Journal of Power Sources 269 (2014) 898–911

Contents lists available at ScienceDirect

Journal of Power Sources

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

Enhancement of proton conductivity of chitosan membrane enabled by sulfonated graphene oxide under both hydrated and anhydrous conditions

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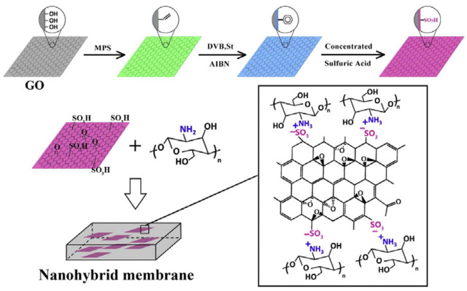
HIGHLIGHTS

- Nanohybrid membranes with polymer-nanosheet (sulfonated graphene oxide) layer were fabricated.
- Inorganic nanosheets (sulfonated graphene oxide) were uniformly dispersed in CS-based membrane.
- The membranes displayed excellent thermal and mechanical stabilities.
- The membranes achieved enhanced proton conductivities under hydrated and anhydrous conditions.
- The membranes afforded acceptable PEMFC performances under anhydrous condition.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 15 May 2014
Received in revised form
12 July 2014
Accepted 12 July 2014
Available online 19 July 2014

Keywords:
Sulfonated graphene oxide
Chitosan
Nanohybrid membrane
Acid–base pair
Proton conductivity
Fuel cell performance

ABSTRACT

In this study, sulfonated graphene oxide (SGO) nanosheets with controllable sulfonic acid group loading are synthesized via the facile distillation–precipitation polymerization, and then incorporated into chitosan (CS) matrix to prepare nanohybrid membranes. The microstructure and physicochemical properties of the resulting membranes are extensively investigated. Compared with CS control and GO-filled membranes, SGO-filled membranes attain enhanced thermal and mechanical stabilities due to the strong electrostatic attractions between $-SO_3H$ of SGO and $-NH_2$ of CS, which inhibit the mobility of CS chains. Additionally, the inhibited mobility reduces the area swellings of SGO-filled membranes, reinforcing their structural stabilities. The incorporation of SGO generates acid–base pairs along CS–SGO interface, which work as facile proton-hoping sites and thus construct continuous and wide proton transfer pathways, yielding enhanced proton conductivities under both hydrated and anhydrous conditions. Meanwhile, the conductivity can be elevated by increasing the sulfonic acid group loading and content of SGO. Particularly, incorporating 2.0% S4GO can afford the nanohybrid membrane a 122.5% increase in hydrated conductivity and a 90.7% increase in anhydrous conductivity when compared with CS control membrane. The superior conduction properties then offered a significant enhancement in H_2/O_2 cell performances to the nanohybrid membranes, guaranteeing them to be promising proton exchange membranes.

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http://dx.doi.org/10.1016/j.jpowsour.2014.07.075

1. Introduction

Fuel cells, which convert chemical energy directly into electrical energy, have been considered as promising energy conversion devices with great potential to alleviate the ever-growing demand for power [1,2]. Among various types of fuel cells, proton exchange membrane fuel cell (PEMFC) has received widespread interest due to the advantages of high energy density, easy fuel handling, environmental friendliness, and feasibility of mobile and transport applications [3–6]. As the indispensable component of PEMFC, proton exchange membrane (PEM) is required to efficiently transport protons, block fuels (i.e., methanol, hydrogen), and possess adequate structural stability for the practical application [7–9].

The commercial PEMs are the state-of-the-art perfluorosulfonic acid-based membranes (e.g., Nafion) in virtue of their high proton conductivity and stable physicochemical properties [3,10]. However, these membranes suffer from the drawbacks such as high cost, serious fuel crossover through the swollen ionic channels, and low proton conductivity under anhydrous condition, degrading their practical application in fuel cell [11]. Therefore, numerous studies have been conducted to develop alternative PEM with adequate properties and low cost [12–14]. Chitosan (CS, a deacetylated form of chitin), bearing amino and hydroxyl groups, is generally discarded as industrial waste around the world with low toxicity and cost [15,16]. Recently, CS has been explored to prepare PEM, considering its excellent film forming and fuel-barrier properties [17–19]. However, proton conduction ability of pristine CS (about 0.0117 S cm^{-1}) is low due to the absence of continuous transfer pathways and the weak conducting ability of base groups [20,21]. To overcome these intrinsic shortcomings, modification is indispensable for CS-based membranes [22–24]. One facile and efficient approach is to incorporate acid groups, such as $-SO_3H$, to CS membrane in virtue of the following advantages: (i) the acid groups can provide additional hoping sites for proton migration; (ii) the acid groups will link the base groups in CS to form acid–base pairs, which could transport protons via a water-free manner with low-energy barrier; (iii) the electrostatic attractions between acid–base pairs will confer enhanced thermal and mechanical stabilities by interfering with the CS chain mobility and packing. To sum up, the acid groups can be incorporated by blending acidic polymers, grafting acidic branched chains, or embedding acidic nanofillers [20–23]. Among these methods, embedding acidic nanofillers is considered as one of the most promising approaches, and the desired nanofillers should be compatible with CS matrix for homogeneous dispersion and meanwhile have high aspect ratio for long-range transfer pathway. Among spherical, tubular, and sheet nanofillers, nanosheet is the most ideal architecture, as its larger surface area and higher aspect ratio can donate more continuous pathways under the same filler content [20,25].

Recently, graphite oxide (GO) has been developed as an attractive nanofiller for PEM due to its unique graphitized plane structure, electric insulativity, and mechanical stability [26–28]. Besides, the oxygen-containing groups (carbonyl, hydroxyl, carboxyl, and epoxy groups) make GO easy to modify [29–32]. During the practical utilization, GO nanosheets have been generally sulfonated to acquire high proton conduction ability. Jiang et al. synthesized sulfonated graphene oxide (SGO) by grafting 3-mercaptopropyl trimethoxysilane to GO surface and then being oxidized by H_2O_2 [29]. Ravi et al. prepared SGO through sulfonation of GO using diazonium salt, which was prepared by adding $NaNO_2$ to the mixture of NaOH and sulfanilic acid, followed by dissolved in ice water and concentrated HCl [32]. For these methods, the sulfonic acid group loading amount is usually limited and/or the modification process is cumbersome and time-consuming.

Herein, SGO with high and controllable sulfonic acid group loading amount was synthesized via a facile distillation–precipitation polymerization for the first time. The SGO was employed to enhance the proton conductivity of CS membrane. The microstructure and physicochemical characteristics of the resulting membranes were investigated in detail. The proton conduction properties under both hydrated and anhydrous conditions were systematically evaluated. Moreover, the PEMFC performances of the membranes were explored. By doing so, it is demonstrated that the SGO gave significant enhancement in the proton conduction and cell performances to CS-based membrane, together with adequate thermal and mechanical properties.

2. Experimental

2.1. Materials and chemicals

CS with the deacetylation degree of 91% was supplied by Golden-Shell Biochemical Co. (Zhejiang, China) and used as received. Natural graphite powders (~45 μm) were purchased from Sinopharm Chemical Reagent. Styrene (St) and 3-(methacryloxy) propyltrimethoxysilan (MPS) were obtained from Aldrich and distilled under vacuum. Divinylbenzene (80% DVB isomers) was supplied as technical grade by Shengli Chemical Technical Faculty, Shandong, China, and was washed with 5% aqueous sodium hydroxide and water, then dried over anhydrous magnesium sulfate. 2,2′-Azobisisobutyronitrile (AIBN), acetonitrile, and sulfuric acid were purchased from Kewei Chemistry Co., Ltd (Tianjin, China). Deionized water was used throughout the experiment.

2.2. Synthesis of SGO

GO nanosheets were prepared by oxidizing natural graphite powders according to the improved method in literature [33]. SGO were synthesized through distillation–precipitation polymerization method [34]: GO (5.0 g) was dispersed into the mixture of ethanol (180 mL), water (20 mL), and aqueous solution of ammonium (15 mL) with vigorous stirring at 25 °C for 24 h. Then, MPS (2.0 mL) was added into the resultant mixture. After being stirred for another 24 h, the MPS-modified GO was purified by centrifugation and followed by drying in a vacuum oven. MPS-modified GO (0.30 g), St (0.50 mL), crosslinker DVB (0.50 mL), and AIBN (0.02 g) were dissolved by ultrasonic treatment in acetonitrile (80 mL) in a dried flask. The mixture was heated and kept boiling state until half acetonitrile was distilled out. Afterward, the modified GO was purified and dried for sulfonation. The resultant modified GO was sulfonated by concentrated sulfuric acid (94%) at 40 °C for 2 h or 4 h to obtain S2GO or S4GO, respectively.

2.3. Preparation of the membranes

CS (1.2 g) was dissolved in acetic acid aqueous solution (30 mL) and stirred for 2 h at room temperature. Simultaneously, a certain amount of GO or SGO was dispersed into water (30 mL) with ultrasonic treatment for 24 h. Afterward, these two solutions were mixed together and stirred vigorously for another 24 h. The resultant homogenous solution was cast onto a clear glass plate and dried at 30 °C for 72 h to obtain a nanohybrid membrane. The obtained membrane was then immersed in 1.0 M sulfuric acid solution for 24 h to completely crosslink the CS matrix, following by extensively rinsing with water to remove the residual acid. After being dried, the nanohybrid membranes were obtained and designated as CS/GO-X, CS/S2GO-X or CS/S4GO-X representing GO, S2GO or S4GO as the nanofillers, where X ($X = 0.5$, 1.0, 1.5, 2.0, and 2.5) represented the weight percentage of the nanofillers to CS. CS