



Ion transport through thermally reduced and mechanically stretched graphene oxide membrane



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ABSTRACT

We investigated the ion transport behavior of graphene oxide (GO) and reduced graphene oxide (rGO) membranes along with thermal treatment and mechanical stretching. The GO membrane with about 400 nm thickness was fabricated onto a polytetrafluoroethylene membrane by vacuum filtration method and then thermally reduced at 120 and 230 °C, respectively. Various ions with different sizes were transported across the membranes via the electric field. As the results, we found that the ion transport linearly depends on the stretching up to 40% of the membrane in most ions. The thermal reduction of the membrane significantly affected the stabilization and modulation the rate of ion transport. Also, we discussed the ion transport mechanism of the stretchable rGO membranes based on the experimental data.

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1. Introduction

Graphene oxide (GO) has emerged as one of the most widely studied nanomaterials and is generally prepared by the exfoliation and oxidization of graphite materials. Recently, GO has attracted great attention due to its unique and outstanding physical properties, which lead to applications such as molecular sieving, desalination, humidity sensing, and insulation [1–9]. GO sheets have a layered structure similar to graphite, but with oxygen-containing functional groups attached to the surface, resulting in a 2D network of sp² and sp³ bonded atoms [10–12]. In particular, as a two-dimensional membrane, GO has shown high permeability and selectivity for specific gases and liquids [13–16]. Nair et al. reported that GO membranes of sub-μm thickness were impermeable to most gases, including helium, and liquids, but allowed water molecules to permeate unimpeded [15]. Kim and co-workers have reported polymer-supported thin GO membranes with a high selectivity for carbon dioxide from a gas mixture [17], while Li et al. presented ultrathin GO membranes (with a thickness approaching 1.8 nm) that exhibited highly selective hydrogen separation in a facile filtration process [18]. They attributed the high selectivity and

permeability for liquids and gases to the formation of nanopores at interlayer spaces and/or the interface of flakes formed between the GO sheets. In particular, they proposed that hydrophilicity and the graphite region of the GO layered structure were responsible for the fast and selective transport of water [14,15]. As for the selective transport of ions, Sun et al. reported the selective transport of sodium salt over copper salt or organic materials, and attributed this to nanocapillary phenomena and electrostatic chemical interactions between functional groups in GO and hydrated ions [19]. Joshi et al. also reported that a GO membrane of 1 μm thickness had an intrinsic sieving diameter of 9 Å, matching the GO interlayer distance, excluding the effective thickness of graphene [20]. Especially, Sun et al. investigated the electric field-assisted transport of ions across the membranes [21]. They found that the electric field strength affected the rate and direction of ion flow. Not only the experiments mentioned above but also some theoretical researchers using computation modeling, such as molecular simulation, which is also an important way to explain the mechanisms of ion transport. They reported that ion transport could be modulated by chemical treatment or deformation of geometry of the materials [9,22–24]. However, in this work, the role of nanopores established

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in the GO structure should be clarified to explain the exact mechanism of ion selectivity, as previous studies have attempted ion transport experiments using only naturally stacked GO membranes without any treatment and/or deformation of the nanopore size [1,6,19,25–27].

In this study, the GO membrane pore size was controlled by mechanical stretching and/or thermal reduction of the membranes, and the ion permeation and selectivity of the membrane were observed. We attempted to determine the mechanism of ion transport through the stretched GO membrane, along with thermal reduction. These trials control the interlayer spacing and pore size using the flake interfaces. Based on experimental data, we suggest a plausible mechanism for ion passage through the membrane and demonstrate the ability to control the membrane physical sieving diameter. Although the exact mechanism of ion transport through the GO membrane is yet to be fully clarified, it is well known that GO membranes have two pathways for ion transport [14,27]. In the first pathway, ion transport is conducted across the interlayer distance formed by direct contact with each basal plane in the stacked GO sheet structure. In the second pathway, ion transport occurs through pores constructed at the boundaries of the edges of GO flakes.

2. Experimental Section

2.1. Materials

A hydrophilic PTFE membrane (47 mm diameter, 0.2 μm average pore diameter) was obtained from Advantec-MFS (Tokyo, Japan). Sucrose, potassium ferricyanide, copper (II) sulfate, magnesium chloride, sodium chloride, and potassium chloride were purchased from Sigma-Aldrich (St. Louis, MO, USA). All chemicals were used without further purification. All solutions were prepared using 18.3 M Ω deionized (DI) water.

2.2. Preparation of graphene oxide membrane

Graphene oxide (GO) dispersed in water (5 g/L, GO flake size 0.5–5 μm) was purchased from Graphene Supermarket (Calverton, NY, USA). To prepare the GO membrane, aliquots of the GO solution (50 μL) were carefully added into DI water (200 mL). A sonic bath (Branson 2510, Danbury, CT) was used for 10 min to completely disperse the GO solution. The GO membranes were attached onto the PTFE membrane by vacuum filtration using the diluted GO solution (1.25 $\mu\text{g}/\text{mL}$). The thickness of the GO membrane was adjusted by changing the volume of the GO solution. Generally, after 200 mL of the GO solution was filtered, the GO membrane was obtained with \sim 400 nm thickness. In order to adjust the interlayer

distance of the GO membrane, thermal reduction (at 120 and 230 $^{\circ}\text{C}$) was performed in a vacuum oven for 1 h under a nitrogen atmosphere.

2.3. Characterization of GO and GO membrane

The surface morphology of the GO membrane was analyzed by scanning electron microscopy (SEM; Quanta 250 FEG, FEI, OR, USA) and atomic force microscopy (AFM; NX10, Park Systems, Santa Clara, CA, USA). The dispersion of the GO solution was analyzed by ultraviolet–visible spectrophotometry (UV–Vis; Agilent Cary 8454, Agilent Technologies, Santa Clara, CA, USA). The diluted GO solution was used as the UV–vis sample, and DI water was used as the reference sample. In addition, the interlayer distance, chemical composition, and surface properties of the GO membrane, were determined using X-ray diffraction (XRD; Cu $K\alpha$ radiation $\lambda = 0.154$ nm, Smartlab, Rigaku, Japan), X-ray photoelectron spectroscopy (XPS; PHI X-tool, Ulvac-Phi, Kanagawa, Japan), and Raman spectroscopy (Raman, LabRam ARAMIS IR2, HORIBA Jobin Yvon, France), respectively.

2.4. Ion transport measurement

In order to measure the ion transport by mechanical stretching of a GO membrane attached to PTFE (GO/PTFE membrane), the GO/PTFE membrane was cut into 2 \times 2 cm dimensions, and then attached to an adjustable ruler using adhesive tape. Next, custom-built 2 mL glass reservoirs were equipped on both sides of the GO/PTFE membrane using a steel holder, and ion transport was measured. To prevent electrolyte leakage due to GO/PTFE membrane stretching, both sides of the custom-built glass reservoirs were sealed with silicone rubber. To exclude ion transport due to concentration differences, the electrolyte concentration in both reservoirs was fixed at 1 M, and Ag/AgCl electrodes were set in each reservoir to apply the potential and measure the current. To prepare the Ag/AgCl electrodes, Ag wire (0.3 mm diameter) was treated with Clorox for 30 min. The ion transport of the stretchable GO membrane was measured by applying a constant voltage and monitoring the ionic current with a potentiostat (versaSTAT3, Princeton Applied Research, USA).

3. Results and discussion

To investigate the ion transport behavior, the measurement of ionic current during ion movement under an electric field was conducted in custom-built glass reservoirs, as shown in Fig. 1a (see Experimental Section). Ion transport through the GO membrane after mechanical stretching is illustrated in Fig. 1b. The ionic current

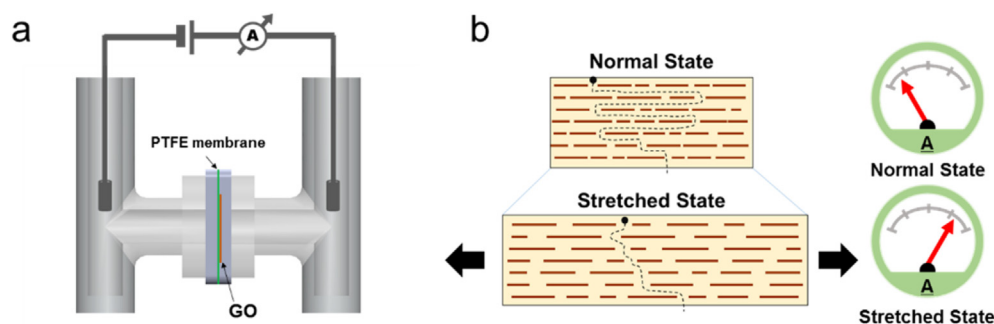


Fig. 1. (a) Schematic illustration of the ion transport measurement set up, (b) Phenomena of GO membrane at mechanical stretching. (A colour version of this figure can be viewed online.)

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