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Improvement of water softening efficiency in capacitive deionization by ultra purification process of reduced graphene oxide

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ABSTRACT

Capacitive deionization (CDI) is the next generation of water desalination and softening technology by using relatively low capacitive current of electrochemical double layer. Among various carbon-based materials used for making electrode, reduced graphene oxide (rGO) has been intensively studied due to its excellent electrical conductivity and high surface area. Although Hummer method for making graphene oxide (GO) and rGO is a simple process, it remains some impurities in inherent GO and rGO which affect negatively to the CDI performance. In this work, we successfully prepared ultra purified GO and rGO by modifying Hummer method in order to remove entirely excess elements degrading the CDI performance. The electrosorption capacity of ultra purified rGO is considerably better than that of previous rGO, and maximum removal achieves 3.54 mg g^{-1} at applied voltage of 2.0 V. Thus, this result could be comparable to other researches in CDI process.

1. Introduction

The water treatment and softening technology applied for drinking and industrial purpose have been widely investigated and already commercialized. Contaminants (Ca^{2+}, Mg^{2+}, Fe^{3+} and Mn^{2+}, etc.) causing water hardness in tap, ground, and river water can be treated by existing methods such as chemical precipitation, ion exchange process, reverse osmosis, and electrodialysis [1]. However, these processes add treatment chemicals into water and require high energy expenditure and operation cost [2]. Thus, a cost-effective and low energy consuming electrochemical method (Capacitive deionization technology) gives reference for this statement.

Capacitive deionization (CDI) technology developed for removal of charged ionic species from salty water, such as salt ions, uses electric fields to temporally adsorb ionic species present in a solution close to a charged surface. Therefore, main requirements of CDI electrode are having large surface area and high conductivity. Reduced graphene oxide (rGO) has been attracted considerable attention over the past few years due to its superiorly electrical, thermal, and electrochemical properties arising from its unique structure [3]. With large theoretical surface area and excellent conductivity [4], rGO is the most promising carbon material applying for energy storage device as well as for CDI.

The rGO fabrication processes consist of two main steps: making graphene oxide (GO) from graphite and chemically reducing GO by hydrazine to form rGO. The Hummers method [5,6] is the most broadly used in GO fabrication. Although the Hummers method is simple, it remains some impurities in inherent rGO. The appearance and reaction of impurity elements in GO and rGO also cause the conductivity problem which negatively affects to the CDI performance. Li et al. studied electrosorption behavior of rGO in desalination and used only HCl solution for washing rGO [7]. The cyclic voltammetry (CV) result showed a pair of small peaks at −0.16 V and +0.05 V of a trace of species (Mn^{2+}, MnO_4^-) residual in rGO. With input conductivity of 50 μS cm^{-1} and the applied voltage of 2 V, maximum ion removal achieved at 1.85 mg g^{-1}. At another research of Wang et al., GO fabricated by Hummers method also shown a pair peaks of residual elements in CV test [8]. Electrosorption capacity with conductivity input of 95 μS cm^{-1} and applied voltage of 2 V was 1.5 mg g^{-1}. Clearly, it was poor result comparing to other materials such as activated carbon or carbon nanotube. The rGO purification to remove negatively effect of

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residuals on ion adsorption is necessary.

In this work, we successfully prepared dispersed rGO in aqueous solution through partly reducing GO and hence enhanced ion adsorption ability of in CDI system. GO was also extremely purified to remove excess elements degrading to CDI performance. Concentration and cleaning time of washing solutions (H_2O_2 and HCl) were increased significantly to totally remove residual elements. Especially, dialysis process was added to remove efficiently impurities. Since rGO was be purified, Faradic reactions was not occurred on any electrode. Ions were adsorbed on the electrode surface by forming an electric double layer instead of negatively affecting of electrochemical reactions. In addition, the ball milling method also was applied into electrode preparation to gain more homogeneous state of rGO, binder and solvent which can enhance ion adsorption in CDI process.

Finally, the different behaviour of rGO and conventional activated carbon in CDI performance was investigated when applied voltage is increase from 1.0 to 2 V. This difference from theoretical, rGO has small surface area comparing with conventional activated carbon materials, so it shows limited CDI performance. In order to overcome this problem, applied voltage can be increased. It is originated in that rGO's 2D structure with all surface area on the material outside, allows ions easily transporting and accessing. The results increase drastically electric double layer and CDI efficiency. Otherwise, conventional activated carbons have 3D structure, where the entire surface area (with much meso- and micro-pore) is within the particles. The sudden increase of applied voltage accelerates electrode resistance and reduces ion transfer by blocking the pores. Even at high applied voltage, electric double layers of meso- and especially micro-pores and ion pathway still are blocked; hence ion adsorption does not tend to increase linearly comparing to rGO.

2. Experimental

2.1. Making and purifying graphene oxide

Our suggestions were changing chemical dosage and adding important steps in GO purification process. Graphite and chemicals used to make GO were provided by Aldrich, USA. With traditional Hummer method, 3 g of graphite power was put into a concentrated sulfuric acid and phosphoric acid (9:1 in volume). Solution was placed into the cooling bath, added 18 g $KMnO_4$ and kept at 80 °C in 24 h. Then, after the dilution with DI water, 10 mL of 30% H_2O_2 and 20 mL of 10% HCl were added and stirred slowly to remove residual $KMnO_4$ and metal ions. Solution was then washed by sonication and centrifuge processes until pH = 7 and finally dried to remove humidity.

At purifying GO step, according to our suggestion, H_2O_2 and HCl solution were increased to 40 and 30 mL, respectively. They converted totally excess Mn^{4+}, Mn^{7+} and metal ions to precipitate state (Mn^{2+}, M^{x+}) before dissolved into solution. The mixture was washed by centrifuge and dialysis processes until pH of 7 and conductivity less than 20 μS cm^{-1}. In dialysis process, membrane can be changed to maintain removing effectively ions. After each step, residuals dissolved in water were gradually removed from rGO. Finally, the purified mixture was washed continuously and dried to remove humidity.

2.2. CDI electrode made by reduction method

Dried graphene oxide was added into DI water to re-disperse, the ratio of GO and DI water is 1 g and 200 mL. Then the solution was sonicated to obtain a homogeneous dispersion. 98% hydrazine solution is added into GO solution with ratio 0.1 mL of hydrazine: 100 mL GO solution and kept at 80 °C for 1 h. After reduced reaction, GO changed its color from dark brown to well dispersed black. Finally, solution was washed with DI water until pH = 7 and dried to remove totally humidity.

rGO and PVdF (Polyvinylidene fluoride) as binder (ratio 9:1) were used to fabricate the electrode. Each graphite sheet electrode was 100 mm wide × 100 mm long × 0.21 mm thick. To achieve adhesion between the carbon mixture and graphite layer, the raw mixture of powders (rGO and PVdF powder) and N-Methyl-2-pyrrolidone (NMP) solvent was sonicated and mixed by ball milling machine about 24 h then coated on graphite sheet by Dr. Blade method. The ball milling method was used instead of simple stirring process to grind rGO powder more smoothly and helped mixture of rGO, binder and solvent gaining better homogeneous state. The rotational speed was 300 rpm in 10 min and repetition was about 35 times. The mixture was checked sticky state after each 5 times of repetitions. Electrode was dried in oven at 60 °C in 12 h to remove entirely humidity and put into a vacuum furnace at 70 °C for 24 h to remove residual organic materials. Finally, the electrodes were assembled into a CDI device for testing (Fig. 1). Hardness water solution was pumped and flowed into CDI system, where the voltage had been applied. The dilute solution flowing from CDI cell was measured by conductivity meter each 30 s. Regeneration process was conducted simply by turning off power supply. Ions adsorbed on electrode surface were desorbed back into stream flow.

2.3. Experimental analysis

The artificial feed solution was prepared by dissolving 28.8 mg L^{-1} of $CaCl_2$, 22.0 mg L^{-1} of $MgSO_4 \cdot 7\,H_2O$, and 39.0 mg L^{-1} of $NaHCO_3$ in DI water. The feed solution was used for all the experiments in this research. Its total hardness and conductivity were 35 ppm (as $CaCO_3$) and about 110 μS cm^{-1}, respectively. Surface analysis of GO and rGO were studied by scanning electron microscope (SEM, S-4700, Hitachi, Japan) and energy dispersive X-ray spectrometry (EDX). In order to measure the hydrophilicity of each electrode depending on the feed solution and DI water, the sessile drop method of a standard goniometer with drop image was used. For a determination of the contact angle, the captured images were analyzed using drop image standard software. The Brunauer–Emmet–Teller (BET) surface area and pore size distribution (PSD) were examined using nitrogen as adsorbate at 77 K. Electrochemical performance of as-obtained electrodes also was evaluated by cyclic voltammetry (CV) at room temperature.

3. Results and discussion

3.1. GO, purified GO and rGO characterization

Fig. 2 shows the SEM and EDX image of the previous GO and purified GO surfaces. It can be seen that both surfaces are similar in many layers. Impurity compounds are not observed due to very small size and amount. However, EDX measurement demonstrates clearly the difference. At EDX of GO image, the weight of K and Mn elements are measured of 0.16 and 4.32% but with purified GO, these elements, especially Mn are disappeared because of many washing and dialysis steps. S element only remains with constant weight since it is not affected by reaction and washing treatments.

In order to examine the wettability of each electrode, contact angle is measured using DI water. As shown in Fig. 2, both purified rGO and previous rGO have high wettability in a short time, thus small droplet formed at the electrode surface. It is explained by partly reduction reaction can maintain several functional groups on rGO's surface and hence increase hydrophilic ability. The contact