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Sulfonated graphene oxide/Nafion composite membranes for high-performance direct methanol fuel cells

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ABSTRACT

An easy and effective method for producing low methanol-crossover membranes is developed by dispersing sulfonated graphene oxide (SGO) into a Nafion matrix. A SGO/Nafion mixture with low SGO content exhibits unique viscosity behavior and allows for better SGO dispersion within the Nafion. After film casting, the composite membranes show lower methanol and water uptakes, a reduced swelling ratio, improved proton conductivity in low relative humidity, and extremely high methanol selectivity, which can be implemented in direct methanol fuel cells (DMFCs). The regular backbone of the composite membrane shows a higher storage modulus, increased α -relaxation (transition temperature), and improved tolerance to pressure during membrane electrode assembly (MEA). The small angle X-ray spectra indicate the shrinkage of the ionic clusters in the composite membranes, which thus reduce methanol crossover. The hybrid membranes applied to DMFCs demonstrate performances superior to that of the commercial Nafion 115 in 1 M and 5 M methanol solutions.

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1. Introduction

Direct methanol fuel cells (DMFCs) have attracted considerable attention from those interested in alternative fuels and merit further investigation. These alternative energy devices can be applied to power a wide range of portable and mobile electronics because DMFCs employ easily manageable liquid

methanol fuel with excellent energy storage densities. DMFCs provide uninterrupted, continuous power as long as the methanol fuel is supplied because they are energy conversion devices rather than energy storage devices. Moreover, DMFCs provide higher energy densities than Li-ion batteries. DMFCs consist of an anode, a cathode, and a proton-conducting electrolyte membrane, which collectively are called a

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membrane electrode assembly (MEA). The current DMFC research is based on polymer electrolyte membranes that provide appropriate fuel cell performance in terms of conductivity, chemical and mechanical stability, durability, and fuel crossover [1–3].

Among the polymer electrolyte membranes, DuPont's perfluorosulfonic acid polyelectrolyte, Nafion, is commonly used because of its excellent chemical stability and high proton conductivity. However, Nafion has a high methanol permeability, referred to as methanol crossover, attributed to the transport of methanol together with water molecules through its ion cluster channels. Moreover, the permeation of methanol from the anode to the cathode is a major challenge for the practical commercialization of DMFCs, due to the degraded cell performance of the mixed potential and catalyst poisoning problems [4,5]. To reduce methanol crossover, thicker membranes such as Nafion 117 (175 μm in thickness) are often preferred for DMFCs. However, this approach causes an increase in resistance and a decrease in power density [6].

To address the methanol crossover problems, many research groups have focused on the modification of Nafion membranes with a variety of nanofillers and polymers, such as SiO_2 , zeolites, zirconium, and polypyrrole [7–13]. The reported strategies for improving the performance of Nafion can be divided into two approaches: either incorporation of dispersed nanofillers [14] or formation of the nanocomposite membranes by in situ formation of inorganic fillers [15]. The composite membranes show high water uptake and low methanol crossover, compared to neat Nafion. However, the organic–inorganic membranes prepared by the above mentioned methods become brittle and poorly conductive, due to the high loading of the inorganic materials. Here, we report a novel strategy for producing low methanol-crossover polymer electrolytes using sulfonated graphene oxide (SGO) [16].

Currently, GO is highly attractive for many applications as a result of its outstanding thermal and mechanical properties [17,18]. Graphene oxide sheets can be thought as an amphiphilic material with hydrophilic regions that contain hydroxyl, carboxylic, and epoxy groups, and hydrophobic regions composed of sp^2 graphite. GO has been used as a surfactant to disperse C_{60} and acts as a hole transporting layer for all-carbon solar cells [19]. Moreover, GO/conducting polymer composites have shown superior capacitance and long cycle life in supercapacitors [20]. The potential advantages of using GO to improve the performance of DMFCs have not been fully realized. Choi group showed outstanding DMFC performance by introducing GO into Nafion solution [21]. However, the image of the GO/Nafion composite membrane revealed inhomogeneous distribution of the GO. Surfactant adsorbed GO has also been investigated on the sulfonated poly(ether ether ketone) (SPEEK) and shown improved proton conductivity and reduced methanol permeability [22]. One of the challenges is to avoid the aggregation of the GO in the polymer matrix. To address this matter, we determined the viscosity changes of the sulfonated GO (SGO)/Nafion solution. The optimal loading percentage of the SGO to Nafion was less than 1.0 wt%. Our investigation revealed a structural reorganization in the composite, showing clearly that the incorporation of the proper amount of SGO in Nafion enhanced proton

conductivity, reduced the water and methanol uptakes, decreased methanol permeability, and improved the mechanical properties.

2. Experimental section

2.1. Materials

Nafion 212 and 18% Nafion DE2020 dispersion were obtained from Ion Power Inc., New Castle, Delaware, U.S. PtRu/C and Pt/C were purchased from Johnson Matthey Inc., and used without further purification. Sulfuric acids (H_2SO_4 , Scharlau, 95–98%) was used without further purification.

2.2. Preparation of sulfonated graphene oxide (SGO)

Graphite oxide was prepared from flake graphite powder by a modified Hummers method [23]. In brief, graphite oxide was synthesized by an oxidation of graphite with KMnO_4 and NaNO_3 in concentrated sulfuric acid. The oxidation was carried out using 250 ml of concentrated sulfuric acid per 10 g of graphite as the dispersion medium. To the graphite dispersion, 5 g NaNO_3 were added and cooled the dispersion to 0 $^\circ\text{C}$ by using the ice water bath. Then 30 g of KMnO_4 were added slowly during 5 h. When the addition was finished, the resulting mixture was stirred at room temperature for another 5 h. The reaction was quenched by pouring ice cold water and adding 5% H_2O_2 to destroy unreacted KMnO_4 . The graphite oxide was collected and washed with $\text{HCl}_{(\text{aq})}$ and DI water. The brown graphite oxide was dried under the vacuum. To prepare graphene oxide (GO), 100 mg graphite oxide was dispersed in 100 ml of DI and ultrasonicated with power 100 W (misonix, sonicator 3000) for hours until the solution became clear. Then the GO solution was centrifuged with 4000 rpm for 10 min to remove any unexfoliated graphite oxide.

50 mg graphene oxide was added to 8 ml 0.06 M sulfanilic acid solution at 70 $^\circ\text{C}$. Under continuous stirring, 2 ml 6×10^{-3} M sodium nitrite solution was added dropwise and the mixture held at 70 $^\circ\text{C}$ for 12 h. After the reaction, the mixture was washed collected by centrifuge and washed with water for several times until the pH reached 7. The SGO particles were characterized by XPS (X-ray photoelectron spectroscopy, Thermo VGESCALab 250).

2.3. Manufacture of proton exchange membranes

Nafion ionomers were transferred to *N,N*-dimethylacetamide (DMAc, Aldrich) by distilling a mixed solution of the Nafion DE2020 solution (500 ml, 18% dispersion in aqueous alcohol) and DMAc (500 ml) under reduced pressure until the solution temperature reached 70 $^\circ\text{C}$, to remove water and solvent. SGO/Nafion solutions with different SGO loadings in DMAc were prepared by adding well-dispersed $\text{SGO}_{(\text{aq})}$ into the Nafion solution and mixing by mild ultrasonication for 6 h. Then, the SGO/Nafion solutions were degassed and dispersed with a planetary mixer before casting. The composite membranes were obtained from bar coating and drying at 50 $^\circ\text{C}$ for 24 h, and post annealing at 140 $^\circ\text{C}$ for 2 h. Nafion composite membranes of the desired sizes were placed into 0.5 M $\text{H}_2\text{SO}_{4(\text{aq})}$ at

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