



# Highly sulfonated poly(ether ether ketone) grafted on graphene oxide as nano hybrid proton exchange membrane applied in fuel cells



Shuitao Gao<sup>a</sup>, Hulin Xu<sup>b</sup>, Zhou Fang<sup>a</sup>, Amina Ouadah<sup>a</sup>, Huan Chen<sup>a</sup>, Xin Chen<sup>c</sup>, Lubin Shi<sup>a</sup>, Bing Ma<sup>a</sup>, Chaojun Jing<sup>a</sup>, Changjin Zhu<sup>a,\*</sup>

<sup>a</sup> School of Chemistry and Chemical Engineering, Beijing Institute of Technology, Beijing 100081, China

<sup>b</sup> Beijing Qintian Science & Technology Development Co., Ltd., China

<sup>c</sup> Department of Chemical Engineering, Columbia University, NY 10027, United States

## ARTICLE INFO

### Article history:

Received 9 April 2018

Received in revised form

14 June 2018

Accepted 27 June 2018

Available online 28 June 2018

### Keywords:

Sulfonated poly(ether ether ketone)

Graphene oxide

Grafting-to

Proton exchange membrane

Fuel cell

## ABSTRACT

Highly sulfonated poly(ether ether ketone) (PEEK) polymer is hydrogenated and then readily grafted on GO to provide nano hybrid material GO-g-SPEEK. The material shows good enough properties for the preparation of proton exchange membranes. First, the GO-g-SPEEK membrane has much more water uptake but less water swelling compared with Nafion<sup>®</sup>, and an excellent proton conductivity of 0.219 S cm<sup>-1</sup> at 90 °C. Then, it demonstrates a peak power density of 112 mW cm<sup>-2</sup> when utilized in a H<sub>2</sub>/air fuel cell at circumstance temperature. Further, blending of the materials with Nafion leads to composite membranes of GO-g-SPEEK/Nafion, which has a close proton conductivity to that of GO-g-SPEEK but far higher cell performances. Of the composite membranes, GO-g-SPEEK/Nafion-33 reveals cell performance of 182 mW cm<sup>-2</sup> at 25 °C and 213 mW cm<sup>-2</sup> at 60 °C. These results indicate that Nafion might serve only as an enhancer of compatibility between membrane and Nafion-supported catalyst phase in the membrane electrode assembly, and therefore suggest that the GO-g-SPEEK may be a promising membrane material for the application in proton exchange membrane fuel cells.

© 2018 Elsevier Ltd. All rights reserved.

## 1. Introduction

To reduce reliance on fossil fuels and increase demands for clean energy technology worldwide, there is currently a growing interest in the use of fuel cells as energy-efficient and environmentally friendly power generators [1]. Among all major types of fuel cell, proton exchange membrane fuel cells (PEMFCs) are in the forefront stage and have gained substantial attention for vehicle and portable applications, owing to a compact structure, room-temperature start-up capacity, high power density features and etc. Proton exchange membrane (PEM) fuel cells, which are composed of a cathode, an anode, and a PEM, convert chemical energy directly into electrical energy cleanly via electrochemical reactions of hydrogen and oxygen, to yield water and heat as the only byproducts [2]. In PEMFCs, one of few pivotal components that underpin the overall performance of fuel cells is the PEM, which serves as the separator of an anode and a cathode along with the

proton conducting channel. Thus, an ideal PEM should possess not only fast proton transport but also superior mechanical properties in the presence of water [3].

Although poly(perfluorosulfonic acid) (PFSA) membranes (for example, Nafion<sup>®</sup>) have been superior to others in overall performance, they still have several disadvantages such as high cost, low thermal stability, and poor function at elevated temperatures (above 80 °C) or low humidity, hindering their worldwide commercialization. In this context, great efforts have been dedicated to developing cost-effective and alternate membranes based on sulfonate aromatic polymers like the sulfonated poly(ether ether ketone) (SPEEK). That is, the SPEEK not only is low at cost, but also holds sufficient mechanical qualities and appropriate thermal strength [4]. Proton conductivity of SPEEK is largely related to the degree of sulfonation. Increasing the degree of sulfonation values helps obtain the ostensible result of “higher conductivity,” while it causes undesirable and excessive dimensional swelling under high humidity conditions. Moreover, the excessive water swelling drawback of the membranes leads to fuel crossover and even deterioration in mechanical stability [5], and it is observed in our work that the membranes with the sulfonation degree of 77% were

\* Corresponding author.

E-mail address: [zcj@bit.edu.cn](mailto:zcj@bit.edu.cn) (C. Zhu).

ready to melt down at 30 °C in hydrate environment and of 84% even at room temperature. This greatly halts the effective application of SPEEK in PEM. Thus, it is of importance to overcome the trade-off effect between the proton conductivity and dimensional stability and comprehensively to promote the performance of SPEEK-based PEM.

Graphene oxide (GO) is an attractive material due to its great promise in a number of application areas. One area where GO has opened up exciting ways as a reinforcement agent is in solid electrolytes owing to its mechanical, thermal, and electrical insulating properties. In particular, GO is a proton conductive material. In-plane and through-plane conductivities of spray-painted GO membrane were reported to be 49.9 and 0.3 mScm<sup>-1</sup>, respectively, reported by Bayer, Lyth and coworker [6]. They also obtained a maximum power density of 33.8 mWcm<sup>-2</sup> for GO membrane at 30 °C, the highest reported so far for pure GO [7], and further conducted a systematic impedance spectroscopy investigation of GO membranes to present information about the nature of the conductivity and permittivity of GO paper [8]. On the other hand, the proton conductivity for GO nearly 10 mScm<sup>-1</sup>, higher than a graphene oxide/proton hybrid, was reported by the different research group [9]. Moreover, bulk GO film exhibits mixed conductivity with different oxidation degrees and its electrochemical behavior may also be influenced by the water content of the film [10,11]. Also, a freestanding sulfonated GO paper showed the in-plane and through-plane conductivity values of 40 and 12 mScm<sup>-1</sup> at 30 °C, respectively [12]. Incorporation of GO into polymer can moderately adjust proton conductivity as a result of rendering the membrane with enhanced hydrophilic property and managing the state of water confined in ionic channels in the polymer matrix, as the presence of oxygen-containing group, such as carboxyl groups and hydroxyl groups [13]. Moreover, the involvement of these functional groups would improve the solubility of GO and afford reaction sites for further use. Apart from that, the existence of substantial band gap due to sp<sup>3</sup>-hybridized carbon atoms, and large surface area in GO also make it a smart nanomaterial with the possibility of facile surface modification, thus providing the opportunity of tailoring the comprehensive properties of GO-based membranes in PEMFC [14,15].

GO-based membranes have been considered to be a very promising alternative to conventional filled polymers or polymer blends of the fuel-cell community, because of their impermeable nature to H<sub>2</sub> and O<sub>2</sub> gases while exhibiting decent H<sup>+</sup> transport, satisfying the important prerequisites for a successful fuel-cell membrane [16,17]. The covalent modification of graphitic materials by functional molecules and various polymers can be obtained generally by “grafting from” and “grafting to” strategies. As for the “grafting from” strategy, the initiator used for polymerization is normally anchored onto the body and in the edges of graphitic materials. In contrast, via “grafting to” strategy, end-group-transformed polymer chains react with the functional groups of substrates [18–21]. In fact, exceptional efforts have been undertaken to show that graphene and graphene oxide (GO) are potentially effective reinforcements [21–25]. Specially, previously reported works about SPEEK/functionalized GO have confirmed the advantage of GO-based materials as PEM [26,27].

In our previous work, we paid great attention to the reinforcement of polymer composites by GO-based additives. Herein, a novel procedure was presented to make a new type of composite PEMs using GO nanosheets as the mechanically-strong barrier for highly sulfonated PEEK. Firstly, the partially hydroxyl-functionalized SPEEK polymers with high sulfonation degree were prepared by the reduction of some benzophenone moieties of SPEEK. Separately, graphite oxides were brominated for further chemical modification using highly reactive C–Br bonds. Then, “graft-to”

reaction between the brominated GO and hydroxyl-functionalized SPEEK polymers yielded final nanohybrid material GO-g-SPEEK. The modified SPEEK chains were found to covalently anchor on graphene surfaces and this afforded reinforcement effects of dimensional stability for GO-g-SPEEK membrane compared to SPEEK. Therefore, it is suggested the improved compatibility and strong interfacial interaction between the graphene and modified SPEEK polymer, and in turn a restriction for their relaxation or segmental motion in the membrane even at higher temperatures. As a result, prevention of excessive water swelling and superior proton conductivity were achieved for the membrane by the combination of materials. Furthermore, polybenzimidazole (s-PBI) and Nafion as blends were combined with the GO-g-SPEEK material, respectively, in order to reinforce the membrane mechanical strength and investigate the electrode assembly behaviour of the GO-g-SPEEK composite membrane. The performances of the resulting membranes were fully tested to illustrate the potential application of GO-composited membranes in PEMs for fuel cells. Our results indicated an effective way to prepare the highly sulfonated SPEEK-based PEMs, which could have excellent membrane and fuel cell performances.

## 2. Experimental

### 2.1. Materials

Polybenzimidazole (PBI) powder was supplied from HEOWNS (Tianjin, China). Concentrated sulfuric acid (95–98%), poly(ether ether ketone)(PEEK) 450G Victrex, N-Methyl-2-pyrrolidinone (NMP), dimethylsulfoxide (DMSO), 2-Propanol, potassium carbonate (K<sub>2</sub>CO<sub>3</sub>) and hydrobromic acid were obtained from TCI Chemical Co. And used without further purification. DMSO was freshly distilled prior to use. Graphene oxide (GO) and Nafion (Du Pont) solution (5 wt%) D520 were produced by Nanjing XFNANO Materials Tech Co., Ltd.

### 2.2. Synthesis of SPEEK

PEEK (4.0 g) was gradually added to 100 ml of concentrated sulfuric acid (95–98%) at ambient temperature under argon atmosphere. After complete dissolution of PEEK, solution was stirred at 70 °C under vigorous mechanical stirring for 3 h. Then, polymer solution was then cooled on ice water bath to terminate the reaction and poured into excess cold water to give a fibrous type SPEEK polymer. Precipitated polymer was filtered and washed several times with distilled water until the pH was neutral and then dried under vacuum at 80 °C for 24 h.

### 2.3. Preparation of hydroxylation of SPEEK (SPEEK-OH)

To a solution of SPEEK (0.48 g) in purified DMSO (30 ml), sodium borohydride (0.12 g) was slowly added and the mixture was stirred for 12 h at 120 °C under nitrogen atmosphere. The mixture was then cooled to room temperature and purified by three cycles of centrifugation with 2-propanol. The precipitate was collected and dried in vacuum at 70 °C for 24 h, resulting in white powders (Scheme S1 in the supplementary data).

### 2.4. Synthesis of brominated graphene oxide (GO-Br)

Graphite oxide (135 mg) and hydrobromic acid (20 ml) were added into a 100 ml reaction flask with a stirrer. After stirring and reflux for 5 h, the reaction product was filtrated and purified by three cycles of centrifugation with deionized water. Finally, the product was dried in vacuum at 80 °C for 24 h. These samples were

Download English Version:

<https://daneshyari.com/en/article/6601978>

Download Persian Version:

<https://daneshyari.com/article/6601978>

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