Electrospun ultrafine carbon fiber webs for electrochemical capacitive desalination†

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Ultrafine carbon fiber webs were prepared from oxidatively stabilized electrospun poly(acrylonitrile) fibers, followed by carbonization or by further activation with steam. Capacitive de-ionization was evaluated in the batch mode. It was found that the webs exhibited considerable electrical adsorption, which was enhanced by activation with a faster electrosorption rate and a higher electrosorption capacity.

The water crisis is expected to get worse in the next few decades, with severe water shortage occurring globally, even in currently-considered water-rich regions, due to environment contamination.[1] Solving this problem demands a tremendous amount of research to identify new methods of purifying water at a low cost and with less energy, while concurrently minimizing the use of chemicals and their impact on the environment.[1,2] Capacitive de-ionization (CDI), which uses ion electrosorption onto the surface of porous materials to remove ions from aqueous solutions, may serve as an energy efficient alternative for the de-salination of brackish water, as compared with more conventional desalination methods like membrane separation and thermal distillation.[2,3] The CDI operates at a low voltage not exceeding the decomposition potential of water. The ions adsorbed are held in the electrical double layer near the charged surface of a flow-through capacitor and can be released back into bulk solution by cancelling the potential difference between the electrodes.[2] No additional chemicals are required for regeneration. In fact, part of the discharging energy can be restored for the sake of energy recycling.

A prerequisite for the high de-ionization efficiency of CDI is the demand for a high electrosorption capacity endowed by the electrode materials. To attain the objective, it is important that a large surface area is created, and thus typical materials such as high specific surface area materials are used. Carbon aerogels,[4–8] activated carbons,[9,10] multi-walled carbon nanotubes and nanofibers,[11–13] ordered mesoporous carbons,[14] graphenes,[15] and oxide-incorporated carbons[16–18] have been investigated as CDI electrodes.

A crucial concern in fabricating CDI electrodes is the production of macroscopic, engineered structures to offer a great opportunity to effectively increase the electroadsorption capacity for the CDI process. Carbonized and activated electrospun fiber webs are attractive for the high efficiency of capacitive de-ionization electrodes. The most important advantage of electrospinning is that it can be used to prepare a macroscopic self-standing web structure in a scalable way.[19] When used as an electrode, the electrospun carbon fibers (e-CF) do not need an extra processing step of adding a binder and an electric conductor, such as carbon black. The webs from electrospinning have important features, such as ease of handling, the non-interference of additives, improved conductivity due to their continuous structure, and the low cost of fabricating such electrodes. In this Letter, electrochemical capacitive de-salination using ultrafine carbon fiber webs prepared by electrospinning is reported for the first time. We demonstrate the potential of electrospun-activated carbon fiber (e-ACF) webs as CDI electrode materials with remarkably enhanced electrosorption capacities.

Poly(acrylonitrile) (PAN) was dissolved in *N*,*N*-dimethylformamide (DMF). The 10% PAN/DMF solution was loaded into a syringe and delivered to the tip of a stainless steel needle with a syringe pump. A 25 kV high voltage power supply was applied to the solution *via* the needle. The electrospun webs through the positively charged capillary were collected on aluminium foil wrapped on a grounded steel sheet. PAN fiber webs were oxidatively stabilized at 280 °C in air for 1 h.[20] The stabilized fiber webs were carbonized by heating at a rate of 5 °C min^{-1} up to 800 °C and holding this temperature for 1 h in an atmosphere of N_2, or further activated with steam at 800 °C under N_2 flow for 1 h. The carbon fiber webs were characterized by scanning electron microscopy and N_2 adsorption at 77 K. A CDI unit consists of two parallel electrode plates separated by a 1.0 mm gap for solution flow (the CDI unit configuration is illustrated in the ESI†). A sodium chloride aqueous solution was pumped into the bottom and extracted from the top of the cell by a peristaltic pump with a flow rate of 6 mL min^{-1}. The voltage used in these experiments was 1.2 V. CDI was performed in batch mode. The solution conductivity was online-monitored at 5 s intervals by a conductivity meter (type 308A, Leici Company). For comparison, activated carbons (AC), activated carbon fibers (ACF) and carbon nanotubes (CNT) were employed to fabricate CDI electrodes with a binder for their interconnection (the characteristics of the carbon materials are provided in the ESI†). The electrodes were fabricated by the following procedure. 0.20 g of the active component (AC, ACF or CNT), 0.08 g of polyvinylidene fluoride (binder) and 0.12 g of

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graphite powder (electric conductor) were mixed with 2 mL of *N*-methyl-2-pyrrolidone. A 5.0 × 5.4 cm graphite paper was coated with the mixture, dried under vacuum at 50 °C for 3 h and then pressed by a roller squeezer to keep a 0.5 mm thickness for each plate. To thoroughly remove the solvent, the electrodes were dried again under vacuum at 130 °C for 3 h.

Fig. 1a shows a typical image of carbonized/activated ultrafine carbon fiber webs prepared by electrospinning. The web is composed of entangled ultrafine fibers distributed at random. Fig. 1b is an enlarged image of the fibers with a slightly rough surface and a fiber diameter of *ca.* 900 nm. No distinct difference between activated and non-activated carbon fibers was observed from the morphology. The macroscopic carbon fiber webs (Fig. 1c) were directly attached to the current collectors when used as CDI electrodes. It is noted that the fiber diameters can be controllably tuned by modulation of the electrospinning parameters, such as polymer concentration, voltage, distance between needle tip and collector, *etc.* A fiber diameter of *ca.* 900 nm herein was used as an example for the application of electrospinning in CDI.

Fig. 2 illustrates the N_2 adsorption/desorption isotherms of activated and non-activated ultrafine carbon fibers. The curve for activated carbon fibers exhibits a type I isotherm, which is the typical adsorption characteristics of microporous materials. The Brunauer–Emmett–Teller (BET) surface area of the activated carbon fibers is 550 $m^2\ g^{-1}$ and the peak of the pore size distribution is 0.6 nm calculated by the MP method, as shown in the inset of Fig. 2. The pore volume of the activated carbon fibers is 0.35 $cm^3\ g^{-1}$. In contrast, non-activated carbon fibers demonstrate a barely measurable BET surface area of 5 $m^2\ g^{-1}$ with a pore volume of 0.01 $cm^3\ g^{-1}$.

Other carbon materials exhibit the following characteristics. The specific surface area of AC (100–200 mesh) is 730 $m^2\ g^{-1}$ according to nitrogen adsorption/desorption measurements. ACF has a smooth surface and a fiber diameter of *ca.* 18 μm with a calculated BET surface area of 670 $m^2\ g^{-1}$. The multi-walled carbon nanotubes were purified by HNO_3 and have an average diameter of 17 nm (see the ESI†).

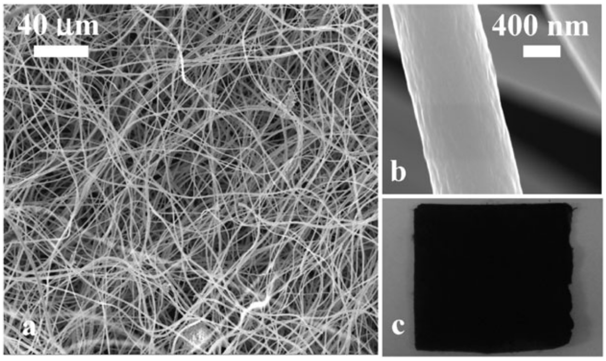

Fig. 1 A typical image of an ultrafine carbon fiber web prepared by electrospinning. (a) A large scale image, (b) an enlarged image and (c) the macroscopic structure of the fiber web.

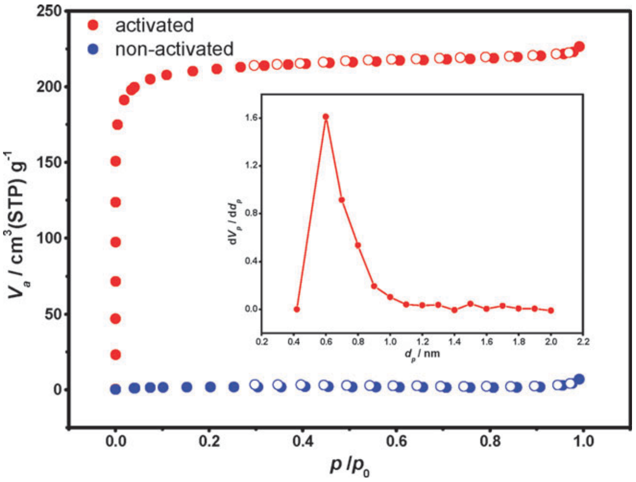

Fig. 2 The N_2 adsorption/desorption isotherms of ultrafine carbon fiber webs and activated carbon fiber webs (inset: the pore size distribution of the activated carbon fiber webs calculated by the MP method).

The de-salination performance of CDI electrodes fabricated by self-standing carbon fiber webs were evaluated by using the CDI apparatus to treat a sodium chloride aqueous solution with a concentration of 60 mg L^{-1}. The electrode assembly was firstly washed with pure water until the conductivity of the solution approached zero, then dried and the de-salination capacity of the webs in salt solution recorded. A repeated wash/record process indicated that the de-salination performance of the webs remained almost constant. Fig. 3 presents the result of the CDI of carbon fiber webs in batch mode. The carbon fibers themselves are capable of adsorbing an amount of NaCl due to the interaction between polar groups on the carbon surface and the ions. Thus, the CDI can be divided into two stages: non-electrosorption and electrosorption. There was no applied electric field during the initial 15 min, and the change in the conductivity of the solution due to non-adsorption was recorded. After this, the CDI electrodes were set at a constant voltage of 1.2 V. At the stage of non-adsorption, a common observation was that the amount of NaCl adsorbed by the activated carbon fiber web was higher than that by the non-activated web, in agreement with the BET surface area of the fibers. Once an electric field was applied to the CDI electrodes, the conductivity of the NaCl solution decreased sharply due to electrical adsorption. Then, the change in conductivity became gradually lower before the electrosorption reached equilibrium. Due to the development of a microporous structure on the activated carbon fiber surface, the e-ACF web exhibits a notably faster electrosorption rate and a higher electrosorption capacity than the non-activated web. The final ion concentration of the treated solution approached zero when using e-ACF web electrodes.

Fig. 4 compares the ion removal capacity of AC, ACF, CNT, e-CF web and e-ACF web electrodes with the same initial concentration of NaCl solution. It is shown that AC electrodes made by the adhesive method exhibit a relatively low ion removal capacity. The CDI unit, which was fabricated by ACF and CNT, shows electrosorption capacities of 0.7–1.3 mg g^{-1}. It is noted that the e-CF web has a distinct ion removal capacity, even though the surface area of the web is much lower than those of the previous three carbon materials. This result is ascribed to the continuous electrical

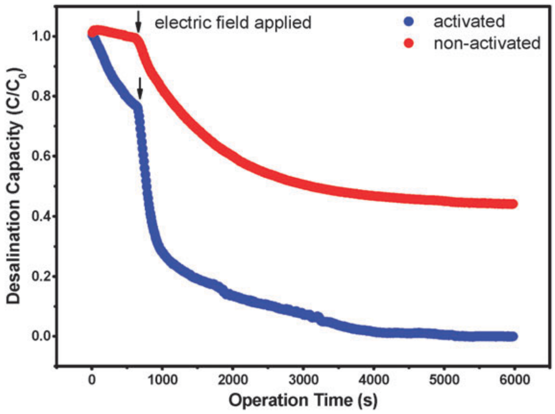

Fig. 3 The de-salination characteristics of electrospun ultrafine carbon fiber webs in a CDI unit.

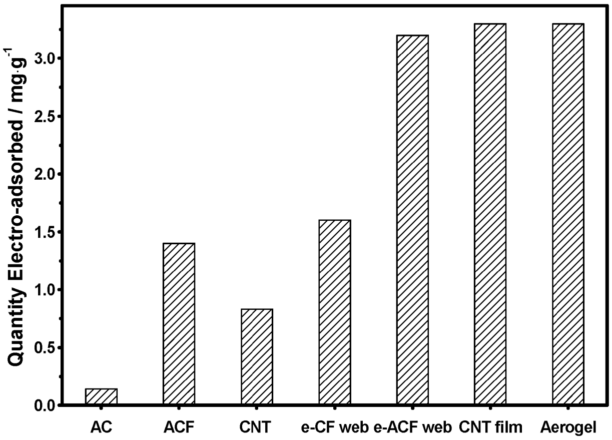

Fig. 4 A comparison of the de-salination capacities for different carbon material electrodes in a CDI unit.

connection and non-interference of the binder. When the e-CF web was treated further by activation, its de-salination capacity was doubled in comparison with the non-activated CF web. The self-standing continuous structure and high surface area are ensured by the electrospun activated carbon fiber web. The ion removal capacity was also compared between e-ACF webs and other reported macroscopic, engineered structures. CNT film (grown directly on a Ni substrate) and carbon aerogel (monolithic form) electrodes show similar ion removal capacities of 3.2 mg g^{-1}.[8,13] The quantity electroadsorbed by e-ACF web electrodes is almost the same as those by CNT film and carbon aerogel electrodes, which indicates electrospinning in combination with activation is an efficient method to produce macroscopic, engineered structures to greatly increase the electroadsorption capacity for CDI processes.

In summary, ultrafine carbon fiber webs exhibit a considerable electrical adsorption that is enhanced by activation with a faster electrosorption rate and a higher electrosorption capacity. Binder-free and self-standing macroscopic carbon webs provide promise for use as electrode materials for capacitive de-ionization.

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