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Original Research

Optimizing the fabrication of carbon nanotube electrode for effective capacitive deionization via electrophoretic deposition strategy

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ABSTRACT

In order to obtain superior electrode performances in capacitive deionization (CDI), the electrophoretic deposition (EPD) was introduced as a novel strategy for the fabrication of carbon nanotube (CNT) electrode. Preparation parameters, including the concentration of slurry components, deposition time and electric field intensity, were mainly investigated and optimized in terms of electrochemical characteristic and desalination performance of the deposited CNT electrode. The SEM image shows that the CNT material was deposited homogeneously on the current collector and a non-crack surface of the electrode was obtained. An optimal preparation condition of the deposited CNT electrode was obtained and specified as the Al $(NO_3)_3$ M concentration of 1.3×10^{-2} mol/L, the deposition time of 30 min and the electric field intensity of 15 V/cm. The obtained electrode performs an increasing specific mass capacitance of 33.36 F/g and specific adsorption capacity of 23.93 mg/g, which are 1.62 and 1.85 times those of the coated electrode respectively. The good performance of the deposited CNT electrode indicates the promising application of the EPD methodology in subsequent research and fabrication of the CDI electrodes for CDI process.

1. Introduction

The capacitive deionization (CDI) technology, also referred to as electrosorption technology, or electrochemical desalting, recently has attracted a range of attentions in the desalination field since the decent procedure with a novel, low-cost and energy-efficient substitute against the traditional desalting methods. A low direct current (DC) potential (normally less than 2 V) is used into this electrochemical process to form an electrode with a variety of advantages, for instance, high capacity, no secondary pollution, and better reversibility. Furthermore, characteristics of CDI without needing high-pressure pumps, frequent routine maintenance and a mass of thermal energy have exposed to scientific researchers and users, leading CDI to be the most promising and attractive desalting strategy in the desalination field of seawater and brackish water [1–3].

As to the ion electrosorption process in CDI, the ions in brine water are absorbed by porous carbon electrode pairs to accomplish the desalination of salty water [1,2,4]. The ion adsorption capacity of CDI electrodes is the key factor influencing CDI performance, which mainly depends on the performance of electrode material and the electrode manufacture techniques [5–7]. At present, carbon nanotube (CNT) is normally utilized as electrode materials of CDI technology, due to CNT (the active materials of CDI electrodes) has high specific capacity, large specific area, and good electroconductivity and has performed excellent ion adsorption capacity in electrodes. Besides, by contrast with other porous carbon materials, such as activated carbon (AC) [8–10], carbon aerogels [11,12] and carbon fibers [13–15], CNTs have a unique hollow structure and network structure of nano-dimension, which is beneficial for the formation of interaction winding and obviously promotes the diffusion and migration of the ions [16–18].

Basically, when it comes to the electrode fabrication methodology, there are two main ways to fabricate electrodes: compressing methodology and coating methodology. The CNTs electrode can be fabricated by compressing the composite material, binder, and conductive agent using compressing methodology. Nevertheless, this fabrication method narrows the ion channels of electrodes, leading to high charge transport resistance. These all have negative impact on the adsorption performance of the electrode [19].

Abbreviations: CDI, Capacitive deionization; EPD, Electrophoretic deposition; CNT, Deposited carbon nanotube; MWCNTs, Multi-walled carbon nanotubes; CV, Cyclic voltammetry; EIS, Electrical impedance spectroscopy

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Besides, the coating methodology can also fabricate the CNTs electrode through casting a slurry mixture of the composite material, binder and conductive agent in specific polymer solution on current collector before a drying process. For example, in Hongsik Yoon et al.'s study [20] Ca-alginate coated electrode can be used as commercial cation exchange membrane, which performs superior improvement in desalination capacity and good charge efficiency. Yue Wang et al. [21] have verified that the coated PPy/CNT electrodes have better structure property, lower charging resistance and higher electrochemical properties comparing with the compressed electrode. However, the advantages of carbon materials with hollow structure and network structure were influenced by polymer binder materials which obstructed ions pores and channels in diffusion and migration, causing lower electrosorption efficiency. In addition, after long-hours immersing into the treated water, the coated electrodes sometimes have the problem of coating shedding which results in poor application in further application [22,23].

Therefore, the electrophoretic deposition methodology (EPD) is a derived CDI fabrication technology, which was drawn from electroplating, coatings and ceramics, continuously developing and supplementing coating methodology in CDI field. This method presents a high-efficient process for fabrication of electrode coatings in colloidal suspensions: deposited materials under a direct-current (DC) electric field and the coatings show high distribution homogeneity and good packing density. The simplicity and advantages of EPD such as low pressure, disuse of polymer binder, low limitation in substrate shape and cost-effectiveness provide the possibility to scale up. In particular, EPD technology can monitor deposition thickness straightforward by adjusting technological parameters to easily master the electrode fabrication process [24,25]. Several articles have manifested that EPD technology was increasingly applied in electrode fabrication technology [26–30], which offer experiences to apply in CDI field.

In order to obtain higher deposition rate and reasonable mass of the deposition coatings, appropriate slurry component concentration, deposition time and electric field intensity were studied and determined [31,32]. Guang Zhu [26] investigated the electrochemical properties and electrosorption performance of the CNTs electrodes which are fabricated by EPD, press and screen printing methods, respectively. The results show that the morphology structure, mass and water wettability can be generally influenced by fabrication methods. And the EPD method demonstrated the advantages of fabricating CNTs electrode, only if the problem of loading mass of CNTs can be effectively optimized. L. Feng et al. [27] prepared well-dispersed multi-walled carbon nanotubes (MWCNTs) on the interface of SiC/zinc aluminum silicate (SiC/ZAS) by EPD method, which reduced the micro-defects at the material interface region and increased the shear strength of joints. This research only studied the load-displacement and sheer strength under different deposited time, which shows that it is essential to optimize the parameters to obtain the best electrode properties. Z. Chen and T. Boström [28] successfully used EPD to prepare functionalized carbon nanotubes (CNTs) on aluminum substrates to be the spectrally selective solar thermal absorbers and studied the effect of CNT coating thickness, deposition parameters and peak heat treatment temperature on the spectral selectivity. The conclusion demonstrated the CNT coatings are uniform; moreover, thickness is one of the key factors of a good spectral selectivity. This research shows the same methodology as that of CDI technology, which provides powerful evidence to use this method into CDI. The research verifies that parameter optimization is the essential research content which results in good foundation for further studies. These investigations indicate that EPD is a viable methodology for electrode fabrication, nevertheless, some underlying research is seldom studied which affects material fabrications and further applications, especially the preparation parameters and their optimization [32]. From above investigations, we can deduce that the comprehensive evaluation of the preparation parameters, especially the mass ratio of slurry components, deposition time and electric field intensity, is obviously essential to conduct for EPD process.

In this paper, in order to obtain superior electrode performances in capacitive deionization (CDI), the electrophoretic deposition (EPD) method is introduced as a novel strategy for the fabrication of carbon nanotube electrode. Preparation parameters, including the concentration of slurry components, deposition time and electric field intensity, are investigated by control variate methodology. Based on the CNT material, morphology of the optimal deposited CNT electrode is characterized by SEM test, its properties are compared with coated electrode in terms of electrochemical characteristic and desalination performance. The studies show the deposited CNT electrode that contributes to the promising application of the EPD methodology in water treatment research and provides a strategy to fabricate the CDI electrodes for CDI process.

2. Materials and methods

2.1. Fabrication of deposited CNT electrodes

To fabricate the deposited CNT electrodes, the solution was blended with 0.15 g CNT (electrode material, bought from Chengdu Organic Chemicals Co. Ltd., Chinese Academy of Sciences. The main technical data is: special surface area 400 m^2/g, outer diameter < 8 nm, inner diameter 2–5 nm and length 10–30 μm) pretreated by concentrated nitric acid, different concentration of $Al(NO_3)_3$ as an additional agent to enhance the deposition effect, and mixed solvent with optimal volume ratio of 1:1 for ethanol and acetone. Specifically, concentrated nitric acid is used to eliminate the oxidant on CNTs which was washed to pH = 7 afterwards; the mixed solvent was used to obtain the higher deposition amount and rate, the most appropriate evaporation rate for better properties of the electrode film [31].

$Al(NO_3)_3$ of various concentrations (0.7×10^{-2}, 1.0×10^{-2}, 1.3×10^{-2}, 1.7×10^{-2} and 2.0×10^{-2} mol/L) were used to determine the optimal slurry component concentration of EPD solution. This solution was then dispersed using ultrasonic for 4 h to ensure homogeneity. The EPD cell was constructed by a groove filled with the slurry, which was inserted in two parallel graphite papers (current collectors) under the same dimension of 3 × 8 cm with groups of various distances between them. This cell was connected to the potentiostatic power supply by governing the direct voltage in diverse stages under multiple deposition time (10 min, 20 min, 30 min, 40 min, 50 min and 60 min) to fabricate CNT electrodes. Whilst attaining the ratio of the direct voltage and the distance to a more persuasive parameter which is electric field intensity (5 V/cm, 10 V/cm, 15 V/cm and 20 V/cm). The electric field (E, V/cm) of the electrode was calculated using the Eq. (1):

$$E = \frac{U}{d} \tag{1}$$

Where E (V/cm) is the applied electric field intensity; U (V) is the applied voltage; d (cm) is the space distance between two electrodes.

2.2. Fabrication of coating-type electrode

To fabricate the coating-type electrode, the coating mixture was prepared by mixing the mixture of the materials under the mass ratio of 8: 1: 1 for the PPy/CNT, polyvinylidene fluoride (binder) and graphite powder (conductivity agent), then stirred for 12 h to ensure homogenetity. The slurry was then cast onto the graphite paper using the H-type coating applicator with the groove depths of 0.3 mm. After the drying process of 40 °C, the coated electrodes were obtained [21].

2.3. Characterization and electrochemical measurements

The top view and cross-section view of the electrodes were observed by scanning electron microscope (SEM, TM3000) and digital