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Activated carbon nanofiber webs made by electrospinning for capacitive deionization

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ABSTRACT

Activated carbon fiber (ACF) webs with a non-woven multi-scale texture were fabricated from polyacrylonitrile (PAN), and their electrosorption performance in capacitive deionization for desalination was investigated. PAN nanofibers were prepared by electrospinning, followed by oxidative stabilization and activation with carbon dioxide at 750–900 °C, resulting in the ACF webs that were characterized by X-ray diffraction, Raman spectroscopy, scanning electron microscopy and nitrogen adsorption. The results show that the as-made ACFs have a specific surface area of 335–712 m^2/g and an average nanofiber diameter of 285–800 nm, which can be tuned by varying the activation temperature. With the ACF webs as an electrode, an electrosorption capacity as high as 4.64 mg/g was achieved on a batch-type electrosorptive setup operated at 1.6 V. The ACF webs made by electrospinning are of potential as an excellent electrode material for capacitive deionization for desalination.

1. Introduction

The reliable supply of clean fresh water is becoming increasingly difficult as the world develops quickly, and this has become a bottleneck issue for the sustainable development of some countries such as China. It is estimated that there is approximately 1.38 billion km^3 of fresh water in the world, unfortunately, only 2.5% of this water resource is drinkable [1]. Seawater desalination is one of the important alternative ways to get fresh drinkable water. Up to now, several processes for desalination including membrane separation such as reverse osmosis (RO) and electrodialysis, and thermal vaporization such as multi-stage flash distillation (MSF) and multi-effect distillation, have been widely explored and used. Among these processes, the RO and the MSF processes have been employed by the majority of water treatment plants (ca. 90%) worldwide for desalination of seawater [2]. The cost of seawater desalination is governed by a number of factors such as the desalination process and the production capacity of the seawater treatment plant [3]. In the case of the RO technique, about 1.5–2.5 kWh of electricity is normally consumed to produce 1 m^3 of fresh water, while in the case of thermal distillation process, the same amount of electricity consumed will produce 10 times more of fresh water. In reality, only those rich countries such as Saudi Arabia can afford to run such seawater desalination facilities. As such, new technologies are highly demanded to further decrease the desalination cost.

Capacitive deionization (CDI) technology is an electrochemically governed method for removing salt from aqueous solutions, in which the carbonaceous electrodes are one of the key materials. When a potential is applied to the electrode, the ions in the solution will be charged, and moved to and adsorbed on the electrode to form an electrical double-layer. After the potential is removed, the adsorbed ions are quickly released back into the bulk solution [4]. The CDI process is an environmental friendly technology for seawater desalination because no contaminants are produced in the whole process, in which the energy consumption is low because the CDI process can be operated at a low potential and no electrolysis occurs at the electrodes [5].

New carbon materials such as carbon aerogel [6], carbon clothes [7], carbon nanotubes [8], graphite [9], and ordered mesoporous carbon [10] have been tested as electrode-active materials for the CDI process. Previous works have demonstrated, to some degree, that carbon aerogels are one of the most promising available materials for CDI [1]. Nevertheless, for carbon aerogels, the obvious shortcomings are their high resistivity and low mechanical strength [11].

In the present work, a CDI unit cell was constructed to evaluate the salt-removal efficiency of electrodes made of activated carbon fiber (ACF) webs prepared by electrospinning [12]. The non-woven ACF webs were stabilized, carbonized and activated in CO_2 before use, which led to ACF webs with a high specific surface area

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and a relatively narrow pore-size. With the web-like ACFs as an electrode, it has more benefits than the traditional powder carbonaceous materials that must be mixed and combined with a polymer binder and an electric conductor such as carbon black [13], and the binder would increase the internal resistance and block some of the pores in the carbon materials, which subsequently resulted in lower adsorption capacity [14].

2. Experimental

2.1. Electrode fabrication

Polyacrylonitrile (PAN) (M_w = 150,000, Aldrich Co.) was dissolved in dimethyl formamide in a weight ratio of 10 wt.% by gently stirring for 4 h at 60 °C, resulting in a PAN solution that was transferred into a 10 mL syringe with a capillary tip (0.8 mm in diameter). The electrospinning was conducted at a high positive voltage (22 kV) that was applied to the polymer solution via the syringe needle tip. The electrospun fibers were collected as a thin web on a rotating metal drum wrapped in aluminum foil, and the drum was rotated at a rate of 400 rpm. The electrospun fiber webs were stabilized in air at 280 °C for 2 h with a heating rate of 1 °C/min, and then activated at 750–900 °C at a ramping rate of 5 °C/min. When the activation temperature was reached, a CO_2 flow of 150 mL/min was introduced into the reactor and continued for 0.5 h, then, the CO_2 flow was replaced by flowing argon. The samples were cooled down to below 50 °C in flowing argon before taken out from the furnace. The as-made ACF webs were denoted as ACF*X*, where *X* stands for the activation temperature.

The electrospun ACF webs were examined using scanning electron microscopy (SEM, Hitachi, S-4700, Japan). The content of carbon, nitrogen and hydrogen in the samples was analyzed using a Vario EL III analyzer (Elementar, Germany). The specific surface area and pore-size distribution were evaluated using the nitrogen adsorption (ASAP2020, Micromeritics, USA). Before the measurement, the ACF webs were degassed at 250 °C for 5 h under vacuum. X-ray powder diffraction (XRD) examination of the ACF web samples was performed on a D/Max-III type X-ray spectrometer with Cu Kα radiation at 40 kV and 100 mA. Raman spectra of the samples were recorded on a LabRam-010 spectrometer with a resolution of 2 cm^{-1}, a 514.53 nm^{-1} laser beam with an intensity of 1000 mW and a slit width of 3.5 cm^{-1}.

2.2. Electrochemical measurements

Electrochemical performance of the electrodes fabricated from the ACF webs was evaluated using cyclic voltammetry (CV). A three-electrode cell assembly was utilized with an Hg/HgO reference electrode, a counter electrode of Pt, and a working electrode with a diameter of ca. 1 cm in 6 M KOH at 25 °C. The potential was swept between −0.9 and −0.1 V at a scan rate of 2–50 mV/s. The gravimetric capacitance (*C*, F/g), i.e. the specific capacitance per mass weight carbon nanofiber, is calculated using the following equation [15]:

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

where *m* is the mass of the carbon nanofiber (g), *v* 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).

2.3. Batch-mode electrosorptive experiment

The ACF webs were used as CDI electrodes and directly attached to the graphite current collectors to make a CDI cell. The adsorption removal efficiency of ions on the ACF web electrodes was measured in a flow-through setup, as shown in Fig. 1. Electrodes were placed face to face at both sides of an insulating nylon net (thickness: 0.2 mm) with an area of 50 mm × 70 mm. The unit cell was prepared by fixing the electrodes with plexiglass on both sides. A flow channel was created by punching a 1-cm-diameter hole in the bottom of the end plate to let the solution run through a spacer to the other end plate. For each run, the solution was continuously pumped into the cell at a flowing rate of 5 mL/min using a peristaltic pump (Loner BT100, China). The total solution volume was maintained at 50 mL and the solution temperature was kept 25 °C. During the measurement, the potential difference between the two electrodes was kept at a constant voltage of 1.6 V using a programmable DC power supply (PST-3202, Gwinstek, Taiwan). The changes of NaCl concentration in the solution were continuously monitored using an ion conductivity meter (ET915, eDAQ TECH, Australia).

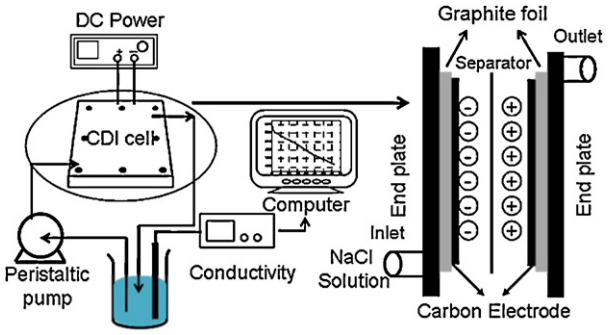

Fig. 1. Diagram of CDI experiment setup.

The electrosorptive capacity (*Q*) is defined as below:

$$Q = \frac{(C_0 - C)V_{NaCl}}{M} \quad (2)$$

where C_0 and *C* (mg/L) are the initial and final concentrations of NaCl, V_{NaCl} is the solution volume (mL), and *M* is the mass of the ACF web electrodes (g).

3. Results and discussion

3.1. Morphology and structure analysis

The white electrospun fiber webs were easily obtained under the electrospinning conditions as described above. After heat treatment, they are turned to black carbon materials with a very smooth surface, as shown in Fig. 2. The ACF webs were directly mounted to

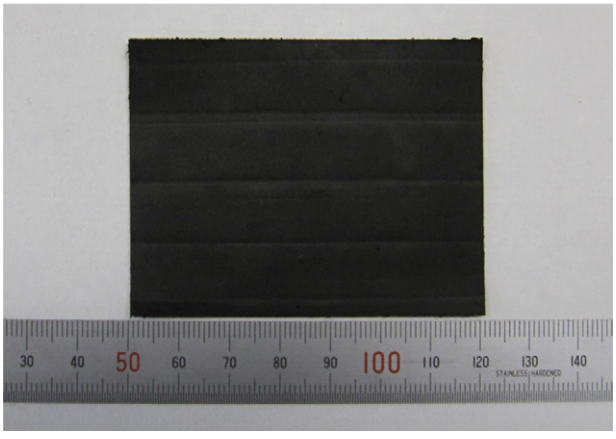

Fig. 2. Photograph of the ACF web after heat treatment.