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Ultrasound-assisted preparation of electrospun carbon fiber/graphene electrodes for capacitive deionization: Importance and unique role of electrical conductivity

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ABSTRACT

The desalination performance of capacitive deionization (CDI) technology is governed by electrode material properties, such as specific surface area, pore size and structure, surface functional groups, electrode geometry, and electrical conductivity. However, few studies have been conducted regarding the impact of the electrical conductivity of electrode materials on the desalination performance of CDI. In this study, monolithic composite web electrodes are fabricated. These electrodes are composed of reduced graphene oxide/activated carbon nanofiber with tuned conductivity by using an ultrasound-assisted electrospinning method. Freestanding monolithic carbon nanofiber webs function as a framework that prevents graphene sheets from restacking. The conductive graphene network helps quickly transfer electrons across the matrix while the ions are efficiently stored in the pores of the electrodes; as a result, a high electrosorption capacity for NaCl of 9.2 mg/g is achieved. The electrical conductivity of the electrodes is correlated with the ion removal efficiency of desalination. Results show that the electrosorption capacity of desalination governed by the electric double-layer scheme can be improved by increasing the electrical conductivity of the electrodes. These findings may provide new insights into the design and fabrication of novel porous electrode materials and elucidate the importance and effects of electrode conductivity on CDI.

1. Introduction

The shortage in fresh water supply is a challenge faced by the world today [1]. An option to ensure freshwater availability is the desalination of seawater. Capacitive deionization (CDI) technology is a promising technology to desalinate water, especially low molar concentration streams, like brackish. In principle, a CDI cell consists of two porous carbon electrodes. Upon applying a voltage difference between two electrodes [2,3] the ions are absorbed. The preferred materials as CDI electrodes are carbon materials because they own high internal surface area and porosity, and the CDI performance is governed by the properties of the carbon electrodes to a great degree [4–7].

In terms of morphological characteristics and textures, carbon electrodes can be classified into two categories: powder and monolith. Powder-like carbon materials, such as commercial activated carbon [8–14], carbon nanotubes (CNTs) [15–17], mesoporous carbon [18–21], and graphene [7,22–24], have been evaluated as CDI electrodes for desalination; these materials should be fixed or bonded by adding a binder before use. The polymer binder likely increases the electrical resistance of the electrode and blocks some of the pores; subsequently, electrosorption capacity is reduced. As such, the carbon materials with free-binder monolithic structures, including carbon aerogel [6,25,26], CNTs/carbon fiber composite [27,28], carbon nanotube sponge [29], and 3D graphene sponge [30–33], have intensively been investigated as CDI electrodes. These monolithic electrodes have shown a high electrosorption capacity, which is partly caused by the continuous monolithic structure with an enhanced electrical conductivity [34]. Considering these findings, we should develop ideal CDI electrode materials with high specific surface area (SSA), tuned porosity, and good conductivity [35]. With the advances in the fabrication of carbon monoliths with optimized SSA and porosity, electrosorption performance has been improved. Nevertheless, few studies have

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been conducted regarding the dependence of salt electrosorption capacity on the electrical conductivity of electrodes; as such, this parameter should be addressed in detail.

Electrospinning is a technology widely used to fabricate continuous nanofiber webs [36]. Researchers [37–39] developed freestanding thin webs consisting of porous activated carbon nanofibers (ACF) for both CDI and energy storage. The ACF webs exhibit good monolithic structure and high electrical conductivity; as such, these components show a high electrosorption capacity as electrode materials in CDI, as demonstrated in our previous work [40]. In addition, as a unique two dimensional structural material, reduced graphene oxide (RGO) has been theoretically and experimentally demonstrated to possess superior electrochemical performance. In particular, the theoretically superior conductivity, mechanical properties and excellent chemical stability make RGO an ideal filler candidate for adding the conductivity of the electrode composites. The present work aims to develop a versatile process to fabricate RGO/ACF composite electrodes and to improve the desalination capacity of the electrodes by tuning their electrical conductivity.

2. Materials and methods

2.1. Materials

2.1.1. Reduced graphene oxide (RGO) synthesis

Graphene oxide (GO) was synthesized from natural graphite powder using a modified Hummers method [41]. Weighted GO was dispersed in *N*,*N*-dimethylformamide (DMF, Tianjin Fuyu Fine Chemical Co., Ltd.) for 1 h under ultrasonication (40 kHz, 100 W); a dark brown suspension was obtained. Ethanediamine was then added to the GO suspension at 90 °C for 30 min; black RGO dispersion in DMF was produced and used for subsequent experiments.

2.1.2. Preparation of RGO/ACF

Polyacrylonitrile (PAN) (M_w = 150,000, Aldrich Chemical Co., USA) was added to the RGO dispersion in DMF and was stirred for 6 h at 60 °C. A homogeneous RGO/PAN suspension was yielded for the preparation of RGO/PAN nanofibers by electrospinning at room temperature. The RGO/PAN solution was put into a 10-mL glass syringe with a spinning needle. The detailed conditions for the electrospinning operation are as follows: the feeding rate of the RGO/PAN solution was 1.0 mL h^{-1}, the applied voltage was 22 kV, the distance between the needle and the collector was 15 cm, and the rotation rate of the collecting drum was 280 rpm. After electrospinning, the paper-like nanofibers were heated to 280 °C at a heating rate of 1 °C min^{-1} in air for 2 h. The temperature was then increased to 800 °C in N_2 for 2 h, and N_2 was replaced with CO_2 to activate the RGO/PAN nanofibers at 800 °C for 1 h. The composite was cooled back to room temperature in N_2, yielding the RGO/ACF web. Pure ACF webs and RGO materials were also prepared under similar conditions mentioned above. The as-made RGO/ACF nanofiber webs with different RGO weight ratio to PAN at 1, 5, 10, and 15 wt% were denoted as RGO/ACF-X (X represents the weight ratio of RGO).

2.1.3. Preparation of RGO/ACF composite webs using the electrospinning coupled with ultrasonic spray process (S-RGO/ACF)

The S-RGO/ACF composite webs were synthesized. First, the precursor PAN was dissolved in DMF under continuous stirring to obtain a polymer solution. GO dispersed in water at 2 mg mL^{-1} was then prepared according to the reference [42]. Subsequently, the PAN-based fiber was created using a traditional electrospinning technique with a flow rate of 1 mL min^{-1}, a tip to collector distance of 15 cm, and a voltage of 22 kV. GO was incorporated through spraying using an ultrasonic atomizer (1.7 MHz, BSW-2A, Beirsi Co., China), as shown in Fig. 1a. Then, the GO-embedded electrospun fibrous polymer webs were stabilized at 280 °C in air for 2 h. The stabilized fibrous webs were then activated in CO_2 at a rate of 5 °C min^{-1} up to 800 °C to obtain S-RGO/ACF composite webs.

2.2. Measurements

The morphology of the samples was examined using a scanning electron microscope (SEM, JEOL S-4800). SSA was measured by nitrogen adsorption and was calculated by the BET equation (ASAP2020, Micromeritics, USA). Before the measurement was performed, the samples were degassed at 250 °C for 5 h under vacuum. The total pore volume was estimated from the amount of nitrogen adsorbed at $P/P_0 = 1$. Raman spectra of the samples were recorded on a LabRam-010 spectrometer with a resolution of 2 cm^{-1}, a laser beam (514.53 nm^{-1}) with an intensity of 1000 mW, and a slit width of 3.5 cm^{-1}. Schematic of four-probe method for measuring sheet resistance was found in Fig. S1. The electrochemical performance of the electrodes was evaluated using cyclic voltammetry (CV). A three-electrode cell assembly was utilized with an Ag/AgCl reference electrode, a Pt counter electrode, and a working electrode with an approximate diameter of 1 cm in 1 M and 10 mM NaCl solution at room temperature. The potential was swept between −0.5 V and 0.5 V at different scan rates. The gravimetric capacitance (*C*, F/g), i.e., the specific capacitance per mass weight carbon electrode, is calculated by the equation below [43]:

$$C = \frac{1}{m\upsilon\Delta V}\int_{V_0}^{V_0+\Delta V} I(V)dV \tag{1}$$

where m is the mass of the carbon electrode (g), υ is the scan rate (V/s), ΔV is the sweep potential range during discharging (V), and $I(V)$ is the corresponding current density (A g^{-1}).

2.3. Batch-mode electrosorption experiment

The electrospun ACF and RGO/ACF series electrodes were evaluated as CDI electrodes, which were directly attached to the graphite current collectors to create a CDI cell. Experimental details of the CDI test system (Fig. S2) can be found in the Supplementary Information (SI). The conductivity of the effluent can be converted into salt concentration according to a calibration curve. The adsorption capacity (Γ, mg/g) and charge efficiency (Λ) can be calculated by Equations (2) and (3), respectively:

$$\Gamma = \frac{(C_0 - C_t)\times V_{NaCl}}{m\times 10^3} \tag{2}$$

$$\Lambda(\%) = \frac{m\times\Gamma\times F}{10^3\times M\times\int i dt}\times 100 \tag{3}$$

where C_0 and C_t are the initial concentration (mg L^{-1}) and the concentration at time t (min), respectively, V_{NaCl} is the volume flow rate of the solution (mL min^{-1}), M is the molar mass of sodium chloride (58.5 g mol^{-1}), m is the total mass of both electrodes (g), i is the absolute value of current response during electrosorption (A) and F is the Faraday constant (96,485 C mol^{-1}).