



Sulfonated reduced graphene oxide as a conductive layer in sulfonated poly(ether ether ketone) nanocomposite membranes



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ABSTRACT

In this work, sulfonated reduced graphene oxide (SRGO) has been synthesized and incorporated into conventional random sulfonated poly(ether ether ketone) (SPEEK) in order to decrease the proton conduction barrier between isolated sulfonic acid groups in SPEEK and improve its conduction properties. SRGO was prepared by a facile arylation of reduced graphene oxide (RGO) with diazonium salt, which allowed the benzene sulfonate groups to be covalently bonded to the RGO layer. By a physical blending approach, the SRGO/SPEEK composite membranes were obtained in a homogenous state, and exhibited considerably improved thermal stability, mechanical strength and *dimensional stability*. Since the sulfonic acid groups presented in SRGO promote ion conduction through both Vehicle and Grotthuss mechanisms, the composite membranes exhibited better proton conductivities (σ), particularly at low relative humidity (RH) conditions. Taking SPEEK/SRGO-1.0 membrane as an example, its σ was as high as 8.6 mS cm⁻¹ at 80 °C/50% RH, which is three times greater than that of the blank. Moreover, the H₂/air single cell test further confirmed the superior performance of the SPEEK/SRGO-1.0 membrane. A higher power output of 705 mW cm⁻² was generated with this composite membrane under the testing conditions, whereas only 636 mW cm⁻² for the pristine SPEEK membrane.

1. Introduction

Proton exchange membranes (PEMs) have been extensively studied for their potential use in PEM fuel cells (PEMFCs), which are considered one of the most promising clean energy conversion technologies [1,2]. The most widely used PEMs, including Nafion (DuPont), Flemion (Asahi Glass), and Aciplex (Asahi Chemical), are mainly based on the perfluorosulfonic acid (PFSA) polymers, due to their good chemical stability, high mechanical strength and high proton conductive ability. Nevertheless, these types of PEMs generally suffer from several drawbacks such as high cost and harsh synthesis methods [3–7].

To overcome those shortcomings, many efforts have been made to design new generation PEMs, particularly based on aromatic ionomers, such as sulfonated poly(ether ether ketone) (SPEEK) [4], sulfonated poly(arylene ether sulfone) (SPAES) [5,6], sulfonated polyphenylenes (SPP) [7,8], etc. Among them, SPEEK is considered as a promising alternative and has been extensively studied over the past decades [9–11]. Its precursor, poly(ether ether ketone) (PEEK), is already commercially available, thus a PEEK-based PEM could be easily prepared by a simple post sulfonation process. Despite its merits such as good

membrane forming ability and high temperature tolerance, the SPEEK polymer generally exhibits considerably large relative humidity (RH) dependence [4,12,24]. In other words, it lacks sufficient ion conductive ability under low water content, which greatly limits its practical applications.

Recently, many researchers have diverted their attentions to *inorganic-organic* composite systems due to the rapid development of many versatile inorganic materials [13,14]. Some unique inorganic fillers, such as zeolites [15], heteropolyacids [16], carbon nanotubes [17], and graphenes [18], have been incorporated into polymers and demonstrated their advantages for use in the PEM. Among these materials, graphene is a particularly interesting choice due to its large surface area and ability to interact with the polymer matrix, which could effectively enhance the mechanical robustness and thermal properties of the membrane [19–21]. However, from the viewpoint of ion carrier, a direct blending or composite preparation procedure using graphene or graphene oxide (GO) remains quite challenging. Such materials cannot actually conduct protons, and in fact, could perhaps inhibit the proton transfer by the barrier blocking effect [22]. Therefore, the functionalization of graphene oxide is of great importance so as to better fulfill synergy mechanism with polymeric

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Nomenclature

SRGO	sulfonated reduced graphene oxide
SPEEK	sulfonated poly(ether ether ketone)
RH	relative humidity
PEMs	Proton exchange membranes
SPAES	sulfonated poly(arylene ether sulfone)
SPP	sulfonated polyphenylenes
MHQ	methoxyhydroquinone
DFBP	4,4'-difluorobenzophenone

6F-BPA	4,4'-(hexafluoroisopropylidene) diphenol A
WU	water uptake
DC	dimensional change
IEC	ion exchange capacity
λ	water sorption
σ	proton conductivity
TGA	thermogravimetric analysis
OCV	open circuit voltage
ORR	oxygen reduction reaction

membranes. For instance, He and his coworkers modified common graphene oxide by polydopamine deposition, and prepared the corresponding nanocomposite membranes with sulfonated poly(ether ether ketone) (SPEEK). The membranes showed improved thermal and mechanical stabilities as well as enhanced proton conductivity [23]. Ko's group also prepared poly(2,5-benzimidazole)-grafted graphene oxide by the surface grafting method and incorporated it into SPAES. Analogously, their membranes also exhibited significant improvement in mechanical stability and proton conductivity [24]. Overall, the above results clearly illustrate the advantages of incorporating functionalized-GO. However, in the above mentioned studies, some relatively complicated synthetic processes or even some noble metal catalysts were utilized, which would make the whole procedure expensive and complex [25,26].

Herein, a facile synthetic strategy has been presented for functionalizing sulfonated reduced graphene oxide nanofillers in order to easily incorporate them into pristine SPEEK polymers and improve their performance. Different from most of the reported work which main-chain-typed sulfonated polymer were always applied, our SPEEK was initially synthesized with the sulfonic acid groups located in the alkyl side chain. The advantage of this kind of chemical architecture has been proved as its superior oxidative stability towards the radicals, which is able to greatly enhance the fuel cell stability [12]. The properties of the SPEEK/SRGO composite membranes including thermal stability, mechanical strength, water uptake, dimensional change, proton conductivity, as well as single cell performance were investigated here in detail to obtain a systematic understanding of this new type of composite membrane.

2. Experimental

2.1. Materials

Methoxyhydroquinone (MHQ), 4,4'-difluorobenzophenone (DFBP), 4,4'-(Hexafluoroisopropylidene) diphenol A (6F-BPA), borontribromide (BBr_3) (1 M in CH_2Cl_2) were purchased from TCI and used as received. Toluene, *N,N*-dimethylacetamide (DMAc), dimethyl sulfoxide (DMSO) and dichloromethane were used after dehydration. 1,4-Butanesultone and sodium hydride were purchased from Energy-Chemical and used as received. Graphite powder, concentrated sulfuric acid (H_2SO_4 , 98%), Sodium nitrite (NaNO_2), potassium permanganate (KMnO_4), hydrochloric acid (HCl), sodium borohydride, 4-aminobenzenesulfonic acid, sodium nitrite, hydrogen peroxide aqueous solution (H_2O_2 , 30%) were obtained from Aladdin and used without further purification.

2.2. Preparation of GO and SRGO

GO was synthesized from commercially available graphite powder by the modified Hummers method [27]. Typically, graphite (1.0 g) powder and NaNO_3 (1.0 g) were mixed with concentrated H_2SO_4 (46.0 mL) in a 500 mL flask which placed in an ice bath. Under a constant stirring, KMnO_4 (4.0 g) was slowly added and the reaction

temperature was controlled of lower than 20 °C. After 1 h, the mixture was transferred to an oil bath and stirred for 1 h at 35 °C and then 60.0 mL of deionized water was carefully added. The solution temperature was raised around 90 °C and kept for another 30 min. Afterwards, deionized water (140 mL) and 30% H_2O_2 (20.0 mL) solution were added to the solution. After centrifuging, the GO sheet was washed with 30% HCl solution and deionized water for several times, and dried at 60 °C under vacuum.

The synthetic route of sulfonated reduced graphene oxide (SRGO) using aryl diazonium salt has been described as previously reported [28]. First, 75 mg of prepared GO was added in water (75.0 mL). After sonication for 2 h, brown dispersion of graphene oxide was formed. Then, 5 wt% sodium carbonate was added into the dispersion to adjust the pH value to 9–10. To prepare the reduced GO (RGO), 600 mg sodium borohydride in deionized water (15 mL) was added into the solution and the mixture was then heated to 80 °C and kept for 1 h. After centrifuging and rinsing with water for several times, the RGO was dispersed in deionized water (75 mL) under ultrasonic treatment. The aryl diazonium salt used for sulfonation was initially prepared from the reaction of 4-aminobenzenesulfonic acid (46 mg) and sodium nitrite (18 mg) in deionized water (10.0 mL) and concentrated HCl solution (1.2 mL) in an ice bath. Then the solution was added to the RGO suspension under N_2 . After 4 h reaction, the sulfonated reduced graphene oxide was centrifuged and washed with deionized water for several times and dried at 60 °C under vacuum.

2.3. Preparation of Sulfonated Poly(ether ether ketone) (SPEEK)

A typical procedure is as follows. MHQ (4.30 mmol, 0.603 g), 6F-BPA (1.20 mmol, 0.402 g), 4,4'-difluorobenzophenone (5.50 mmol, 1.200 g), DMAc (11.0 mL) and K_2CO_3 (8.25 mmol, 1.140 g) were added into a 100 mL three-neck flask, equipped with a stirrer and nitrogen inlet/outlet. After the addition of toluene (15 mL), the solution was heated to 140 °C and kept for 2 h under stirring to remove the water from the system. Then, the temperature was increased to 165 °C, and the reaction continued for another 4 h. After that, the viscous solution was diluted by another portion of DMAc and poured into deionized water for isolation. Finally, the fiber-like polymer (P1) was washed with water, methanol, and dried in a vacuum oven at 80 °C overnight (Yield: 89%). ^1H NMR (DMSO- d_6 , ppm): $\delta=3.71$ (s, 3H, $-\text{OCH}_3$), and 6.74–7.81 ppm (bs, Ar-H).

To an ice bath, P1 (1.0 g, 0.56 mmol) and CH_2Cl_2 (20 mL) were added into a 50 mL double-neck flask with a stirrer. Under a nitrogen atmosphere, $\text{BBr}_3/\text{CH}_2\text{Cl}_2$ (10 mL, 1 M) was slowly added dropwise to the solution and allowed to react overnight. After that, the orange precipitation was washed with deionized water until neutral. After filtration and drying, the solid was re-dissolved in DMSO (10 mL), and re-precipitated into isopropanol (IPA). P2 was then obtained by drying the product under vacuum at 80 °C overnight (Yield: 84%). ^1H NMR (DMSO- d_6 , ppm): $\delta=10.1$ (s, $-\text{OH}$), and 6.53–7.79 ppm (bm, Ar-H).

P2 (0.840 g, 1.87 mmol), NaH (0.090 g, 3.75 mmol), and DMSO (12 mL) were mixed in a double-neck flask. To this mixture, 1,4-butanediol (3.75 mmol, 0.383 mL) was added by a syringe, the

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