



Improvement in the mechanical properties, proton conductivity, and methanol resistance of highly branched sulfonated poly(arylene ether)/graphene oxide grafted with flexible alkylsulfonated side chains nanocomposite membranes



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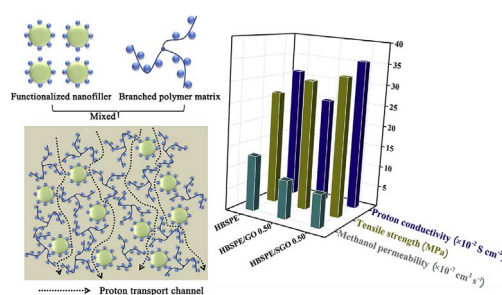
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HIGHLIGHTS

- A novel alkylsulfonated graphene oxide (SGO) was synthesized for the first time.
- Branched sulfonated polymer/SGO nanocomposite membranes were prepared.
- The membranes exhibited excellent mechanical properties and high proton conductivity.
- The membranes achieved high power density (82.36 mW cm^{-2}) in DMFC tests.

GRAPHICAL ABSTRACT



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ABSTRACT

Sulfonated polymer/graphene oxide (GO) nanocomposites exhibit excellent properties as proton exchange membranes. However, few investigations on highly branched sulfonated poly(arylene ether)s (HBSPE)/GO nanocomposites as proton exchange membranes are reported. In order to obtain HBSPE-based nanocomposite membranes with better dispersibility and properties, a novel GO containing flexible alkylsulfonated side chains (SGO) is designed and prepared for the first time in this work. The HBSPE/SGO nanocomposite membranes with excellent dispersibility are successfully prepared. The properties of these membranes, including the mechanical properties, ion-exchange capacity, water uptake, proton conductivity, and methanol resistance, are characterized. The nanocomposite membranes exhibit higher tensile strength (32.67 MPa), higher proton conductivity (0.39 S cm^{-1} at 80°C) and lower methanol permeability ($4.89 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$) than the pristine membrane. The nanocomposite membranes also achieve a higher maximum power density (82.36 mW cm^{-2}) than the pristine membrane (67.85 mW cm^{-2}) in single-cell direct methanol fuel cell (DMFC) tests, demonstrating their considerable potential for applications in DMFCs.

1. Introduction

Direct methanol fuel cells (DMFCs) have attracted substantial interest

as promising alternative energy conversion devices that directly convert chemical energy into electrical energy [1,2]. As an indispensable component of DMFCs, the proton exchange membrane (PEM) must meet

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several demanding requirements for practical applications, including efficient proton transport, good mechanical properties, and methanol permeability resistance. To date, only perfluorosulfonated polymers (commercial DuPont Nafion) have been extensively used as membrane materials for DMFCs. However, these materials suffer from several drawbacks, such as serious methanol crossover, low conductivity at high temperature, and high cost [3,4]. Therefore, to overcome these problems, numerous studies have been conducted, such as developing novel modified perfluorosulfonated ionomer derivatives and sulfonated aromatic hydrocarbon polymers as alternative commercial membranes [5,6].

Among sulfonated aromatic polymers, sulfonated poly(arylene ether)s are considered promising alternative materials. However, the majority of these materials have short lifetimes because of hydrolysis and oxidative degradation [7,8]. Although cross-linking is accepted as an effective method for prolonging the lifetimes of these materials, cross-linked membranes are not suitable for commercial applications because of their insolubility [9,10]. In recent years, a series of branched PEMs have been reported [7,11]. Our group has developed a series of highly branched sulfonated poly(arylene ether)s (HBSPE), most of which exhibit excellent solubility, promising oxidative stability and high proton conductivity [12–16]. However, these branched membranes exhibit poor mechanical properties and low methanol resistance because of their three-pronged branched structure and increased free volume. Blending highly branched PEMs with organic or inorganic fillers may be an effective method to balance the properties of a set of PEMs for satisfying the requirements for fuel cells; however, this strategy has seldom been reported.

On the other hand, graphene oxide (GO) has attracted considerable interest in the area of new and high-performance materials for use as an inorganic filler in composite PEMs [6,17,18]. However, pristine GO possesses few proton-conducting groups, which negatively influences the proton conductivity of the PEM when GO is used as a filler. Therefore, grafting GO with a sulfonated group ($-\text{SO}_3\text{H}$) using various methods has been studied, as this strategy not only improved the proton conductivity of the PEM but also enabled better dispersibility of the GO in the nanocomposite PEMs compared to pristine GO. Moreover, there are strong interfacial interactions between polymers and GO or its derivative, and these interactions can improve the mechanical properties to a certain degree. Introducing sulfonated GO into Nafion, sulfonated polybenzimidazole, poly(ether ether ketone), and polyimide has been reported to improve properties such as fuel permeability and their performance in the PEMs of fuel cells [19–22].

Utilizing the advantages of highly branched PEMs and sulfonated GO, in this work, we attempt to combine these materials to obtain nanocomposite membranes with improved properties. However, there was a limited improvement in the mechanical properties obtained by using sulfonated GO [19–22]. We designed GO with flexible alkylsulfonated chains (SGO), as these flexible alkyl side chains may considerably improve its mechanical properties. SGO improves not only the strong interfacial interactions between the sulfonated PEM and SGO by forming new hydrogen bridges but also the entanglement interactions between the flexible alkyl side chains in the SGO and polymer backbones. Here, the novel material SGO was designed and synthesized for the first time through an amidation reaction between GO and tris(hydroxymethyl)methyl aminomethane, followed by a nucleophilic substitution with 1,4-butylenesulfone. Then, GO and SGO were combined with HBSPE to obtain the nanocomposite membranes. The effect of introducing different SGO or GO nanofiller contents into the nanocomposite membranes on properties such as mechanical properties, methanol resistance and proton conductivity was investigated in detail.

2. Experiments

2.1. Materials

GO was purchased from Chengdu Organic Chemicals Co. Ltd.,

Chinese Academy of Sciences (purity: > 99 wt%, layers: < 3, thickness: 0.55–1.2 nm, and diameter: 0.5–3 μm). Tris(hydroxymethyl)methyl aminomethane, 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC), 4-dimethylaminopyridine (DMAP), N,N-dimethylformamide (DMF), 1,4-butylenesulfone, N,N-dimethylacetamide (DMAc), dimethyl sulfoxide (DMSO), and sodium hydroxide were purchased from Shanghai Energy Chemical. Anhydrous potassium carbonate was dried at 150 °C for 24 h under vacuum before use. All other solvents and reagents were of reagent grade and were used as received.

2.2. Synthesis of GO grafted with tris(hydroxymethyl)methyl aminomethane (NGO)

NGO was obtained from GO according to the synthetic procedure reported in the literature [23]. First, 0.5 g of GO and 50 mL of DMF were added to a 100 mL three-neck round-bottom flask under nitrogen and treated with ultrasound for 8 h. Then, 2.5 g of EDC, 0.5 g of DMAP, and 2.5 g of tris(hydroxymethyl)methyl aminomethane were added to the suspension, and the mixture was refluxed with magnetic stirring at 70 °C for 7 days. The resulting mixture was filtered through a 0.45 μm PTFE syringe filter, washed with deionized water and ethanol repeatedly and then dried at 60 °C overnight under vacuum.

2.3. Synthesis of NGO grafted with 1,4-butylenesulfone (SGO)

SGO was synthesized as described in a previous work [24]. Briefly, SGO was obtained by immersing NGO in 50 mL of dried DMSO under nitrogen, treating it with ultrasound for 8 h, and adding NaOH to the mixture at room temperature under magnetic stirring. Next, 5 mL of 1,4-butylenesulfone was added to the reaction mixture, which was heated at 80 °C for 7 days. The resulting mixture was filtered through a 0.45 μm PTFE syringe filter, washed with deionized water and ethanol repeatedly, and dried under vacuum at 60 °C overnight.

2.4. Preparation of the nanocomposite membranes

HBSPE was synthesized according to the literature [13], as shown in Scheme S1. First, 1.0 g of HBSPE was mixed with a certain amount of GO or SGO in 10 mL of DMAc under ultrasonic treatment and was stirred for 12 h at room temperature to form a homogeneous solution. The resulting solution was cast onto a glass plate and dried under vacuum at 60 °C for 12 h to obtain tough and smooth membranes. The obtained nanocomposite membranes were named HBSPE/GO X and HBSPE/SGO X, representing GO and SGO as the fillers, respectively, where X (X = 0.25, 0.50, 0.75, and 1.00) indicates the weight percent of the filler to HBSPE. The resulting composite membranes had an average thickness of 70 μm .

2.5. Characterization

Fourier transform infrared spectra (FT-IR) over the range from 4000 to 700 cm^{-1} were obtained on a Thermo Scientific Nicolet 6700 FT-IR spectrometer. Elemental analysis was performed on a vario EL elemental analyzer. Thermogravimetric analysis (TGA) of the composite membranes was conducted under a 40 mL min^{-1} flow of N_2 at a heating rate of 10 °C min^{-1} on a Q50 TGA instrument. The mechanical properties of the membranes were measured at room temperature using a testing machine (CMT4204, MTS Systems, China). Surface and cross-sectional images of the membranes were recorded using a scanning electron microscope (SEM, SU-70, Hitachi).

Detailed procedures for determining the water uptake, swelling ratio, and IEC were reported in a previous work [12,25].

The proton conductivity (σ) was calculated using a four-probe technique on an impedance analyzer (Zahner IM6ex, Germany) with an oscillating voltage of 20 mV over the frequency range from 10 Hz to 10⁶ Hz under 100% relative humidity (RH) conditions over the

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