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An effective methanol-blocking membrane modified with graphene oxide nanosheets for passive direct methanol fuel cells

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ABSTRACT

Methanol crossover through the proton exchange membrane from the anode to the cathode is a major obstacle for the development of the direct methanol fuel cells (DMFCs). This work focuses on the exploration of a novel methanol-blocking membrane prepared by layer-by-layer assembly of poly(diallyldimethylammonium chloride) (PDDA) and graphene oxide (GO) nanosheets onto the surface of Nafion® membrane. Results demonstrate that the bilayers are methanol-blocking, which formed a dense and uniform thin film structure on the surface of Nafion® film. The methanol permeability measurement across the composite membrane shows a decrease in methanol diffusion coefficient by 67% in comparison to the pristine membrane. The limiting current density on the cathode due to methanol crossover across the membrane with PDDA-GO bilayer structure is about 1/3 of that with pristine membrane, indicative of a reduction of methanol crossover by 63%. The use of Nafion®-PDDA-GO leads to the enhanced power density and improved energy efficiency of the passive DMFC. This study highlights the perspective of the application of GO as methanol-blocking thin film on the surface of Nafion® membrane in the DMFC.

1. Introduction

Passive direct methanol fuel cells (DMFCs) are potentially applicable as portable power sources due to their high energy density, low pollution, simple structural design and easy re-fueling [1–3]. However, at present, DMFCs face critical technical problems that hamper their practical applications including low power density, slow reaction kinetics of methanol oxidation, and methanol crossover from the anode through the proton exchange membrane (PEM) to the cathode [4], among which, methanol crossover is the most serious one.

Nafion® membrane as the state-of-the-art PEM is widely used in the DMFC due to its excellent mechanical, thermal and chemical stability, as well as its relatively high proton conductivity [5,6]. However, methanol readily migrates from the anode through the Nafion® membrane to the cathode [7]. Methanol crossover in the DMFCs not only results in a mixed potential effect at the cathode but also causes a significant loss in both cell's performance and fuel utilization. Thus, many efforts have been focused on the modification of existing Nafion® membrane by blending inorganic components, such as sulfonated organic silica [8], zirconium phosphate [9], zeolite [10], and montmorillonite [11], and various polymers, such as chitosan [4], poly(vinylidene fluoride) [12], and polybenzimidazole [13] to fabricate a composite membrane to block methanol permeation. For this purpose, the layer-by-layer (LbL) deposition technique has been successfully employed to suppress methanol crossover in the DMFCs, which is based on the alternated deposition of charged materials, such as purple membrane [14], phosphotungstic acid [15,16], and Au nanoparticles [17] on Nafion® membrane surface by means of electrostatic interaction, leading to the formation of thin films of controlled architecture and composition at the nanometer scale. LbL deposition of a thin film on a Nafion® membrane has been shown to suppress the methanol crossover, however, its proton conductivity decreases with the increase in the layer thickness. Thus, extensive research efforts have been placed on finding new materials that can suppress the methanol crossover without much loss in the proton conductivity of the PEM.

Graphene oxide (GO) nanosheets have abundant functional groups on the surfaces which can be used as anchoring sites [18,19]. Owing to the ionization of the carboxylic acid and phenolic hydroxyl groups on the surface, GO is highly negatively charged. The negative charge can help to stabilize the colloidal GO solution but also can lead to deposition of GO particles on positively charged surfaces. Whereas poly(diallyldimethylammonium chloride) (PDDA), a linear cationic polyelectrolyte, is commonly used as the agent to bind negatively charged Nafion® membrane and negatively charged materials to suppress methanol

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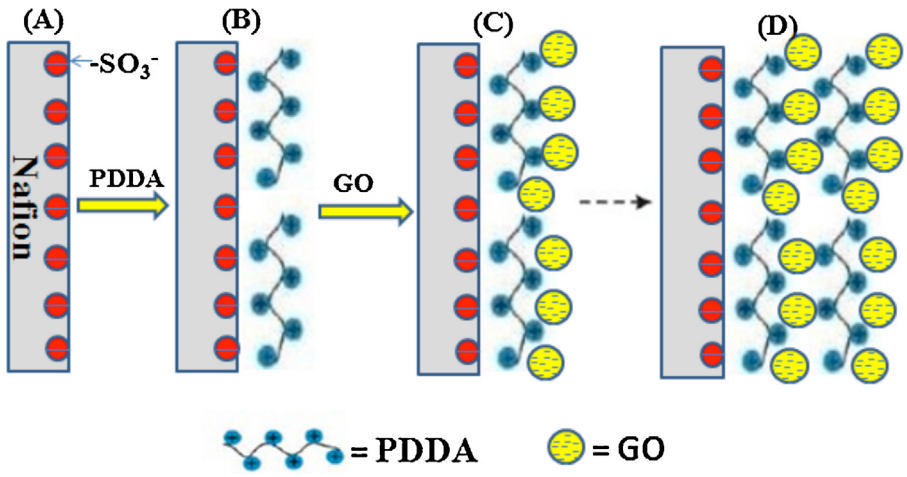

Fig. 1. Schematic diagram of the LbL self-assembly of PDDA/GO bilayers on Nafion® membranes.

crossover. The PDDA has been successfully employed to bind PSS (poly(sodium styrene sulfonate)), PAZO (poly(1-(4-(3-carboxy-4-hydroxyphenylazo)benzene sulfonamido)-1,2-ethanediyl, sodium salt)) [20], PWA (phosphotungstic acid, $H_3PW_{12}O_{40}$) [15] and PM (purple membrane) [14] onto Nafion® membranes to suppress methanol crossover. However, to the best of our knowledge, there is no report on the LbL assembly of PDDA-GO thin film onto the surface of Nafion® membrane.

In this present study, a novel approach for preparing an effective multilayer methanol-blocking film on Nafion® membrane by means of the LbL deposition of polycation PDDA and negatively charged GO is described. The methanol permeability of the composite membranes has been studied in detail for potential application of GO in the DMFCs.

2. Experimental

2.1. Materials and reagents

Oxidized graphite was synthesized from graphite powder (99.9995%, 325 mesh, purchased from Alfa Aesar) by the modified Hummers method. After removal of residual salts and acids, the resultant dispersion of graphite oxide was subjected to ultrasonic treatment to obtain the exfoliated GO. Poly(diallyldimethylammonium chloride) (PDDA) (average MW< 8500) was obtained from Nittobo Co. as an aqueous solution. PDDA was diluted to 20 mmol/L with Milli-Q water. Nafion® 212 membrane was purchased from Dupont.

2.2. LbL deposition

The preparation procedure of multilayer composite membranes is schematically shown in Fig. 1. Before the LBL deposition, Nafion® membranes were pre-treated as described in our previous report [21]. Subsequently, the membranes were immersed into a PDDA solution and a GO solution in succession, respectively. Repetition of these steps can form the multilayer films on the supports. The PDDA-GO thin film was described as a bilayer.

2.3. Physical and electrochemical characterization

The zeta-potential of the GO in the solution was determined using a Malvern Zetasizer 9000 series instrument. Lambda17 series UV-vis spectroscopy (Perkin-Elmer) was used to evaluate the possible incorporation of GO on the surface of Nafion® membrane. In addition, the surface of the composite membranes was examined by scanning electron microscopy (SEM) Hitachi S-4700 operated at an accelerating voltage of 20.0 kV.

The methanol permeability of the membranes was determined using a diffusion apparatus which contains two compartments A and B, separated by the membrane under study. The initial concentration of methanol in compartment A is 2 M, while the compartment B contains ultrapure water. The increase of methanol concentration in compartment B over time was detected by a gas chromatograph (GC 9890, Shanghai Linhua Instrument).

To evaluate the methanol crossover and the performance of the DMFCs, the membrane electrode assembly (MEA) was prepared by hot-pressing anode and cathode on both sides of a membrane at 130 °C and 6 MPa for 3 min. The anode and cathode catalysts used in this work were Pt-Ru black with an atomic ratio 1:1 (HiSpec 6000, Johnson Matthey) and Pt/C (HiSpec 9100, Johnson Matthey). The metal loading was ca. 4.0 ± 0.2 mg/cm^2 for both cathode and anode, and the ionomer loading was 20 wt.% for the cathode and 15 wt.% for the anode, respectively. Both the anode and cathode catalyst layer were coated on the micro porous layer (MPL), which was fabricated from coating Vulcan XC-72R carbon slurry with 20 wt.% PTFE as binder on the carbon paper. The loading of carbon was ca. 1 mg/cm^2 on the carbon paper (TGPH060, 0 wt.% PTFE, Toray) for the anode and ca. 2 mg/cm^2 on the carbon paper (TGPH060, 20 wt.% PTFE, Toray) for the cathode, respectively.

The performance of MEAs was evaluated in the single cell as our previous report [21]. The polarization curves of the passive DMFCs under air-breathing mode were obtained on an Arbin FCT testing system (Arbin Instrument Inc. USA) by using 2 M methanol solution at room temperature. The discharging curves at constant voltage of 0.35 V were obtained for the passive DMFCs fueled with 6.0 mL of 2 M methanol solution to compare the energy efficiency before and after the modification of GO on the surface of Nafion®. In order to explore the effect of PDDA-GO bilayers on the conductivity of membrane, electrochemical impedance spectra (EIS) were obtained at a frequency range between 100 kHz and 0.01 Hz by a Solartron SI 1287& SI 1255 B, and the amplitude of the sinusoidal voltage signal did not exceed 10 mV. The resulting impedance spectra were analyzed based on electrical circuit element model. The values of the model elements were determined by fitting the experimental data with Z-view software. Besides, the limiting oxidation current of methanol on the cathode due to crossover was determined to reflect the methanol-blocking properties of the membranes during cell test. Pure nitrogen was fed to the cathode as protection gas and 2 M methanol solution was injected into fuel reservoir. The linear sweep voltammetry was carried out when the open circuit voltage