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Preparation optimization on the coating-type polypyrrole/carbon nanotube composite electrode for capacitive deionization

Yue Wang[a,b,c,*], Xinyu Han[a,b,c], Ruguo Wang[a,b,c], Shichang Xu[a,b,c], Jixiao Wang[a,b,c]

[a] Chemical Engineering Research Center, School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, China
[b] Tianjin Key Laboratory of Membrane Science and Desalination Technology, Tianjin 300072, China
[c] Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Tianjin 300072, China

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ABSTRACT

In order to obtain the high electrode performance in capacitive deionization (CDI), the coating methodology was introduced and incorporated in the fabrication of the novel polypyrrole/carbon nanotube (PPy/CNT) composite electrode. A typical optimization on the major preparation parameters of the coating-type PPy/CNT electrode was conducted, including the mass ratio of electrode material mixture, the coating thickness and the drying temperature. Based on the PPy/CNT composite, the performance of the optimized coated electrode and the compressed electrode was typically compared in terms of the electrochemical characteristic and desalination performance. The experimental results indicated that the performance of the coated electrode got to the optimum under the mass ratio of 8:1:1 for the PPy/CNT, polyvinylidene fluoride and graphite, the coating thickness of 0.3 mm and the drying temperature of 40 °C. The coated electrode was markedly superior to the traditional compressed electrode in terms of the specific mass capacitance and specific adsorption capacity. The specific mass capacitance and specific adsorption capacity of the coated electrode reached 180.61 F/g and 93.68 mg/g respectively, which were 1.57 and 1.37 times that of the compressed electrode. These conclusions would lay a good foundation for the practical application of the coating methodology and also the novel electrode composite materials in the CDI field.

1. Introduction

With globally growing concerns about the environment and freshwater crisis in recent years, the capacitive deionization (CDI) technology, also referred to the electrosorption technology, has attracted an increasing attention in the desalination market due to its advantages of lower energy consumption and no secondary pollution compared with the traditional technologies such as thermal and membrane desalination processes [1–3]. Basically, CDI can be described as a potential-induced adsorption of the ions on the surface of the charged electrode. During the adsorption process, ions are adsorbed on the electrode surface by applying a potential difference between a pair of electrodes. When the ion-adsorption of the electrode reaches its saturation, the adsorbed ions will then be released back to the bulk solution by removing or reversing the potential between the electrodes. In this way, the electrode can be regenerated and prepared for the next adsorption process [4–6].

The key factor that affects the performance of CDI is the ion adsorption capacity of the electrode, which mainly depends on the performance of the electrode material and the proper electrode fabrication methodology [7,8]. Concerning the electrode material, recent studies [9,10] have shown that the composite which combines the carbon material and conducting polymer is a good candidate material which commonly represents a high ion adsorption capability by utilizing the excellent electrical conductivity of carbon material and the high specific capacitance of conducting polymer. As a typical composite material, the polypyrrole/carbon nanotube (PPy/CNT) composite has been successfully synthesized via chemical oxidation method and the saturated adsorption capacity of composite based electrode was about four times that of the carbon nanotube (CNT) based electrode [11].

As for the electrode fabrication methodology, there are basically two ways for fabricating an electrode: compressing methodology

* Corresponding author at: Chemical Engineering Research Center, School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, China. Tel.: +86 22 27406889.
E-mail address: tdwy75@tju.edu.cn (Y. Wang).

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and coating methodology. The compressing methodology is to fabricate the electrode by compressing the composite material, binder and conductive agent under a high pressure [12]. Some researchers have reported that the CNT electrode could be prepared by the compressing method and used for CDI process [13,14]. However, the application of the high compressing pressure may cause a narrow ion pathway and a high charge-transfer resistance in the electrode, which may reduce the adsorption performance of the electrode. Besides, the compressing method may be not applicable in practice since there exists a bottleneck for the scaling-up electrode fabrication.

Different from the compressing method, the electrode can also be obtained through a drying process after casting a slurry mixture of the composite material, binder and conductive agent in a polymer solution on current collector, namely the coating methodology [15,16]. For this method, the performance of the composite material could be well exerted since the pressure-related charge-transfer resistance is eliminated. Moreover, the fabrication process is comparatively simplified and has the potential for the scaling-up electrode preparation. Therefore, the coating methodology has been increasingly used to fabricate the electrode in the investigations of the CDI electrode materials [17–19]. However, the preparation optimization and specific analysis about the coating-type electrode itself were rarely cared and reported.

Generally, three preparation parameters, including the mass ratio of electrode material mixture, the coating thickness and the drying process are believed to play a key role in the fabrication and performance of the coating-type electrode. The coating-type electrode prepared under the optimized parameters could be fabricated well and obtain the high electrode performance. In this regard, recent research efforts have begun to focus on optimizing some specific preparation parameters. Chia-Hung Hou et al. [20] had investigated the effect of polyvinylidene fluoride (PVDF) binder on the electrode performance, finding that increasing the PVDF content could enhance the mechanical strength of carbon electrode, but decrease the electrosorption efficiency at the same time. Jae-Hwan Choi et al. [21] fabricated the carbon electrode by using the water-soluble polymer binder, polyvinyl alcohol (PVA), in its coating process to increase the wettability of carbon electrode. The results showed that the specific capacitance of PVA-bonded carbon electrode was improved by 13.3-30.1% compared with that of the PVDF-bonded carbon electrode. But recent publications still lack the comprehensive evaluation about the preparation parameters. Therefore, it is necessary to conduct a typical optimization on the major preparation parameters of the coating-type electrode.

Traditionally, the carbon material was often used and studied in the coating methodology of the CDI electrode. The viability of adopting this methodology to fabricate the novel composite material electrode also needs to be investigated. As is known, the composite electrode prepared by different fabrication methods may attain the varying electrode performance. But no previous study has investigated this issue. Hence, it is essential to make a comparison about the performance between the coating-type and compressing-type electrode to identify the effective electrode fabrication technology for enhancing the electrode performance.

In this paper, the coating methodology was adopted to fabricate the PPy/CNT electrode, and the main preparation parameters, including the mass ratio of electrode materials, the coating thickness and the drying temperature were tested and optimized by using control variate methodology. Based on the PPy/CNT composite, the performance of the optimized coating-type electrode and the compressing-type electrode was typically compared in terms of the surface morphology, electrochemical characteristic and desalination performance.

2. Experimental

2.1. Fabrication of coating-type PPy/CNT electrode

To fabricate the coating-type PPy/CNT electrode, the slurry was prepared by mixing a solution of the PPy/CNT composite synthesized by chemical oxidation method, PVDF (binder) dissolved in N-methyl-2-pyrrolidone (NMP) and graphite powder (conductivity agent). Various mass ratios of the PPy/CNT, PVDF and graphite were used to determine the optimal composition of the slurry mixture. The mixture was stirred for 12 h to ensure homogeneity. The slurry was then cast onto the graphite paper using the H-type coating applicator as seen in Fig. 1 to form the electrode with a dimension of 2.5×4.5 cm. The cast electrodes with different coating thicknesses (0.2, 0.3 and 0.4 mm) were obtained by altering the coating applicator with different groove depths. The resulting electrodes were then dried in the oven for 12 h to obtain the coated electrode. Different drying temperatures (20, 40, 60 and 80 °C) were used to determine the optimum drying temperature.

2.2. Fabrication of compressing-type PPy/CNT electrode

To fabricate the compressing-type PPy/CNT electrode, the mixture of the PPy/CNT, PVDF and graphite was grinded adequately and then pressed in the self-manufactured mould at a pressure of 10 MPa for 10 min. The mass ratio of the PPy/CNT, PVDF and graphite was the same with the optimal mixture composition of the coated electrode. After mold-releasing, the PPy/CNT plate with diameter of 15 mm and thickness of 0.16 mm was adhered on the graphite paper to obtain the compressed electrode.

2.3. Physical characterization and electrochemical measurements

The surface and cross-section of the electrode were observed by scanning electron microscope (SEM, TM3000) and digital microscope (KH-7700). Electrochemical measurements were carried out in 1 M NaCl solution by using a three-electrode system, including a prepared PPy/CNT electrode as working electrode, a platinum electrode as counter electrode and a saturated calomel electrode (SCE) as reference electrode. Cyclic voltammetry (CV) measurements were made within the potential range of −0.2 to 0.6 V vs. SCE and at the scan rate of 0.005 V/s. The specific mass capacitance (C_m, F/g) of the electrode was calculated by the equation (1). In electrical impedance spectroscopy (EIS) measurement, the frequency was in the range of 0.01 Hz–10 kHz and the applied bias voltage was set at open-circuit potential.

$$C_m = \frac{\int_{E_1}^{E_2} i(E)dE}{(E_2 - E_1)/mv} \quad (1)$$

Fig. 1. The picture of the H-type coating applicator.