



Contents lists available at ScienceDirect

Journal of Membrane Science

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

Enhanced physical stability and chemical durability of sulfonated poly(arylene ether sulfone) composite membranes having antioxidant grafted graphene oxide for polymer electrolyte membrane fuel cell applications

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ARTICLE INFO

Keywords:

Sulfonated poly(arylene ether sulfone)
Graphene oxide
Antioxidant grafted graphene oxide
Composite membranes
Fuel cell

ABSTRACT

Sulfonated poly(arylene ether sulfone) (SPAES) composite membranes were prepared using antioxidant grafted graphene oxide as a filler for polymer electrolyte membrane fuel cell (PEMFC) applications. SPAES was synthesized *via* condensation polymerization of 4,4'-dihydroxybiphenyl, 4,4'-dichlorodiphenylsulfone and 3,3'-disulfonate-4,4'-dichlorodiphenylsulfone. The antioxidant grafted graphene oxide was prepared by grafting hindered amine, 4-amino-2,2,6,6-tetramethylpiperidine, onto the surface of graphene oxide (GO). The SPAES composite membrane containing the antioxidant grafted GO showed improved physicochemical properties such as mechanical strength, chemical and thermal stabilities, and proton conductivity compared to pristine SPAES membrane. In particular, the antioxidant grafted GO was much more effective in enhancing the chemical stability of SPAES than GO without the antioxidant. For example after Fenton's test, the SPAES composite membrane with grafted antioxidant showed smaller decrease of both the weight and proton conductivity values than the pristine SPAES and SPAES composite membrane with GO. The enhanced chemical stability of SPAES composite membrane with antioxidant grafted GO can be explained by the combined antioxidant effect of both grafted antioxidant functional groups and GO.

1. Introduction

Polymer electrolyte membrane fuel cells (PEMFCs) have been studied intensively as an eco-friendly and efficient energy conversion system for automotive, stationary, and portable applications [1–3]. The polymer electrolyte membranes (PEMs) that can transfer proton from anode to cathode and block the reactant gas and electron in the fuel cell system are regarded as the key component of PEMFCs [4]. Perfluorosulfonated ionomers such as Nafion® have been widely used as commercial benchmark PEMs due to their high proton conductivity and outstanding chemical stability [5]. However, these membranes have a number of drawbacks including low glass transition temperature, poor thermo-mechanical property above 80 °C, severe fuel cross-

over, and high cost [6–9]. These drawbacks have prompted the development of alternative PEMs based on sulfonated hydrocarbon polymers including sulfonated poly(arylene ether sulfone) (SPAES) [10–12]. Although the sulfonated hydrocarbon membranes have exhibited considerable potential as alternative PEMs in terms of proton conductivity and mechanical properties, their chemical stability including oxidative stability should be improved for practical application in PEMFC [13]. The sulfonated hydrocarbon PEMs normally suffer from significant deterioration of their physical properties in a short period of time under operation because reactive oxygen species (ROs) such as oxygen radicals and hydrogen peroxide formed at both cathode and anode of the membrane electrode assembly (MEA) as redox reaction byproduct can cause polymer chain scission (i.e., unzip

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<http://dx.doi.org/10.1016/j.memsci.2016.10.038>

Received 9 August 2016; Received in revised form 20 October 2016; Accepted 24 October 2016

Available online xxxxx

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scission, midpoint scission, and loss of sulfonic acid groups) [14,15]. Therefore, several approaches have been taken to prepare the sulfonated hydrocarbon membranes with improved chemical stability by preparing polymer blends containing free radical stabilizers [16], layered structures with polystyrene [17], and composite membranes with redox active transition metal ions such as Ce(III) [18,19]. Although they showed improved chemical stability, these approaches have disadvantages such as the decrease in the proton conductivity, the complicated process for the membrane fabrication, and the leakage of metal ions from the membranes during the operation, respectively.

Recently, the antioxidant behavior of carbon nanomaterials, such as carbon nanotube, graphene, and graphene oxide (GO), in the polymer matrix and their effect on the physicochemical properties of the polymer composites have gained much attention in scientific researches and practical industry applications [20–22]. The remarkable improvement in the thermal and chemical stabilities of the polymer composites containing carbon nanomaterials has been known to be closely related to the inherent radical scavenging ability of the carbon nanomaterials because of their lattice defects, such as lattice vacancies, phenol, and other oxygen functional groups that can stabilize the radicals [21–23]. Our group recently proposed an effective approach to improve the mechanical and thermal properties of polyketone composites by adding a very small amount of GO derivatives containing antioxidant functional groups [24]. In this current study, we attempted to improve the physicochemical properties of the sulfonated hydrocarbon PEM without deteriorating the proton conductivity using antioxidant grafted GO as a filler of SPAES membrane. The detailed synthetic procedures for the preparation of the antioxidant grafted GO and SPAES composite membranes including their physicochemical properties such as water absorption behavior, mechanical properties, chemical stability, morphology, thermal stability, and proton conductivity are discussed in this manuscript.

2. Experimental

2.1. Materials

4,4'-Dihydroxybiphenyl (BP, 97.0%, Aldrich) and 4,4'-dichlorodiphenylsulfone (DCDPS, 98.0%, Aldrich) were recrystallized from methanol and toluene, respectively. 3,3'-Disulfonate-4,4'-dichlorodiphenylsulfone (SDCDPS) was synthesized from DCDPS as described by Ueda et al. [25]. The yield of SDCDPS after recrystallization from a mixture of *iso*-propylalcohol and deionized water (7/3, v/v) was 83%. Graphite powder and 4-amino-2,2,6,6-tetramethylpiperidine (hindered amine compound, HA, 97%) were purchased from BASF and TCI, respectively, and used as received. Potassium carbonate (K_2CO_3 , 99.0%, Aldrich) was dried under vacuum at 80 °C for 48 h, prior to use. Fuming sulfuric acid (65% SO_3 , Merck), sodium chloride (NaCl, 99.5%, Daejung), sodium hydroxide (NaOH, 98.0%, Daejung), phosphorous pentoxide (P_2O_5 , 99.9+%, Aldrich), sodium nitrate ($NaNO_3$, 99.0%, Daejung), and potassium permanganate ($KMnO_4$, 97.0%, Aldrich) were used as received. *N*-Methyl-2-pyrrolidone (NMP, 99.0%, Junsei) and *N,N*-dimethylformamide (DMF, 99.5%, Junsei) were stored over molecular sieves under nitrogen and toluene (99.5%, Junsei) was refluxed over calcium hydride and distilled. All other solvents and reagents were used as received from standard vendors.

2.2. Synthesis of sulfonated poly(arylene ether sulfone) (SPAES)

SPAES was synthesized *via* step-growth polymerization of BP with DCDPS and SDCDPS as described in our previous report [6]. The off-white product polymer was obtained in 93% of yield after being dried in a vacuum oven at 60 °C for 24 h. SPAES: 1H NMR (DMSO- d_6 , 400 MHz): δ 8.31 (br, 2H, ArH), 7.96 (br, 4H, ArH), 7.87 (br, 2H, ArH), 7.73 (br, 8H, ArH), 7.22 (br, 8H, ArH), 7.13 (br, 4H, ArH), 7.02 (br, 2H, ArH).

2.3. Preparation of graphene oxide (GO)

Graphene oxide (GO) was prepared by the modified Hummer's method using graphite as starting materials [26,27]. 1.0 g of graphite powder and 0.5 g of P_2O_5 were added into a reactor charged with 6 mL of concentrated sulfuric acid (98.0%). The mixture was heated at 80 °C and stirred for 6 h, and then 200 mL of deionized water was added into the mixture. The mixture was filtered and washed with deionized water several times. The obtained solid (pre-oxidized graphite) was dried in a vacuum oven at 60 °C for 24 h. The dried solid and 0.5 g of $NaNO_3$ were added into a reactor in an ice bath and 23 mL of concentrated sulfuric acid was added drop wisely into the reactor without stirring. 6.0g of $KMnO_4$ was slowly added into the mixture with stirring and temperature was kept at 0–5 °C. The mixture was heated to 35 °C and stirred for 18 h, and then 200 mL of deionized water and 10 mL of 30% H_2O_2 were added. The mixture was centrifuged (10000 rpm for 30 min) and supernatant was decanted. Then the mixture was filtered through 0.2 μm AAO membrane filter and the solid was rinsed with 250 mL of 10.0% HCl (aq) followed by excessive deionized water until the PH value was 7. The resulting product, GO, was dried in a vacuum oven at 80 °C for 24 h.

2.4. Preparation of hindered amine grafted graphene oxide (HA-GO)

0.1 g of GO was added to 30 mL of DMF by sonication for 30 min and 0.2 g of 4-amino-2,2,6,6-tetramethylpiperidine (HA) was added to the GO solution. The mixture solution was refluxed under nitrogen for 12 h with stirring and the reaction temperature kept at 80 °C. Then, the mixture was filtered through 0.2 μm PTFE membrane filter and rinsed with DMF several times. The product was further purified by dissolving in DMF, filtering, and rinsing with DMF. The resulting product, hindered amine grafted GO, was dried in a vacuum oven at 80 °C for 24 h and named as HA-GO.

2.5. Preparation of composite membranes

The SPAES composite membranes were fabricated by typical solution casting method. The mixture containing 0.5 mg of HA-GO and 3.3 g of DMF was sonicated for 40 min and stirred at 60 °C for 1 h to make a homogeneous dispersion of HA-GO in DMF. 0.5 g of SPAES was then mixed with the DMF solution and the mixture was cast onto a clean glass plate. Thickness of the mixture solution on the glass plate could be controlled using a doctor blade film applicator. The casted solution was heated at 80 °C for 12 h in a vacuum oven. After cooling to room temperature slowly, the membrane was immersed in deionized water and peeled off from the glass plate. The membrane in salt form (K^+) was transformed to its acid form (H^+) by soaking in 1 M H_2SO_4 aqueous solution at 30 °C for 24 h and washed with deionized water several times. The obtained membrane was dried in a vacuum oven at 80 °C for 24 h and named as SPAES/HA-GO-0.1, where 0.1 is the weight percent of HA-GO to SPAES. Other SPAES/HA-GO membranes with 0.5, 1.0, and 3.0 wt% of HA-GO to SPAES were also fabricated, and named as SPAES/HA-GO-0.5, SPAES/HA-GO-1.0, and SPAES/HA-GO-3.0, respectively. For comparison, pristine SPAES and SPAES composite membranes with GO were prepared by the same procedure used for the fabrication of the SPAES/HA-GO membranes except for using GO instead of HA-GO. When 0.1, 0.5, 1.0 and 3.0 wt% of GO were used, they were named as SPAES/GO-0.1, SPAES/GO-0.5, SPAES/GO-1.0, and SPAES/GO-3.0, respectively. The thicknesses of all the membranes are in the range of 15–20 μm . The photo images of prepared SPAES and composite membranes were provided in Fig. S1.

2.6. Characterization

The 1H NMR spectra were obtained on an Avance-400 (Bruker, Germany) with a proton frequency of 400 MHz. Deuterated dimethyl-

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