subsequently, the suspension was washed with H_2O for 3 times and finally dispersed in 20 mL of DMF.

The GO was functionalized by histidine through an amidation reaction. Firstly, the above suspension was added into a three-necked flask containing 100 mL of thionyl chloride under N_2 atmosphere. The flask was equipped with a water-cooled reflux condenser and heated at 65°C for 24 h. The GO with acid chloride groups (denoted as GO-COCl) was washed with THF until the pH of filtrate reached neutral. Secondly, GO-COCl was mixed with aqueous solution of histidine (5 mg mL^{-1}), and the suspension was heated at 100°C for 40 h. Finally, the histidine-functionalized GO (denoted as GO-his) was filtered, washed with H_2O , and dried under vacuum at 40°C for 48 h.

2.3. Preparation of sulfonated poly (ether ether ketone) (SPEEK)

SPEEK was prepared by a post-sulfonation method. Typically, 18 g of dried PEEK was dissolved gradually in 200 mL of concentrated sulfuric acid (98%) for 4 h at room temperature, then the mixture was stirred vigorously at 45°C for 8 h. After reaction, the solution was slowly precipitated in water under mechanical agitation. The obtained SPEEK precipitate was filtered, washed several times with water until the pH reached neutral. Finally, the SPEEK polymer was dried at room temperature for 24 h and at 60°C for another 24 h. The sulfonation degree of as-prepared SPEEK was measured to be 66% by acid-base titration.

2.4. Preparation of hybrid membranes

0.6 g of SPEEK was dissolved in 4 g of DMF under stirring at 25°C . A premeasured amount of GO-his was dispersed in 4 g of DMF under ultrasonication, then the GO-his suspension was added into the SPEEK solution, followed by vigorously stirring for 12 h to ensure a fine dispersion. The mixture was degasified and cast onto a glass plate, followed by successively dried at 60°C for 12 h and annealing at 80°C for another 12 h. The prepared hybrid membranes were designated as SPEEK/GO-his-X, where X was the weight ratio percentage of inorganic fillers to SPEEK. As a comparison, plain SPEEK membrane and hybrid membranes incorporated with pristine GO (SPEEK/GO-X) were also fabricated. The thickness of all the membranes was in the range of 60–65 μm .

2.5. Characterizations

Transmission electron microscopy (TEM) observation was performed by a Tecnai G2 F20. Fourier transform infrared spectra (FTIR) of GO and membranes were recorded on a Nicolet MAGNA-IR 560 spectrometer in the wavenumber range of $4000\text{--}400 \text{ cm}^{-1}$. The elemental composition of GO was investigated by X-ray photoelectron spectroscopy (XPS, PHI-1600). The cross-sectional morphologies of the membranes were observed using magnified field emission scanning electron microscope (FESEM, Hitachi S-4800) operated at 3 kV and FESEM (Nanosem 430) operated at 10 kV. The crystalline structure was characterized with X-ray diffractometer (XRD, RigakuD/max2500 v/Pc) using $\text{Cu K}\alpha$ radiation, the scanning angle ranged from 2° to 55° with a scanning rate of 2° min^{-1} . Glass transition temperature was measured by differential scanning calorimetry (DSC, 204 F1 NETZSCH), samples were preheated under N_2 atmosphere from 25 to 150°C at $10^\circ\text{C min}^{-1}$, then cooled to 90°C and reheated to 260°C . Thermal stability was characterized by thermogravimetric analyzer (TGA, Perkin-Elmer Pyris), each sample was heated under N_2 flow over the temperature range of $20\text{--}800^\circ\text{C}$ at a heating rate of $10^\circ\text{C min}^{-1}$. The mechanical properties of the membranes were measured using an electronic tensile machine (WDW-2, Yangzhou Zhongke Measuring Apparatus Co., China) with an elongation rate of 10 mm min^{-1} at room temperature.

Download English Version:

<https://daneshyari.com/en/article/182976>

Download Persian Version:

<https://daneshyari.com/article/182976>

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