Journal of Membrane Science 507 (2016) 1–11

Contents lists available at ScienceDirect

Journal of Membrane Science

journal homepage: www.elsevier.com/locate/memsci

Graphitic carbon nitride nanosheets/sulfonated poly(ether ether ketone) nanocomposite membrane for direct methanol fuel cell application

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ARTICLE INFO

Article history:
Received 18 October 2015
Received in revised form
14 January 2016
Accepted 2 February 2016
Available online 8 February 2016

Keywords:
Carbon nitride
Nanocomposite membranes
Proton conduction
Methanol permeation
Fuel cells

ABSTRACT

As a novel kind of two-dimensional soft nanomaterial, graphitic carbon nitride (g-C_3N_4) has been boomingly explored in diverse fields such as photocatalysis and heterogeneous chemical catalysis, however, its potential application in proton exchange membranes (PEMs) fuel cells remains disclosed. In this study, nanocomposite membranes with varying g-C_3N_4 nanosheets content are fabricated by incorporating g-C_3N_4 nanosheets into sulfonated poly(ether ether ketone) (SPEEK). An increase in proton conductivity from 0.0606 S cm^{-1} of the SPEEK control membrane to 0.0786 S cm^{-1} of the nanocomposite membrane is achieved at the g-C_3N_4 nanosheets content of 0.5 wt% at 20 °C, stemming from that the improved connectivity of the ionic groups renders the acid-base pair effect and facilitates the Grotthuss-type transport of proton. Methanol permeability at room temperature decreases with the increase of the g-C_3N_4 nanosheets content, stemming from that the periodic vacancies in the lattice of g-C_3N_4 render the molecular sieving effect and the consequent high resistance for methanol permeation. An increase up to 39% in maximum power density is obtained, indicating the potential of g-C_3N_4 nanosheets for fuel cell application. Moreover, the superior mechanical properties of the g-C_3N_4 nanosheets lead to a 68% increase in ultimate tensile strength of the nanocomposite membranes (54.31 MPa at the g-C_3N_4 nanosheets content of 0.5 wt%).

1. Introduction

In recent years, proton exchange membrane fuel cells (PEMFCs) as alternative energy conversion devices have received much attention and are expected to become a source of low-emission power generation for both portable and stationary applications owing to their high energy efficiencies and environmental-benign nature [1,2]. Proton exchange membrane (PEM) is a key component for PEMFCs. At present, Nafion® membranes are commonly used PEMs with high proton conductivity at a certain range of temperature and humidity, but they still have some drawbacks such as high fuel permeability and high cost [3–6].

Studies have been focused on alternative solutions, including fabrication of nanocomposite membranes by incorporating different nanofillers [7–9]. Till now, zero-dimensional (0D) materials (such as silica nanoparticles [10–12], ceramic oxides nanoparticles [13,14], etc. [9,15–17]) and one-dimensional (1D) nanomaterials (such as carbon nanotube [18,19], titania [20,21] and titanate [22] nanotube) have been incorporated into polymer matrix as versatile nanofillers. These nanocomposite membranes exhibited great enhancement in performance, endowing strong competitiveness in fuel cell application. Recently, two-dimensional (2D) nanomaterials as novel fillers for PEMs have been actively exploited due to their unique properties such as high aspect ratio and large surface area, which contribute to the following distinct merits as nanofillers for PEMs: (i) finely tuning the microstructure of the membrane, rendering a better connectivity of the ionic clusters, and thus donating more continuous pathways for protons transport [23–25]; (ii) serving as high-resistance fuel barriers, creating longer and more tortuous paths to effectively decrease the fuel crossover [26]. For instance, Zarrin et al. fabricated nanocomposite membrane filled with functionalized graphene oxide (GO), and both proton conductivity and single cell performance were significantly enhanced [27]; Feng et al. employed an "*in situ* growth of MoS_2" strategy to prepare MoS_2/Nafion composite membranes

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http://dx.doi.org/10.1016/j.memsci.2016.02.004
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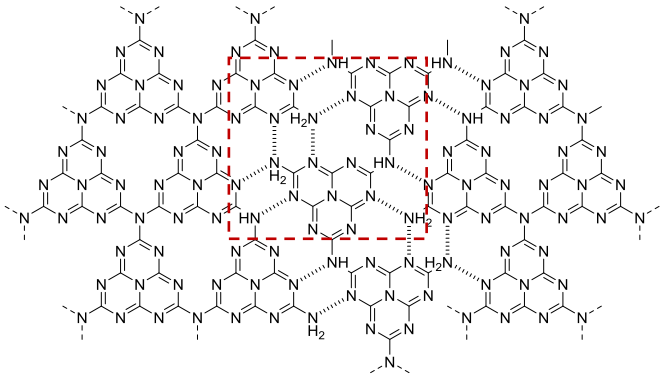

Fig. 1. Structural model of g-C_3N_4 with defects in red rectangle. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

and obtained highly selective PEMs [28].

Graphitic carbon nitride (structural model is shown in Fig. 1) is a promising 2D soft nanomaterial with a similar stacked 2D structure as graphene [29,30], which is becoming increasingly popular in the fields of photocatalysis, heterogeneous catalysis and other promising applications [31–33]. However, its application in proton exchange membranes (PEMs) remained unexplored. Due to some unique attributes, g-C_3N_4 should have potential in enhancing the performance of the PEMs. For instance, the amino (–NH_2) and imino (–NH) groups of g-C_3N_4 could interact with the acid groups (sulfonate groups) in the polymer matrix to form acid–base pairs, facilitating the dissociation of sulfonate groups and enhancing the Grotthuss-type transfer of protons [34–39]. The interfacial acid–base interactions between g-C_3N_4 nanofillers and polymers also ensure that the mechanical properties of g-C_3N_4 could be conferred to the nanocomposite membranes, which would result in elevated mechanical properties. In addition, g-C_3N_4 possesses periodic vacancies in the lattice with an appropriate geometric size smaller than that of methanol molecule but bigger than that of hydrated proton, and molecular sieving effect could be expected which can lead to a decrease in methanol crossover [40,41] without impeding proton transfer.

In this study, g-C_3N_4 nanosheets were synthesized, and subsequently incorporated into SPEEK to prepare nanocomposite membrane. The structures and thermal properties of g-C_3N_4 were characterized by Fourier transform infrared spectroscopy (FTIR), thermal gravimetric analysis (TGA), X-ray diffraction and transmission electron microscopy (TEM). Proton conductivity, methanol permeability, single cell performance, water uptake, dimensional stability, thermal properties, mechanical stability of the resultant membranes were evaluated.

2. Experimental

2.1. Materials

Melamine, hydrochloric acid, and methanol were purchased from Tianjin Guangfu Technology Development Co. Ltd. (Tianjin, China). Concentrated sulfuric acid (98 wt%, AR) was bought from Tianjin Jiangtian Chemical Scientific Ltd. N,N-Dimethylacetamide (DMAc, GR), isopropanol were purchased from Shanghai Aladdin Industrial Corporation. Poly(ether ether ketone) (Victrex®PEEK, grade 381G) was purchased from Nanjing Yuanbang Engineering Plastics Co. Ltd. Pt/C catalyst and carbon paper were received from Shanghai Hesen Electric Co., Ltd. Nafion 5% solution was obtained from DuPont. All the materials and chemicals were of analytical grade and used as received. Deionized water was used throughout the study.

2.2. Synthesis of g-C_3N_4 nanosheets

Bulk g-C_3N_4 was prepared by directly heating melamine at 550 °C for 4 h in air, with heating/cooling rate of 3 °C min^{-1}. The obtained bulk g-C_3N_4 was milled into powder. Then, a direct thermal oxidation "etching" process was adopted by heating bulk g-C_3N_4 at 500 °C (ramp rate: 5 °C min^{-1}) under air condition for 2 h [42]. The obtained light yellow powder was then dispersed in water with a concentration of 1 mg ml^{-1} for ultrasound exfoliation of 12 h [43]. After centrifugation and drying, g-C_3N_4 nanosheets were acquired.

2.3. Sulfonation of PEEK and determination of DS

Dried PEEK pellets were gradually added in 20 min into mechanically stirred concentrated sulfuric acid under room temperature and vigorously agitated for 3 h. After thorough dissolution, the reaction mixture was heated to 50 °C and kept under stirring for another 9 h. The sulfonated PEEK (SPEEK) was recovered by precipitating the solution into excess cold water. The polymers were washed with water until pH of the rinse water was at neutral, and then dried in vacuum [44].

The degree of sulfonation (DS) of SPEEK polymers was determined using ^{1}H NMR spectroscopy by integration of the distinct aromatic signals as reported in previous literatures. Fig. 2 showed the ^{1}H spectrum of SPEEK sample and the assigned peaks. The presence of sulfonic acid groups results in a distinct signal for H_E together with other two types of protons H_C and H_D as shown in Fig. 2. With the increase of DS, the intensity of these peaks could be expected to enhance as well [45]. In fact, the DS could be quantitatively determined based on the following formula:

$$\frac{n}{12-2n} = \frac{A_{H_E}}{\sum A_{H_{AA'BB'CD}}} (0 \le n \le 1) \quad (1)$$

$$DS = n \times 100\% \quad (2)$$

where A_{H_E} is the peak area of distinct H_E signals, $\sum A_{H_{AA'BB'CD}}$ is the integrated areas of the signals related to all the other aromatic hydrogens. The DS was calculated to be 67%.

2.4. Preparation of the membranes

The nanocomposite membrane was fabricated by solution-casting method. SPEEK (0.6 g) was dissolved into DMAc (3 mL)

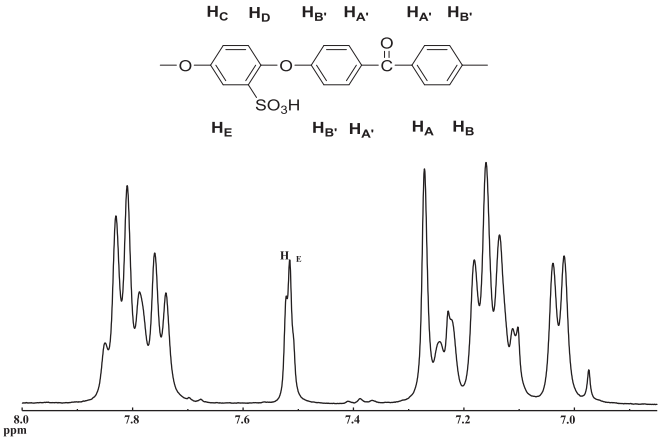

Fig. 2. ^{1}H NMR spectrum of sulfonated PEEK sample.