



Diamines cross-linked graphene oxide free-standing membranes for ion dialysis separation



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ABSTRACT

Design and tuning of the permeation channels of graphene oxide (GO) membranes are crucial for separation. Herein, GO membranes were covalently cross-linked by a series of diamines utilizing two cross-linking methods (carboxyl activation/amidation, catalytic amidation) for the first time. The effects of cross-linking parameters (temperature, diamines concentration, diamines molecular structure) on the elastic modulus, contact angle, swelling degree and ion dialysis separation of GO membranes were systematically studied. It was found that the carboxyl activation/amidation cross-linking method does not favor the fabrication of free-standing GO membranes. In the catalytic amidation cross-linking, with the increase in chain length of aliphatic diamines, the elastic modulus and the contact angle with water generally increase, while the swelling degree in water decreases. The cross-linked GO membranes display higher fluxes and K^+/Mg^{2+} separation factor than those of the pristine membrane. The *p*-phenylenediamine (PPD) cross-linked membranes shows excellent elastic modulus (10.5402 GPa) and high K^+/Mg^{2+} selectivity factor (7.15) along with low swelling degree due to its rigid structure, demonstrating its great potential in ion dialysis separation.

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1. Introduction

Graphene oxide (GO) is an important derivative of graphene, and can be prepared by strong oxidation of graphite [1]. The surface of GO contains large numbers of hydrophilic functional groups, such as carbonyl, carboxyl, epoxy, and hydroxyl. Therefore, GO can be easily exfoliated to produce aqueous colloidal suspensions which exhibit excellent liquid crystalline behavior [2], and can be used for fabricating free-stand laminates membranes with interlocked layered structure [3]. Although the single layered GO flake possesses high mechanical strength, the GO membranes exhibit brittleness and weak mechanical performance due to the weak interaction between GO flakes. Therefore, the integral mechanical strength of GO membranes is considered as the critical challenge for the practical separation.

Chemical cross-linking of GO membranes with metal ions [4], borate [5], isocyanates, dopamine [6], polyetheramine [7], polyallylamine [8], etc., has been reported to prepare robust membranes [9]. Nevertheless, the design and tuning of the permeation channels of GO membranes have been seldom addressed. In our previous work [10], dicarboxylic acids, diols and polyols were

employed to cross-link the basal plane or the edges of GO flakes, and the membrane performances were successfully adjusted. To cross-link the edges and basal plane of GO flakes simultaneously, in this paper, a series of diamines (including aliphatic and aromatic diamines) were used as cross-linkers, and two cross-linking methods (carboxyl activation/amidation, catalytic amidation) were explored for the first time. The effects of cross-linking parameters (temperature, diamines concentration, diamines molecular structure) on the elastic modulus, contact angle, swelling degree and ion dialysis separation of GO membranes were systematically studied. This work provides a deep understanding on tuning the properties of GO membranes by varying the structures of cross-linkers.

2. Experimentals

2.1. Materials

H_2SO_4 (> 98.0%), hydrochloric acid (37%), $KMnO_4$, $NaNO_3$, anhydrous ethanol, acetone, N, N-dimethylformamide (DMF), thionyl chloride, hydrogen peroxide (30%), ethylene diamine (EDA), propylene diamine (PDA), butane diamine (BDA), hexamethylene diamine (HMDA), *p*-phenylenediamine (PPD), *o*-phenylenediamine (OPD), $MgCl_2$, KCl, NaCl and $NiCl_2$, were analytical grade

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(Beijing Chemical Factory). Graphite was provided by Tianjin Bodi Chemical Co. Ltd. Chloroform and DMF were dehydrated with anhydrous MgSO_4 prior to usage.

2.2. Preparation of cross-linked GO membranes

GO was prepared using the modified Hummers' method [11]. The GO membranes were cross-linked by the following two methods. (1) Carboxyl activation/amidation: The carboxyl on GO was first activated by thionyl chloride and then reacted with diamines. In a typical procedure, the GO dispersion was freeze-dried in vacuum and then dispersed in anhydrous chloroform containing thionyl chloride and DMF (catalyst). The mixture was stirred and refluxed at 70°C for 24 h, evaporated to remove the solvent and excess thionyl chloride, washed with chloroform several times, and then dried. Then the as-obtained anhydrous GO-COCl powder was reacted with diamines in chloroform at 80°C , washed, and filtrated with a polypropylene (PP) microfiltration membrane ($0.45\ \mu\text{m}$, $\Phi\ 25\ \text{mm}$) under vacuum to obtain cross-linked GO membranes. (2) Catalytic amidation: A certain volume of diamine solution was added in GO colloidal suspension. After ultrasonic dispersion, the mixture was filtered with a PP microfiltration membrane. Then hydrochloric acid (0.5 mL) was added onto the membrane, and kept at fixed temperature for a certain time to catalyze the reaction. Lastly, the membrane was washed with deionized water and dried at room temperature.

2.3. Characterization

The FT-IR spectra of GO were measured with a Nicolet 380 FT-IR spectrometer (USA). The morphology was observed by cold-field scanned electron microscopy (SEM S-4800, Japan). The mechanical performance was tested by a universal mechanical testing machine (INSTRON-3366, USA) at a stretching speed of 100%/min. The swelling degree (SD) was measured by gravimetric method. The dried membrane with a weight of W_d was soaked in DI water or salt solution at room temperature for 3 h. Then the swollen membrane was taken out and the surface water was wiped off, and the weight (W_s) was measured. The swelling degree was calculated as $\text{SD} = (W_s - W_d) / W_d \times 100\%$.

Ion dialysis experiments were conducted using a U-tube dialyzer, which was divided by GO membrane ($\Phi\ 13.0\ \text{mm}$) into two compartments. The feed side contained the mixed salts aqueous solutions (KCl, NaCl, MgCl_2 and NiCl_2), and the permeate side contained DI water. Both sides were stirred magnetically to promote mass-transfer. The ion concentration in the permeate side was measured by ICP-AES (iCAP 6000 SERIES, Thermo Scientific). The permeation flux was obtained from the concentration change in the permeate compartment. The selectivity factor of the cations is expressed as

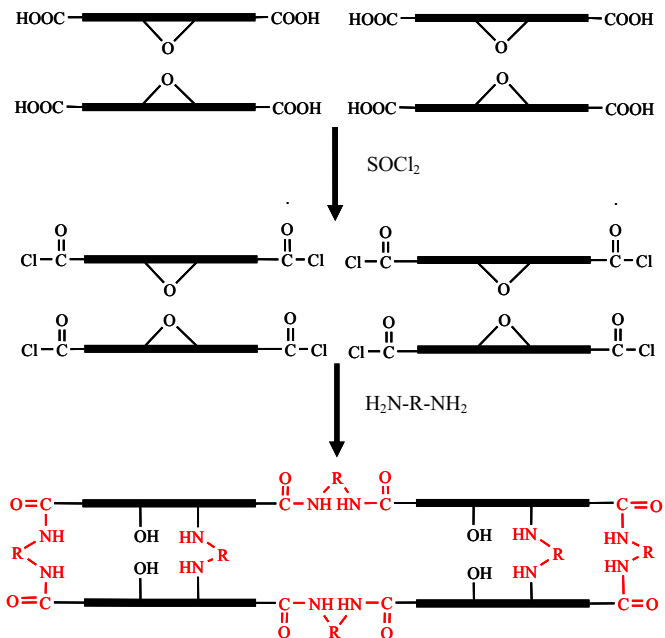
$$\alpha = \frac{C_i/C_j}{C_i/C_j} \quad (1)$$

where C_i and C_j are the concentrations of cations i and j in the permeate compartment, and C_i and C_j are the concentrations in the feed compartment.

3. Results and discussions

3.1. Cross-linking GO by carboxyl activation/amidation

To accelerate the reaction between carboxyl on GO and diamines, the freeze-dried GO powder reacts with thionyl chloride in anhydrous chloroform at the catalysis of DMF [12,13]. Then the as-



Scheme 1. Reaction mechanism of GO carboxyl activation/amidation cross-linking.

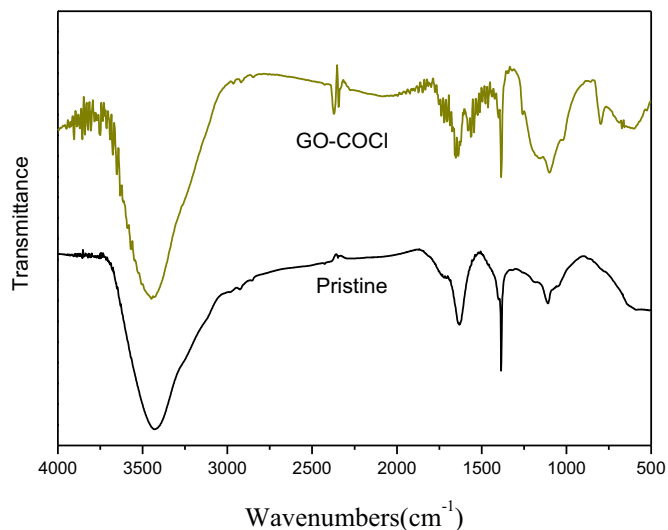


Fig. 1. FTIR spectra of GO and GO-COCl powder.

obtained GO-COCl on the edges of GO reacts with diamines to form amide. The -COCl groups may also react with hydroxyl on GO basal plane. Meanwhile, the amine group attacks the three membered epoxide ring on GO and forms C-OH and C-N bonds [14]. Condensation reaction between amine and hydroxyl can also occur [15]. Scheme 1 gives the carboxyl activation/amidation mechanism.

Fig. 1 gives the FTIR of the pristine and carboxyl activated GO. The pristine GO membrane shows the vibrations of O-H ($3430\ \text{cm}^{-1}$), C=C ($1630\ \text{cm}^{-1}$), carboxyl ($1720\ \text{cm}^{-1}$), C-O ($1380\ \text{cm}^{-1}$) and C-O-C (epoxy, $1130\ \text{cm}^{-1}$) [16,17]. After carboxyl activation, a new peak at $760\ \text{cm}^{-1}$ appears which is related to C-Cl vibration, confirming the formation of GO-COCl. Fig. 2 gives the SEM images of GO. The freeze-dried GO powder displays two dimensional flakes with some wrinkles (Fig. 2a). After carboxyl activation/amidation and filtration with PP membrane, the as-obtained GO membrane is fragile and not valuable for usage (Fig. 2b). The plausible reason is that the -COCl groups on the

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