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Enhanced proton conductivity of Nafion nanohybrid membrane incorporated with phosphonic acid functionalized graphene oxide at elevated temperature and low humidity

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ABSTRACT

Nafion-based nanohybrid membranes doped with phosphonic acid-functionalized graphene oxide (PGO) are fabricated for an ideal prospect in the application of proton exchange membrane fuel cells (PEMFCs). Graphene oxide (GO) is synthesized with a modified Hummers method and coated with polydopamine *via* the self-polymerization of dopamine, followed by grafting with alendronic acid through Micheal addition reaction. This method enables abundant phosphonic acid groups to be grafted on the GO nanosheets. The incorporation of such phosphonic acid-functionalized graphene (PGO) into Nafion matrix generates additional proton-conducting sites and improves the water adsorption and retention capacity of nanohybrid membranes. More importantly, the distribution of phosphonic acid groups in membrane is controlled by the unique structure of GO nanosheets, which benefits the formation of new pathways for proton hopping at low humidity conditions. Consequently, the nanohybrid membranes show improved proton conducting capacity, especially under high temperature or low relative humidity. The nanohybrid membrane with 2 wt% PGO exhibits a proton conductivity of 0.277 S cm^{-1} at 100 °C and 100% RH, and 0.0441 S cm^{-1} at 80 °C and 40% RH, which are 1.2 and 6.6 times higher than that of pristine Nafion membrane. Meanwhile, the Nafion/PGO-2.0 membrane displays the best fuel cell performance with the highest power density of 213.12 mW cm^{-2} and open circuit voltage of 0.939 V.

1. Introduction

Proton exchange membrane fuel cells (PEMFCs) are regarded as promising power sources due to their attractive features such as high power density, simple modular design, high efficiency and rapid start up [1]. As the core components of PEMFCs, proton exchange membranes (PEMs) have attracted extensive attention, especially on membrane materials. Nafion® series membranes commercialized by DuPont Co. are the representatives of the current state-of-art PEMs. Nafion® series membranes are a kind of perfluorosulfonic acid ionomer membrane composing of hydrophobic poly-(tetra-fluoroethylene)-like backbone and hydrophilic pendant side chains with terminated sulfonic groups [2,3]. The unique structure endows Nafion® membranes with not only good chemical stability but also desirable proton conductivity under 100% relative humidity (RH) [1]. Nevertheless, the proton conductivity of Nafion® membrane depends critically on the presence of water. At elevated temperature or low RH, a sharp decline of proton conductivity is observed for Nafion® membrane due to its dehydration [4,5]. Currently, the following two approaches are usually used to improve the membrane conductivity at low RH and elevated temperatures by incorporating hydrophilic inorganic additives into Nafion to improve its water retention capacity [6–10] or by introducing specific water-independent proton-conducting groups to conduct protons without the aid of water [11] such as phosphonic acid, imidazole, butyl methyl imidazolium triflate, etc. [12–15].

Graphene oxide (GO) is an important kind of derivative of graphene. GO is considered as an amphiphilic material with hydrophilic regions containing oxygenic groups (such as carboxylic, hydroxyl, and epoxy groups) and hydrophobic regions composed of sp^2 graphite [16,17]. GO is used as an attractive inorganic additive for hybrid membranes for its unique two-dimensional structure and high surface area [18,19]. It has been reported that the incorporation of GO can adjust proton conductivity by

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endowing the membrane with enhanced hydrophilic property and controlling the state of water confined in ionic channels in the polymer matrix [20–22]. Moreover, GO is a good proton conductor after modified with proton conductive groups in its interlayer space [21,23,24]. The modification of GO is mostly realized *via* chemical reactions between modifiers and oxygenic groups on GO [23]. So far, sulfonic acid-functionalized GO are intensively studied as fillers in hybrid membranes [19,25,26], whereas few efforts have been dedicated to other proton conducting groups owing to the limitation of possible reactions.

It is well known that dopamine can undergo self-polymerization to produce an adherent polydopamine which is coated on a wide range of substrates (*eg.* polymer surfaces, metal and metal oxide) at a weak alkaline pH [27,28]. The above process is accompanied by oxidizing catechol groups to form the quinone, which can react with various functional groups *via* Schiff base reaction or Michael addition and form covalently functional layers [29,30]. Inspired by the above feature, GO surface can be further modified making use of dopamine as a capping agent to obtain more kinds and larger amount of proton-conducting groups.

In this study, a novel kind of nanohybrid membrane composed of Nafion and phosphonic acid-functionalized graphene oxide is fabricated. To increase the loading amount of phosphonic acid groups, GO is firstly modified by dopamine, and then grafted with amino-terminated alendronic acid *via* Michael addition reaction. The resultant phosphonic acid functionalized GO (PGO) is incorporated into Nafion matrix with the aim of improving the proton conducting property of membrane, especially at evaluated temperature and low RH. The as-prepared PGO and membranes are characterized by TEM, SEM, XRD, TGA, XPS and FTIR. Meanwhile, the membrane property is evaluated in terms of proton conductivity, water uptake, swelling degree and single fuel cell performance.

2. Experimental

2.1. Materials

5% Nafion solution was produced by Dupont and purchased from Shanghai Hesen Scientific Co., Ltd. Tris-Cl ($>99.9\%$) and flake graphite were supplied by Sigma-Aldrich, as well as the dopamine ($>95\%$). Alendronic acid ($>98\%$) was purchased from TCI (Shanghai) Development Co., Ltd. Hydrogen peroxide (H_2O_2, 30%), potassium permanganate ($KMnO_4$), sodium nitrate ($NaNO_3$), and dimethylacetamide (DMAc, $>99.8\%$) were supplied by Aladdin-reagent. Hydrochloric acid (HCl, 36–38%) was purchased from Guangfu Fine Chemical Research Institute (Tianjin, China), as well as concentrated sulfuric acid (H_2SO_4, 95–98%).

2.2. Synthesis of phosphonic acid-functionalized graphene (PGO)

GO was successfully prepared *via* a typical Hummers method using graphite powder[31]. The detailed synthetic steps were as follows: 150 mL of concentrated sulfuric acid (H_2SO_4) was added into a round-bottomed flask while cooled in an ice-water bath. Then 2.5 g of sodium nitrate ($NaNO_3$) and 2 g of powdered graphite were added with vigorous stirring and 15 g of crystal $KMnO_4$ was added in batches. The mixture was stirred at 35 °C. After 30 min, a certain quantity of water was added slowly to dilute the mixture and stirred continuously for another 30 min. When adding more deionized water and 5% H_2O_2, the reaction mixture was filtered immediately. Subsequently, the oxidation product was circularly washed with 5% HCl and water until neutral pH. Lastly, collected by centrifugation, the obtained powdered GO was dried at 25 °C.

To prepare the PGO, 30 mg of dopamine and 30 mg of GO were dispersed in 150 mL of 0.01 mol L^{-1} Tris-Cl solution ($pH=8.5$) and treated by sonication in an ice-water bath for 10 min. The mixture was stirred continuously at 30 °C. After 24 h, the polydopamine modified GO (DGO) was separated by centrifugation. Subsequently, 49 mg of alendronic acid was added into DGO solution. The mixed solution was stirred at 30 °C for 24 h. Then the product was collected through centrifugation and washed until neutral pH. Finally, the prepared phosphonic acid-functionalized GO (PGO) was freeze-dried and grinded into powder.

2.3. Membrane preparation

Nafion-based nanohybrid membranes were prepared by the solution casting method. First of all, a certain amount of PGO was dispersed in 4 mL of DMAc under stirring and ultrasonication for 24 h. Then 0.2 g of Nafion which had been dried for 24 h under 60 °C was redissolved in the solution and stirred at 25 °C to make the solution mixed completely. The obtained casting solution was poured onto a clean flat glass plate in an oven at 80 °C for 12 h and heated up to 120 °C for 12 h to remove the solvent. Afterwards, peeled off from the glass, the nanohybrid membranes were successively immersed in boiling H_2O_2 (3 vol%), boiling deionized water, boiling H_2SO_4 (1 M) and deionized water respectively. The resultant nanohybrid membranes were named as Nafion/PGO-X, where X refers to weight percentage of PGO relative to Nafion. Nafion-based nanohybrid membranes doped with GO and DGO were prepared at the same time and named as Nafion/GO-X and Nafion/DGO-X respectively.

2.4. Characterizations

The morphology of the as-prepared GO, DGO and PGO was observed by transmission electron microscopy (TEM, JEOL), while their chemical composition was determined by fourier transform infrared spectra (FTIR, 4000–400 cm^{-1}). X-ray photoelectron spectroscopy (XPS) was utilized with a PHI-1600 spectrometer using Al Kα radiation for excitation to further confirm the chemical composition of PGO.

Field emission scanning electron microscopy (FESEM, Nanosem 430) was utilized to examine the microstructure of cross-sectional morphology in the as-prepared Nafion membranes. And to investigate the nanostructure of both pristine Nafion and nanohybrid membranes, X-ray diffraction scattering (XRD) was used with a scanning rate of 5° min^{-1} with an angular range of 5–50°. Tested under the heat-up rate of 10 °C min^{-1}, thermo gravimetric analysis (TGA) of prepared membranes was recorded by a Perkin-Elmer Pyris instrument to evaluate the thermal stability under N_2 atmosphere from 30 °C to 800 °C.

2.5. Water uptake and swelling degree

The membranes were cut into rectangular-shaped samples drying in an 80 °C oven. Each of these dried samples which had a weight of W_{dry} (g) and an area of A_{dry} (cm^2) was soaked in room-temperature water. 24 h later, the samples were wiped by tissue paper. Its weight (W_{wet}), as well as area (A_{wet}) were measured again at 25 °C. The water uptake as well as swelling degree of membranes can be calculated using the following equations:

$$\text{water uptake}\ (\%) = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100\% \tag{1}$$

$$\text{swelling degree}\ (\%) = \frac{A_{wet} - A_{dry}}{A_{dry}} \times 100\% \tag{2}$$