Journal of Energy Chemistry 25 (2016) 354–360

Contents lists available at ScienceDirect

Journal of Energy Chemistry

journal homepage: www.elsevier.com/locate/jechem

http://www.journals.elsevier.com/journal-of-energy-chemistry/

Development of high quality Fe_3O_4/rGO composited electrode for low energy water treatment

Ngoc Tuan Trinh[a], Sangho Chung[a], Jae Kwang Lee[b], Jaeyoung Lee[a,b,c,*]

[a] Electrochemical Reaction and Technology Laboratory, School of Environmental Science and Technology, Gwangju Institute of Science and Technology (GIST), Gwangju 61005, South Korea
[b] Center for Chemical Energy Storage System, Research Institute for Solar and Sustainable Energies, GIST, Gwangju 61005, South Korea
[c] Ertl Center for Electrochemistry and Catalysis, GIST, Gwangju 61005, South Korea

ARTICLE INFO

Article history:
Received 26 January 2016
Revised 2 March 2016
Accepted 3 March 2016
Available online 10 March 2016

Keywords:
Electrochemical water treatment
Capacitive deionization
Water softening
Grapheme
Fe_3O_4/rGO nanocomposite
Fe_3O_4 nanoparticle

ABSTRACT

Electrochemical water treatment is an attractive technology for water desalination and softening due to its low energy consumption. Especially, capacitive Deionization (CDI) is promising as a future technology for water treatment. Graphene (rGO) has been intensively studied for CDI electrode because of its advantages such as excellent electrical conductivity and high specific surface area. However, its 2D dimensional structure with small specific capacitance, high resistance between layers and hydrophobicity degrades ion adsorption efficiency. In this work, we successfully prepared uniformly dispersed Fe_3O_4/rGO nanocomposite by simple thermal reactions and applied it as effective electrodes for CDI. Iron oxides play a role in uniting graphene sheets, and specific capacitance and wettability of electrodes are improved significantly; hence CDI performances are enhanced. The hardness removal of Fe_3O_4/rGO nanocomposite electrodes can reach 4.3 mg/g at applied voltage of 1.5 V, which is 3 times higher than that of separate rGO electrodes. Thus this material is a promising candidate for water softening technology.

1. Introduction

The water treatment and softening technology recently has been developed to apply for drinking and industrial purposes. Metallic cations (Ca^{2+}, Mg^{2+}, Fe^{3+} and Mn^{2+}, etc.) causing water hardness in tap, ground, and river water can be treated by popular methods such as chemical precipitation, ion exchange process, nanofilteration, reverse osmosis, and electro-membrane systems [1]. However, these processes still bear shortcomings such as the addition of chemicals into water, especially, high energy consumption and operation cost [2–4]. Therefore, it is necessary to find an effective method to overcome these problems [5,6].

Capacitive deionization (CDI) is a novel technology developed for the removal of charged ionic species from salty water, such as salt ions [7]. The basic concept of CDI is to force charged ions toward oppositely polarized electrodes by imposing a direct electric field to form a strong electrical double layer and hold the ions. Once the electric field disappears, the ions are instantly released back to the bulk solution. In a configuration of CDI cells, the feed stream flows between each pair of high capacity electrodes, i.e., porous carbon electrodes. By polarizing both electrodes, the charged ions are adsorbed on each electrode surface; positively charged ions are attracted on a surface of the negatively charged electrode and vice versa [8]. CDI is an alternative low-energy consumption desalination technology. Although numerous researches have been reported applying CDI technique to desalination [9], heavy metal [4] and biomass removal [10], few studies have focused on applying CDI to water softening. Therefore, the investigation of water softening performance using CDI process is needed.

As typical porous electrode materials of CDI cell, carbon based materials including activated carbon [11,12], carbon aerogels [13], and carbon nanotubes [14,15] are always attractive with researchers to be employed as electrosorptive electrodes due to their good conductivity, high surface area, and suitable pore size distribution. Graphene (rGO), a two-dimensional sp^2 bonded carbon material, has attracted considerable attention over the past few years due to its amazing electrical, thermal, and electrochemical properties arising from its unique structure [4]. With large theoretical surface area and excellent conductivity [16,17], graphene is a remarkable candidate for application in energy storage device as well as CDI.

Even though graphene exhibits good electrochemical performance in terms of energy storage, its hydrophobic property and small specific capacitance could lower the wettability and

* Corresponding author at: Electrochemical Reaction and Technology Laboratory, School of Environmental Science and Technology, Gwangju Institute of Science and Technology (GIST), Gwangju 61005, South Korea. Tel: +82 62 715 2440; Fax: +82 62 715 2434.
E-mail address: jaeyoung@gist.ac.kr (J. Lee).

http://dx.doi.org/10.1016/j.jechem.2016.03.008
2095-4956/

electrolyte accessibility, resulting in the decrease in ion transfer rates in CDI process. So far, to improve and develop the potential electrochemical properties of graphene, several methods were proposed such as: mixing graphene with other materials [18,19], modifying graphene fabrication [20,21], and compositing with transition metal oxides (MnO_2 [22], NiO [23], SnO_2 [24], Co_3O_4 [25]) for batteries, super-capacitors, and fuel cell. Yet limited studies have mentioned the idea of applying them to CDI. Recently, only MnO_2, TiO_2, Fe_3O_4, and SnO_2/rGO compositions were studied as electrodes for desalination purpose. Ahmed G. El-Deen prepared nanostructured-MnO_2@graphene sandwich [26] with controlled morphology. The prepared electrode showed the CDI performance improvement of 26% comparing to pristine graphene electrode. In his other research [27], TiO_2 nanoparticles were loaded into graphene by hydrothermal treatment method. This unique morphological structure exhibited impressive features, high wettability, prevented the release of TiO_2 and hence improved ion adsorption. Gu et al. [28] fabricated mesoporous graphene electrode using etching method of Fe_3O_4 nanoparticle on rGO in acidic media. The prepared rGO/Fe_3O_4 electrode showed electrosorptive capacity which is 1.5 times higher than that of pristine rGO.

In this work, we prepare uniformly-dispersed Fe_3O_4/rGO nanocomposites by simple thermal reactions. The main focuses are to improve hydrophilicity and specific capacitance of electrodes. It is explained that the Fe_3O_4 composited on rGO forms anchors to increase interfacial contact surface and decrease ion mass transfer resistance in electrodes and between electrodes and electrolytes. This introduced material with cost effectiveness is expected to significantly enhance ion adsorption ability of CDI system.

2. Experimental

2.1. Materials

All chemicals including commercial graphite powder, potassium permanganate, phosphoric acid (85%), sulphuric acid (95%–97%), hydrogen peroxide (30%), hydrochloric acid (37%) and iron (III) chloride were purchased from Sigma-Aldrich and used without any further purification.

2.2. Graphite oxide preparation

Graphite oxide was fabricated by modified traditional Hummer method. Three grams of graphite powder were put into a concentrated sulfuric acid and phosphoric acid with ratio 9:1 in volume. This solution was placed into a cooling bath, added with 18 g $KMnO_4$ and kept at 80 °C for 24 h. Then, after being diluted with DI water, 40 mL of 30% H_2O_2 and 30 mL of 10% HCl were added and the solution was stirred slowly to remove the residual $KMnO_4$ and metal ions. The mixture was washed by centrifuge and dialysis processes until a pH of 7 and conductivity of less than 20 μS/cm were reached. Finally, the solution was washed again and dried to remove humidity.

2.3. Graphene preparation

Dried graphene oxide was added into DI water to re-disperse, the ratio of GO and DI water is 1 g per 200 mL. Then the solution was sonicated to obtain a homogeneous dispersion. 98% hydrazine solution was added into GO solution (the ratio being 0.1 mL hydrazine per 100 mL GO) and kept at 80 °C for 1 h. During the reduction process, the color of dispersed GO solution turned from dark brown to black. Subsequently, this solution was washed with DI water until a pH of 7 was reached and dried to totally remove humidity.

2.4. Fe_3O_4/rGO nanocomposite preparation

In a typical procedure, Fe_3O_4/rGO composites were prepared by a simple thermal hydrolysis process. The amount of $FeCl_3$•$6H_2O$ powder was varied (0.125, 0.25, and 0.5 g) in order to control the ratio of Fe_3O_4 and rGO. The amounts of rGO and KOH were fixed at 1 and 3.75 g, respectively. $FeCl_3$•$6H_2O$ and rGO powder were mixed and sonicated in alkaline condition (KOH) until a homogeneous solution was obtained. $Fe(OH)_3$ will be formed by the following reaction:

$$rGO + 3KOH + FeCl_3 = rGO + Fe(OH)_3 + 3KCl \quad (1)$$

The products of this reaction were heated at 850 °C for 1 h in nitrogen condition. At high temperature and lack of oxygen, a small amount of rGO was partly reduced and CO was formed. Then CO and $Fe(OH)_3$ reacted to form Fe_3O_4, CO_2, and H_2O vapor.

$$6Fe(OH)_3 + CO = 2Fe_3O_4 + CO_2 + 9H_2O \quad (2)$$

Formed Fe_3O_4/rGO samples were washed by 10% HCl and DI water until pH =7, and then dried in an oven to remove humidity. The samples notated as FG-0.125, FG-0.25, and FG-0.5, in accordance with the amounts of $FeCl_3$•H_2O mentioned above, were compared to separate rGO to investigate water softening efficiency.

2.5. Electrode preparation for CDI test

Fe_3O_4/rGO nanocomposites 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 secured adhesion between the carbon mixture and graphite layer, the raw mixture of powders (Fe_3O_4/rGO and PVDF powder) and N-Methyl-2-pyrrolidone (NMP) solvent was sonicated and mixed by a ball milling machine for about 24 h then coated on graphite sheet by doctor blade equipment. The ball milling method was used instead of simple stirring process to finely grind Fe_3O_4/rGO powder more smoothly and helped the mixture, binder as well as solvent gain more homogeneous slurry. The rotational speed was set at 300 rpm in 10 min and repetition was approximately 35 times. The mixture was checked for sticky state every 5 times of repetition. The electrodes were dried in oven at 60 °C for 12 h to remove entirely humidity, and then put into a vacuum furnace at 70 °C for 24 h to evaporate residual organic materials. Finally, the electrodes were assembled into a CDI device for testing. Hardness water solution was pumped into the CDI system, where the voltage had been applied. The dilute solution flowing from CDI cell was measured every 10 s by a conductivity meter. Regeneration process was conducted simply by turning off the power supply. Ions adsorbed on the electrode surface were desorbed back into the stream flow.

2.6. Experimental analysis

The artificial feed solution was prepared by dissolving 28.8 mg/L of $CaCl_2$, 22.0 mg/L of $MgSO_4$•$7H_2O$, and 39.0 mg/L of $NaHCO_3$ in DI water. The feed solution was used for all the experiments in this research and its total hardness and conductivity were 35 ppm (as $CaCO_3$) and about 110 μS/cm, respectively. Surface analysis of rGO and Fe_3O_4/rGO were studied by scanning electron microscope (SEM), transmission electron microscopy (TEM), energy dispersive X-ray spectrometry (EDX) and X-ray diffraction (XRD). 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