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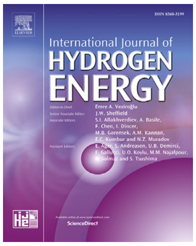

In-situ preparation of cross-linked hybrid anion exchange membrane of quaternized poly (styrene-*b*-isobutylene-*b*-styrene) covalently bonded with graphene

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ARTICLE INFO

Article history:
Received 22 September 2017
Received in revised form
2 November 2017
Accepted 7 November 2017
Available online xxx

Keywords:
Anion exchange membrane
Quaternized polymer grafted graphene
Covalent bond
Ion conductivity
Compatibility
Alkaline stability

ABSTRACT

Introducing graphene into polymer matrix is an effective way to enhance performances of anion exchange membrane (AEM). However, utilizing the advantages of graphene by physical approach is limited due to the weak interface interaction between graphene and polymer matrix. Herein, we report an effective strategy to covalently bond graphene with polymer matrix to improve the interface interaction and further to improve the properties of AEM. A series of cross-linked quaternized graphene-based hybrid AEM were fabricated by covalently bonding poly (vinylbenzyl chloride) grafted graphene (GN-*g*-PVBC) copolymer with chloromethyl functionalized poly (styrene-*b*-isobutylene-*b*-styrene) (SIBS) through the cross-linker (*N*,*N*,*N*′,*N*′-tetramethyl-1,6-hexanediamine) by *in-situ* synthetic approach. The interface interaction between graphene and QSIBS is greatly enhanced according to micromorphology characterization of the hybrid membrane. The cross-linked quaternized hybrid AEM containing 0.55 wt% of GN-*g*-PVBC exhibits obviously improved dynamical mechanical properties (storage modulus: 418 MPa), ion conductivity (1.81×10^2 S cm^{-1}), methanol barrier property (5.19×10^{-7} cm^2 s^{-1}), selectivity (3.49×10^4 S s cm^{-3}) at 60 °C and especially a comparably excellent chemical stability to that of Nafion 115 due to the enhanced interface interaction between graphene and the polymer matrix.

Introduction

Fuel cells are green energy devices which directly translate chemical energy into electric energy by electrochemical reaction of methanol, ethanol or hydrogen. Ethanol and hydrogen source can be generated from fermentation of biofuel [1] and oxidation of water [2], respectively. Direct methanol fuel cell (DMFC), one kind of fuel cell, has also been considered as an alternative power source to batteries for their instant refueling, high efficiency and low emission of pollutants [3,4]. Ion exchange membrane, such as proton

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https://doi.org/10.1016/j.ijhydene.2017.11.064

Please cite this article in press as: Mo Z-H, et al., *In-situ* preparation of cross-linked hybrid anion exchange membrane of quaternized poly (styrene-*b*-isobutylene-*b*-styrene) covalently bonded with graphene, International Journal of Hydrogen Energy (2017), https://doi.org/10.1016/j.ijhydene.2017.11.064

exchange membrane (PEM) or anion exchange membrane (AEM), is one of the most important components of DMFC. As a commercial PEM, Nafion, possesses a combination of high proton conductivity and excellent chemical stability. Nevertheless, its fatal drawback of high methanol permeability restricts its performance in DMFC [5]. To overcome the problem, some inorganic fillers [6,7], such as silicon dioxide [8], titanium dioxide [9], carbon nanotube [10,11] or graphene oxide (GO) [12–30] were introduced into polymer for manufacturing high performance PEMs. Among these inorganic fillers, the functionalized GO have been caught much attention due to its large surface area [31], outstanding physicochemical stability and electrochemical properties [32–36].

AEM has relatively lower fuel crossover rate than PEM, but suffers lower ion conductivity for the lower mobility of hydroxide ions compared to protons. In order to improve the ion conductivity as well as alkaline stability and to further decrease the fuel permeability of AEMs, the functionalized GO, including non-ionized GO [37,38] and ionized GO [39–43], were introduced into polymer matrixes. However, the improvement of these nanocomposite membranes was still limited due to the lack of covalent bond interaction between the functionalized GO and polymer matrix. Recently, the reduced GO (rGO) was introduced into quaternized polysulfone (QPSF) as both inorganic nanofiller and crosslinker to enhance the compatibility and interaction between GO and the matrixes in the resultant crosslinked QPSF-rGO nanocomposite AEM, but led to a decrease in anion conductivity with rGO content increasing [44]. The covalently functionalized GO and quaternized QPSF nanocomposite membranes were also fabricated for fuel cells, in which the ion conductivity was also seriously reduced [45].

In our recent reports, the cross-linked quaternized polystyrene-based thermoplastic elastomers with a small amount (0.5%) of octadecylamine-functionalized GO (GOA) composite AEM with an improved performance have be successfully *in-situ* prepared [37,38]. In this paper, in order to further enhance the interaction between GO and the matrixes and further to improve the comprehensive properties of poly (styrene-*b*-isobutylene-*b*-styrene) (SIBS)-based AEMs, poly (vinylbenzyl chloride) grafted ionized graphene (GN-*g*-PVBC) copolymer was introduced into polymer matrix with covalent bond *via* PVBC macromolecular bridge. A series of cross-linked QSIBS covalently bonded with GN-*g*-PVBC (QSIBS-*cb*-(GN-*g*-PVBC)) hybrid AEMs were prepared in the presence of *N*,*N*,*N*′,*N*′-tetramethyl-1,6-hexanediamine (TMHDA) by *in-situ* synthetic approach. The cross-linked QSIBS-*cb*-(GN-*g*-PVBC) hybrid AEM with high anion conductivity, excellent alkaline stability and thermal dynamic mechanical property could be achieved at very low content (*ca*. 0.14%) of graphene. The QSIBS/GOA nanocomposite membrane was also prepared under the same conditions for comparison.

Experimental section

Materials

Natural graphite flakes were supplied by Jinrilai graphite company (Qingdao, China) with an average diameter of 2 μm. Concentrated sulfuric acid (H_2SO_4, 98%), sodium nitrate ($NaNO_3$, AR), potassium permanganate ($KMnO_4$, AR), hydrogen peroxide (H_2O_2, 30% aqueous solution), concentrated hydrochloric acid (HCl, 36–38%), ethanol (AR), barium chloride ($BaCl_2$, AR), trichloromethane (TCM, AR) and sodium hydroxide (NaOH, AR) were purchased from Beijing Chemical Factory (China). 1-Amino-3-dimethylaminopropane (DMAPA, 99%) was purchased from Alfa Aesar (China). *N*,*N*,*N*′,*N*′-tetramethyl-1,6-hexanediamine (TMHDA, AR) was purchased from Fluka (U.S.A.). *N*,*N*-dimethyl-butylamine (DMBA, 98%) and 1,2-Dichlorobenzene (o-DCB, AR) were purchased from Aladdin(-China). Poly (vinylbenzyl chloride) (PVBC, 60/40 mixture of 3- and 4- isomers, $M_n = 55{,}000$ g mol^{-1}, PDI = 1.82) was purchased from Aldrich (China). All the above reagents were used as received. Poly (styrene-*b*-isobutylene-*b*-styrene) triblock copolymer (SIBS) ($M_n = 92{,}000$ g mol^{-1}, PDI = 1.8, styrene content = 43 wt%) and chloromethyl functionalized SIBS (CSIBS) (functionality = 35% based on polystyrene segments) were synthesized by living cationic polymerization and chloromethylization in our laboratory according to our previous works [37,38,46,47].

Chemical modification of GO with 1-amino-3-dimethylamino-propane

GO was prepared based on a modified Hummers method as previously reported [38,48]. A typical procedure was described as follows. 3 g of $NaNO_3$ was added to 69 mL of pre-cooled (0 °C) concentrated H_2SO_4. After the $NaNO_3$ was dissolved, 3 g of natural graphite was added to this $NaNO_3/H_2SO_4$ solution. 9 g of $KMnO_4$ was then added gradually with stirring and the temperature of the mixture was maintained below 5 °C. The mixture was then stirred at 35 °C for 30 min 138 mL of distilled water was slowly added to the mixture, simultaneously, increased temperature to 98 °C and then maintained at 98 °C for 15 min. The reaction was terminated by adding 420 mL of distilled water followed by 30 mL of 30% H_2O_2 solution. The solid product was separated by centrifugation, washed repeatedly with 5% HCl solution until sulphate could not be detected by titration with $BaCl_2$ solution. The resultant GO was dried at 65 °C.

200 mg of GO was dispersed in 100 mL deionized water *via* ultrasonication, and then 1 mL of DMAPA was added with mechanical stirring. The mixture was refluxed at 90 °C for 12 h, and then was filtrated with organic membrane having an average pore size of 0.22 μm. The filtrated powder was further rinsed in 20 mL of ethanol with the aid of ultrasonication for 10 min and then filtrated. The rinsing-filtration process was repeated for 4 times. The rinsed functionalized GO (GN) was further washed with o-DCB for 3 times to remove the absorbed DMAPA and ethanol. The octadecylamine-functionalized GO (GOA) could be also prepared under the same conditions.

Synthesis of PVBC grafted GN (GN-g-PVBC) graft copolymer

20 mL of GN in o-DCB suspension (1 mg mL^{-1}) was added into the solution of PVBC (2 g of polymer in 30 mL of o-DCB) with stirring and ultrasonication for 10 min. The mixture was stirred and refluxed at 100 °C for 6 h, filtrated by organic membrane with 0.22 μm average pore size, and then washed

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