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# Non-destructive modification on Nafion membrane *via* in-situ inserting of sheared graphene oxide for direct methanol fuel cell applications

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ABSTRACT

Based on a swelling-filling modification strategy, sheared graphene oxide (SGO) sheets are *in*-situ inserted into the Nafion membrane and act as bi-functional fillers to simultaneously improve the methanol-permeation resistivity and proton conductivity. Proton/methanol selectivity, as a key descriptor of overall performance of the proton exchange membrane, of the Nafion membrane is therefore 4-fold increased. At the same time, the mechanical, oxidative and thermal stabilities of the Nafion membrane are also improved by the SGO sheets due to the interaction between SGO and Nafion. As a result, the swelling-filling modified SGO -Nafion membrane is therefore considered as a promising electrolyte for direct methanol fuel cell (DMFC) application and the power of the Nafion based DMFC can be improved by ca. 50% during the polarization measurement.



## 1. Introduction

Direct methanol fuel cell (DMFC) has been considered as one of the most promising long-term power supply for portal electronic devices and electric motor-bicycles [1–3]. Compared to the lithium ion batteries currently dominating the market, energy density of DMFC is ca. one order of magnitude higher [4–9]. More importantly, the conventional refueling of DMFC makes the uninterrupted operation of the electronic devices possible [1–3,5,7]. However, dependence of DMFC performance on noble-metal catalyst and sever methanol permeation issue hinder the large-scale commercialization of DMFC technology [10,11]. In spite of the development of noble-metal-free electrochemical catalysts [12–14], plenty research efforts were made on methanol permeation reduction through the proton exchange membrane (PEM) [15–19]. Modification on the currently commercial PEM, Nafion membrane, was considered as the most straightforward and effective strategy [20–24]. Organic [25,26] and inorganic [27,28] fillers were composited with Nafion membrane to physically block the methanol molecules. Among these organic/inorganic fillers, graphene oxide (GO) [29–33] was found to be extraordinary effective due to the nano-sheet structure of GO is more effective on methanol blocking than the traditional nano-particle fillers. Unfortunately, huge size of the GO sheets would break the continuity of proton conductive channel (PCC) in the composited Nafion membrane [22,32–35] and hence ruin the proton conductivity of the Nafion membrane. At the same time, large-scale phase-separation between GO and Nafion would lead to decay on the mechanical strength of the Nafion membrane [33]. In order to overcome the shortage of the traditional composition methanol resistant strategy, a non-detective swelling-filling (SF) modification strategy on Nafion membrane was proposed in our previous work [36,37] by *in*-situ inserting the nano fillers into the Nafion framework during swelling of solvents. However, the GO sheets are difficult to enter the Nafion framework *via* the SF strategy due to

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their large sizes. Sheared Graphene Oxide (SGO), which keeps the nano-sheet structure of GO but has much smaller size [38–42], are therefore considered.

Here in this work, aqueous solution of SGO was facilely prepared from GO [41] and subsequently applied as precursor for SF modification on Nafion membrane. The SGO nano-sheets therefore insert into the Nafion framework together with the swelled water and immobilize in the membrane after the removal of water as illustrated in Scheme 1. During the DMFC operation, methanol molecules can be effectively blocked by SGO and the proton conductive efficient would not be faded since the proton conductive channel (PCC) in the Nafion membrane is kept intact. Instead, the hydrogen bonding interaction between the functional groups on SGO surface and the $-SO_3H$ groups on Nafion chain can participate in the PCC reconstruction. Both methanol-permeation resistivity and proton conductivity of the SGO-Nafion membrane are therefore remarkably improved. At the same time, mechanical stability of Nafion membrane is strongly reinforced and the SF treated SGO-Nafion membrane therefore exhibits 50% greater power output in practical DMFC application compared to the pristine Nafion membrane.

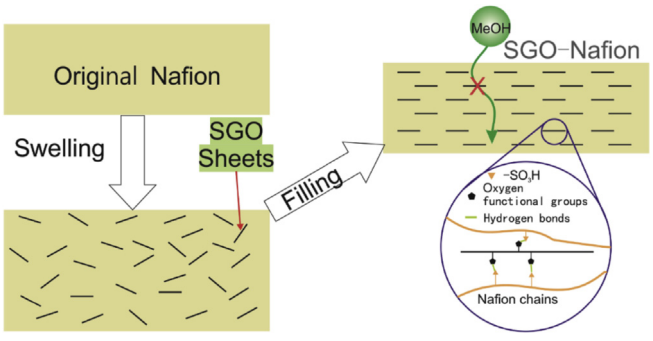
## 2. Experimental

### 2.1. SGO synthesis

GO sheets were prepared from natural graphite powder by a modified Hummers method [43] and graphene sheets were obtained by thermal deoxidization of GO sheets in a tube furnace at 300 °C for 2 h with a heating rate of 5 °C/min in a nitrogen atmosphere. According to the previously reported literature [41], graphene sheets (0.05 g) were subsequently oxidized in mixed acid (10 mL concentrated $H_2SO_4$ + 30 mL concentrated $HNO_3$) for 20 h under ultra-sonication. To remove the residual acid, the mixture was diluted to 300 mL with deionized water, filtered and washed repeatedly. 0.2 g purified oxidized graphene sheets were re-dispersed in 40 mL deionized water. The suspension was transferred to a PTFE lined autoclave (50 mL) for hydrothermal reaction at 200 °C for 10 h after the pH was tuned to 8 with $NH_4OH$ solution. The resulting black suspension was filtered through a 0.22 μm micro-porous membrane and a brown SGO (<220 nm) solution was separated with the scanning electron microscope (SEM) and transmission electron microscope (TEM) images shown in Fig. S1.

### 2.2. SGO-Nafion membrane preparation

Before the SF treating, three Nafion 212 membranes (size: 3 × 5 cm) was pretreated sequentially by 5% $H_2O_2$ solution, 1 M $H_2SO_4$ solution and deionized water at 100 °C for 1 h. The pretreated Nafion membranes were subsequently soaked in the prepared SGO solution for 3 day at 20 °C, 40 °C and 60 °C, respectively, to get the SGO-Nafion-20, SGO-Nafion-40 and SGO-Nafion-60 membranes. During the swelling process, SGO were *in*-situ inserted into the Nafion framework together with water. Afterward, surface of the SF treated Nafion membranes was washed by deionized water to remove loosely adsorbed SGO filler. 80 °C dry under vacuum for 12 h was carried out to remove the water solvent in the membrane to obtain the SGO-Nafion membranes. The SGO-Nafion membranes are standardly treated (sequentially treated in boiling 5% $H_2O_2$ solution and 1 M $H_2SO_4$ solution) before further measurements.




**Scheme 1.** Schematic illustration of the SF SGO inserting process of the methanol-permeation resistant SGO-Nafion membrane.

### 2.3. Characterizations

#### 2.3.1. Proton conductivity and electron conductivity

Cross-plane proton conductivity and electron conductivity of the prepared membranes were measured using an electrochemical workstation (VMP3, Bio-Logic). A piece of membrane (diameter: 1.5 cm) was assembled between two Pt meshes (diameter: 1.5 cm) for the measurement of proton/electron conductivity using a two-probe method at various temperatures in deionized water [44]. Impedance spectra were recorded by varying the frequency from 1 MHz to 0.1 Hz with AC amplitude of 5 mV at a bias potential of 0 V, and the proton resistance was determined by extrapolating the Nyquist curve at high frequencies to the real axis [45,46]. The measurements were conducted at temperature ranging from 30 to 80 °C. Proton conductivity $\sigma_p$ was calculated from the impedance data according to the following equation:

$$\sigma_p = \frac{d}{R_p A} \tag{1}$$

where $d$ (cm) is the thickness of the membrane, $A$ ($cm^2$) is the area of the Pt meshes. $R_p$ (Ω) is the resistance associated with the proton conductivity of the membrane recorded from the impedance data.

The I–V curves were recorded by using the same device at the voltage window of -1 V~ 1 V. The slopes of the linear portions in the recorded I–V curves were used to calculate the electron resistances of the membranes and electron conductivity $\sigma_e$ was calculated from the impedance data according to the following equation:

$$\sigma_e = \frac{d}{R_e A} \tag{2}$$

where $R_e$ (Ω) is the electron resistance calculated from the I–V curves.

#### 2.3.2. Methanol permeability

Methanol permeability through the membranes was measured at room temperature using an "H" type diaphragm diffusion dialysis cell, which was widely used for permeation measurement of methanol [47,48] or vanadium ions [49,50], with two glass cells separated by the membrane sample. 50 mL 1.0 M methanol solution was filled in the diffusion cell and 50 mL deionized water was filled in the receiving cell. To accelerate the methanol diffusion, magnetic stirring was performed in both glass cells and 5 μL sample was taken from the receiving cell every 1 h during the 6 h continuous diffusion. The methanol concentration of the samples was measured using a gas chromatographer (9790II Zhejiang Fuli Analytical Instruments Co., Ltd.) and the 1 h methanol permeability was obtained according to Eq. (3):