Electrochimica Acta 263 (2018) 40–46

Contents lists available at ScienceDirect

Electrochimica Acta

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

Water-enhanced performance in capacitive deionization for desalination based on graphene gel as electrode material

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ARTICLE INFO

Article history:
Received 20 December 2017
Received in revised form
5 January 2018
Accepted 7 January 2018
Available online 8 January 2018

Keywords:
Graphene
Capacitive deionization
Water
Desalination
Electrode

ABSTRACT

Graphene gel is an excellent material for capacitive deionization (CDI) because of its high specific surface area, three-dimensional structure and binder-free preparation. Current studies have been primarily focused on the design and synthesis of new graphene gel materials. However, there have been no studies comparing the desalination performance of graphene hydrogel (GH) and graphene aerogel (GA), the two primary CDI materials. In this work, GH and GA were synthesized and applied in CDI. A range of characterization methods were used to analyze the microstructure of the GA and GH electrode materials. The results showed that the electrosorption capacities of GH and GA were 49.34 and 45.88 mg g^{-1}, respectively, in sodium chloride solution with an initial concentration of 500 mg L^{-1} at 2.0 V. A water-enhanced function mechanism was proposed to explain the differences in desalination performance.

1. Introduction

With the growing global population and worsening quality of fresh water resources, the scarcity of drinking water is becoming an increasingly serious issue. To solve the problem, sea water and brackish water have been explored as alternative sources of potable water using desalination technology [1,2]. Common desalination technologies based on membrane separation or thermal evaporation (e.g., thermal vapor compression (TVC), reverse osmosis (RO), multistage flash distillation (MSF), electrodialysis) have drawbacks such as high energy consumption, high maintenance costs, and regeneration difficulties [3,4]. Capacitive deionization (CDI) is a novel technology for the removal of ions from water. CDI uses electrostatic force; therefore, it only requires a low direct voltage (<2 V). Additionally, CDI functions by removing ions, a minor component, instead of water, the major component. Compared to the traditional methods, CDI is a power-saving, easily regenerated and low-cost technology [5–7].

The electrode, the heart of CDI, is generally fabricated with carbon materials, such as activated carbon (AC) [8,9], activated carbon nanofibers (ACF) [10,11], carbon aerogel (CA) [12,13], carbon nanotubes (CNTs) [14,15], and graphene [16,17]. Traditional carbon materials show a range of problems, such as low capacitance and low electrical conductivity. Graphene has a two-dimensional planar structure composed of conjugated carbon atoms, which confers an ultrahigh specific surface area (2600 $m^2 g^{-1}$) with superior electrical conductivity (7200 m s^{-1} at ambient temperature) and electrical double-layer capacitance (21 $\mu F\ cm^{-2}$) in theory [18–20]. However, the desalination performance of graphene fabricated by the reduction method is undesirable in CDI, due to the restacking of graphene sheets caused by Van der Waals and π-π interactions [21–23]. Hence, it is crucial to prevent the aggregation of the graphene sheets during reduction. One approach is to create a three-dimensional graphene structure. For example, Xu et al. [24] fabricated a three-dimensional graphene sponge to reduce the aggregation. The specific surface area was 356 $m^2 g^{-1}$, which was more than two times that of pristine graphene, at 150.5 $m^2 g^{-1}$. Wang et al. [25] reported a three-dimensional macroporous graphene material that possessed loosely stacked graphene sheets and showed a higher specific surface area. Therefore, it has been demonstrated that a three-dimensional structure can prevent the aggregation of graphene to enhance CDI performance.

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https://doi.org/10.1016/j.electacta.2018.01.041

Graphene aerogel (GA) is a common form of three-dimensional graphene structures. For example, Yin et al. [26] synthesized a GA/TiO_2 hybrid composite, which had an electrosorption capacity of 15.1 mg L^{-1}. El-Deen et al. [27] fabricated a GA composite with a high specific surface area and charge efficiency using a facile synthetic method. However, freeze drying is required following the reduction process, which slows production and increases cost. Furthermore, during the drying process, the pore structure is decomposed to a certain extent. Finally, it is difficult for water to be absorbed through the GA pores because of their hydrophobicity.

Recently, another three-dimensional form of graphene, graphene hydrogel (GH), was reported [28,29], which avoided using both the freeze drying process and the binder, which is usually added to prepare the electrode [30]. It would be expected that this material would show higher electrical conductivity and be quicker to prepare compared with graphene powder and other three-dimensional graphene architectures, e.g., graphene sponge [1] and graphene aerogel [31]. Gu et al. [32] prepared graphene hydrogel-polypyrrole-Mn composites, which showed an electrosorption capacity of 18.4 mg g^{-1} in 1000 μs cm^{-1} NaCl solution. Konget et al. [33] reported a type of graphene hydrogel that showed a high specific capacitance and electrosorption capacity. The studies of graphene gel in CDI have focused on designing new materials; however, there have been no reports exploring the differences between GH and GA or their capacitive deionization mechanisms.

The purpose of this work is to study the mechanism underlying the different CDI performances of GH and GA to find a better fundamental material for the CDI electrode. In this study, GH and GA were synthesized by the reduction method and applied in CDI. BET, SEM, TEM, Raman and XPS were used to analyze the microstructures and to explain the difference in CDI performance between GH and GA. Finally, a water-enhanced model was proposed to explain the different performances.

2. Experiment

2.1. Synthesis of graphene hydrogel and graphene aerogel

Graphite oxide was prepared by the modified Hummers method [34]. Preparation method of Graphene hydrogel (GH) and graphene aerogel (GA) resembled our previous work [35]. Two milligrams of graphite oxide was first dispersed in 250 mL deionized water and later sonicated in an ultrasound bath for 1 h to obtain a 4 mg mL^{-1} graphene oxide (GO) dispersion. 1 g ascorbic acid was then added to a 12.5 mL GO dispersion and mixed well. The mixture was then heated at 95 °C for 12 h to obtain the graphene hydrogel. Then graphene hydrogel was soaked in water for three days to remove the residual reducing agent. The obtained the GH was first freezed at −70 °C for 4 h and then dried at ambient temperature under vacuum for 48 h in the freezer dryer.

2.2. Electrosorption experiment

The electrode was prepared by directly pressing the supporting electrode with a pressure of 1 Mpa for 1 min. To avoid corrosion, titanium was used as the collector electrode in the desalination test. The CDI performance was investigated by the batch-mode method, which used a continuous system, including a unit cell, conductivity meter, an ampere meter, a dc power supply and a peristaltic pump. The initial concentration and volume of NaCl was ~500 mg L^{-1} and 45 mL, respectively. The system operated at 2.0 V with a flow rate of 10 mL min^{-1}. The mass of electrode was the pure graphene gel mass, i.e., the water in GH was not accounted for. The variation of conductivity was continuously measured by a conductivity meter (METTLER TOLEDO S230) and the concentration was calculated according to conversion relation between them, which was calibrated before the experiment. The electrosorption capacity (q_e, mg g^{-1}) was calculated using the following formula in our experiment:

$$q_e = \frac{(C_o - C_e) \times V}{m} \tag{1}$$

where C_0 and C_e are the initial and final concentrations of the NaCl solution, respectively (mg L^{-1}), V is the volume of NaCl solution (L), and m is the mass of electrode previously reported (g).

2.3. Characterization

The surface morphologies of GA and GH were characterized by scanning electron microscopy (SEM Hitachi 54800, Japan) and environmental scanning electron microscopy (ESEM), respectively. Transmission electron microscopy (TEM JEOL-2010F, Japan) was used to study the structure of the materials. The X-ray photoelectron spectroscopy spectra (XPS) and Raman spectra were obtained using a Kratos Axis Ultra^{DLD} (SHIMADZU, Japan) and XploRA™ Plus (Horiba, Japan), respectively. The Brunauere-Emmette-Teller (BET) surface areas were evaluated using a nitrogen adsorption–desorption isotherm at 77 K, and the distribution of pore size was fitted using the Barrett–Joyner–Halenda (BJH) model and Nonlocal Density Functional Theory (NLDFT) calculations using an ASAP 2020 instrument (MICROMERITICS INSTRUMENT CORP, USA). The results of GH was substituted by the material derived from supercritical carbon dioxide drying method because the instrument could not test samples containing water and supercritical carbon dioxide drying can prevent the formation of the liquid-vapor meniscus, reduce the liquid surface tension and avoid the pore collapse phenomenon [36] to remain the original nanostructure of GH as whole as possible. The contact angle was obtained using an SL 200 KB (Kono group, USA). The cyclic voltammogram (CV) measurements and electrochemical impedance spectra (EIS) were obtained using a CHI 600D electrochemical workstation (Shanghai CH Instruments Co., China) using a 1 mol L^{-1} NaCl solution in a three-electrode cell. The specific capacitance (C, F g^{-1}) was calculated from the CV curves according to the following formula:

$$C = \frac{\int IdE}{2m\nu E} \tag{2}$$

where I is the respond current (A) during the experiment, E is the potential (V), m is the mass of electrode (g) and v is the potential scan rate (V s^{-1}).

3. Results and discussion

3.1. Morphology and structure of GA and GH

The morphology of GA is shown at low and high magnification in Fig. 1a and b, respectively. GA exhibits a crisscross, interconnected structure, which prevents the aggregation of graphene sheets. The high magnification SEM image provides further verification of this structure. Fig. 1c shows the structure of GH, which is composed of planar sheets. The sheets are wrinkled and curved at the edges, which distorts the original planar structure of graphene and provides more adsorption sites for ions. And GH exhibits larger and tighter graphene sheets rather than crisscross structure like GA which probably caused by the rupture of graphene sheets during drying process. The structure of GA revealed by TEM is shown in