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Parameter optimization on the compressed polypyrrole/carbon nanotube composite electrode for capacitive deionization

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ABSTRACT

For the capacitive deionization technology, it is vitally important to explore a proper electrode moulding technology to sufficiently perform the electrode performance. In this work, a compression moulding method was adopted for the fabrication of the novel polypyrrole/carbon nanotube (PPy/CNT) composite electrode and a typical optimization on the major preparation parameters was conducted, including the mass ratio of electrode material mixture, the electrode thickness and the moulding pressure. In the optimization process, the flexural strength tests were first introduced to optimize the moulding pressure. The results indicated that the performance of the PPy/CNT electrode fabricated by the compression moulding method got optimum at the moulding pressure of 10 Mpa, the mass ratio of 9:1:2 (PPy/CNT : polyvinylidene fluoride (PVDF) : graphite powder) and the thickness of 0.6 mm. Under the optimal conditions, the specific area capacitance and the area surface adsorption capacity of the PPy/CNT electrode were significantly improved and could reach up to 5.30 F/cm^2 and 1.97 mg/cm^2, respectively.

Keywords: Capacitive deionization; Polypyrrole; Carbon nanotubes; Compression moulding method

1. Introduction

With growing demands for fresh water, seawater desalination has emerged to become the strategic supply of water for many arid countries such as Qatar and the United Arab Emirates in particular [1,2]. Capacitive deionization (CDI), as a novel desalination technology, has received increasing attention due to its significant advantages of efficient energy use, low operating cost, high recovery rate and eco-friendliness as compared with conventional desalination processes such as thermal distillation and reverse osmosis [3–6]. In CDI, the treatment is realized via two basic processes of the charging and the discharging. During the charging process, ions in feed solution are driven toward oppositely charged electrodes when an external potential is applied to polarize the electrode pair, which results in a purified stream with lower ion concentration. In the following step, the adsorbed ions are released back into the bulk solution by reversing or removing the external potential and thus the electrodes are regenerated. Thus, the feed solution can be continuously desalinated through the CDI cycle [7–9].

The prerequisite for high deionization efficiency of CDI is the demand for the electrode with the high ion adsorption capacity, which mainly depends on the performance of the electrode material and the proper electrode fabrication method [10,11]. To achieve this goal, one of the most effective ways is to develop novel electrode materials with high specific surface area, good electrical conductivity and excellent electrochemical stability [12]. Recently, carbon-based composite materials have been thoroughly investigated to overcome defects of single carbon material. Especially,

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the combination of carbon materials with conducting polymers can largely enhance the ion adsorption capacity of pristine carbon materials by adjusting the intrinsic pore structure or improving the wettability and surface chemistry with functional groups [13–16]. As a typical composite material, the polypyrrole/carbon nanotube (PPy/CNT) composite has been successfully prepared by chemical oxidation method in our research team. The prepared composite exhibits a high affinity to ions due to their synergistic effects [17].

In CDI, electrode moulding technology also plays a key role in electrode performance which affects the desalting efficiency [18]. Compared with the coating method, the compression moulding method as one of the electrode fabrication methods has some merits such as convenience in operation and good desalting stability of the prepared electrode. According to the recent studies, the compression moulding method based on carbon materials has been designed and optimized. Kim et al. [19] had investigated the effect of active carbon electrode thickness on the rate capability of the CDI cell. The result showed that compared with the thicker electrodes, the thinner electrode retained higher deionization capacity with the increase of scan rate. This research illustrates that the electrode thickness is one of important parameters affecting the desalting performance. In our previous work, the influence of the moulding pressure and the proportion of the binder on the CNT electrode had been studied and analyzed. The CNT electrode obtained the best performance when the weight content of PVDF was 10% and the moulding pressure was 10 MPa [20]. However, the novel composite materials are very different from carbon materials in the aspects of microstructure, conductivity and mechanical strength. Hence, the feasibility of the compression moulding method to prepare the composite electrode needs to be investigated and further exploration is required to understand how the preparation parameters affect the performance of the composite electrode.

Although some parameters have been investigated in the preparation process of the carbon electrode, the parameters such as the mass ratio of the electrode material mixture, the electrode thickness and the moulding pressure need to be comprehensively evaluated for the preparation of the composite electrode. These fabrication parameters are viewed as significant factors affecting the CDI performance. Actually, the typical optimization and analysis about these parameters of the compression moulding method are scarcely cared and reported in the fabrication process of composite electrode.

In this paper, the typical optimization for the PPy/CNT electrode as a novel composite electrode fabricated by the compression moulding method is first proposed and investigated. The major preparation parameters were optimized, including the mass ratio of the electrode material mixture (PPy/CNT : PVDF : graphite powder), the electrode thickness and the moulding pressure. Based on the compression moulding method, the capacitive behavior of the compressing-type electrode in different preparation conditions was specifically analyzed by the electrochemical characteristics. In particular, the performance of the PPy/CNT electrode was studied in terms of the desalination performance test. Moreover, the mechanical strength of the compressing-type electrode at different pressures was measured to study the effect of the moulding pressure on the performance of the PPy/CNT electrode.

2. Experiments

2.1. Synthesis of PPy/CNT composite

The PPy/CNT composite was synthesized by chemical oxidation method. First, CNT suspending solution was obtained by dispersing CNT into ethanol under ultraphonic oscillation for 30 min. Then the purified pyrrole monomer by distillation with N_2 protection, HCl solution and oxidant $FeCl_3$ were added into the CNT suspending solution orderly and reacted at the temperature of 0°C for 12 h. Finally, the reaction solution was filtered and washed thoroughly with deionized water to collect the product of PPy/CNT composite. The obtained composite was dried under vacuum at 60°C for 24 h.

2.2. Fabrication of PPy/CNT electrode by the compression moulding method

Based on the certain mass ratio, the active materials (PPy/CNT), the binder (PVDF) and the conductive agent (graphite powder) were mixed and grinded adequately. Diverse proportions of the PPy/CNT, PVDF and graphite powder were used to determine the optimal composition of the electrode material mixture. Then the well mixed powders were put into the self-manufactured mould and pressed at a certain pressure for 10 min. Different moulding pressures (5, 10, 15, 20 and 25 MPa) were used to determine the optimum moulding pressure. After mould-releasing, the round PPy/CNT plate with the diameter of 15 mm was adhered on the disposed graphite paper as the current collector to obtain the PPy/CNT electrode. The resulting PPy/CNT plates with different thicknesses (0.2, 0.4, 0.6, 0.8 and 1.0 mm) were obtained by altering the total mass of electrode material mixture. Here, the thickness of the resulting PPy/CNT plates was measured by the vernier caliper.

2.3. Electrochemical characterization

The electrochemical performance of the PPy/CNT composite electrodes was measured by cyclic voltammetry (CV). These electrochemical tests were carried out in 1.0 M NaCl solution by using electrochemical workstation (LK2005) in a three-electrode system, including a prepared electrode as working electrode, a platinum electrode as counter electrode and a standard calomel electrode (SCE) as reference electrode. The CV behaviors were tested within the potential range of –0.2 to 0.6 V vs. SCE and at the scan rate of 0.005 V/s. For the prepared electrode, the specific mass capacitance (C_m, F/g) and specific area capacitance (C_s, F/cm^2) from the CV were calculated by Eqs. (1) and (2), respectively:

$$C_m = \frac{\int_{E_1}^{E_2} i(E)dE}{2mv(E_2 - E_1)} \tag{1}$$

$$C_s = \frac{\int_{E_1}^{E_2} i(E)dE}{2sv(E_2 - E_1)} \tag{2}$$

where E_1, E_2 (V) are the initial and final potential, respectively; i (A) is the response current; v (V/s) is the potential scan rate; m (g) is the mass of active component in the electrode and s (cm^2) is the area of the electrode.

2.4. Flexural strength tests

In order to measure the flexural strength of the PPy/CNT electrodes, three-point bending tests were conducted by the electron universal testing machine. The schematic diagram of three-point bending test is shown in Fig. 1. In this experiment, the electrode samples with the same electrode mass of 0.45 g were prepared at different pressures. The dimension of the electrodes was all 20 mm × 6 mm (length × width) while the thickness of the electrodes prepared at different pressures was distinct. Therefore, the flexural strength of the PPy/CNT electrodes was calculated by the following Eq. (3):

$$\sigma = \frac{3FL}{2bh^2} \tag{3}$$

where σ (MPa) is the flexural strength; F (N) is the maximum load on the electrode sample, which is recorded before fracture; L (mm) is the span between the supports, which is set as 15 mm; b (mm) is the width of the electrode sample and h (mm) is the thickness of the electrode sample.

2.5. CDI performance tests

Fig. 2 shows a schematic diagram of the CDI system used in this study. The CDI cell was assembled with the prepared PPy/CNT electrode as anode and the graphene nanoribbons electrode as cathode, and the desalination performance was tested in a NaCl solution that has an initial conductivity of 1,000 μS/cm. In the experiment, the working voltage provided by the power controller was set as 1.4 V. Regeneration of the electrodes was achieved by interrupting the applied potential. Conductivity of the NaCl solution was monitored and collected in real time during the experiments. In addition, the specific mass adsorption capacity (m_g, mg/g) and specific area adsorption capacity (m_s, mg/cm^2) of the CDI cell were calculated by Eqs. (4) and (5), respectively:

$$m_g = \frac{\alpha\left(k_0 - k_1\right)V}{m} \tag{4}$$

$$m_s = \frac{\alpha\left(k_0 - k_1\right)V}{s} \tag{5}$$

where k_0 and k_1 (μS/cm) are the initial and final conductivity of the NaCl solution, respectively; α is the coefficient bridging between the conductivity and the concentration of the NaCl solution, and is measured as 6.8×10^{-4} mg/(μS·cm^2); V (mL) is the volume of the feed solution; m (g) is the total mass of active materials of the two paired electrodes and s (cm^2) is the total area of the two paired electrodes.

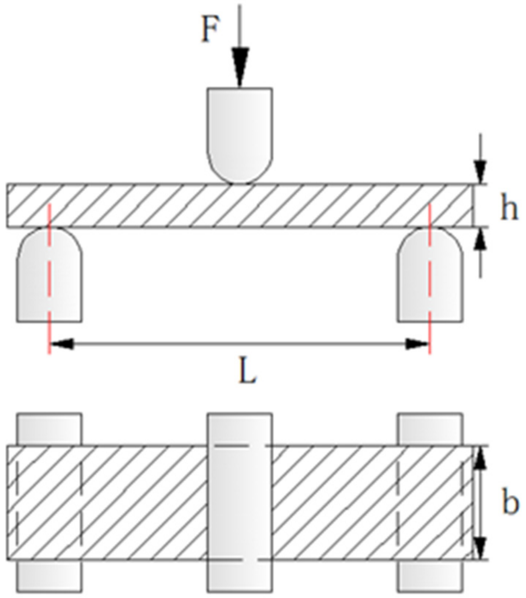

Fig. 1. Schematic diagram of three-point bending test.

3. Results and discussion

3.1. Mass ratio of electrode material mixture

The mass ratio of PPy/CNT, PVDF and graphite powder was investigated to achieve superior electrode performance. These electrode components play different roles in the fabrication and performance of the PPy/CNT composite electrode. Using the compression moulding method, the mass ratio of electrode material mixture was optimized under the moulding pressure of 10 MPa.

The mass ratio of PPy/CNT and PVDF from 3:1 to 15:1 was studied when the mass ratio of PVDF and graphite powder was fixed on 1:1. Fig. 3 shows CV behaviors of the PPy/CNT electrodes as a function of the mass ratio of PPy/CNT and PVDF. The CV curves are similar to each other and present nearly rectangular in shape, which indicate the excellent electrochemical stability and reversibility of the composite electrode [21]. From the CV curves, it can be observed that the electrode prepared with the mass ratio of PPy/CNT and PVDF of 9:1 has larger voltammetric current response compared with those prepared with the remaining mass ratio of PPy/CNT and PVDF, which reveals the higher charge storage capability of the PPy/CNT electrode in the mass ratio of PPy/CNT and PVDF of 9:1. The mass ratio of PPy/CNT and PVDF declines from 9:1 to 3:1 which implies that the PVDF content correspondingly increases. As can be seen from Table 1, the specific mass capacitance of the PPy/CNT electrode decreases with the increase of the PVDF

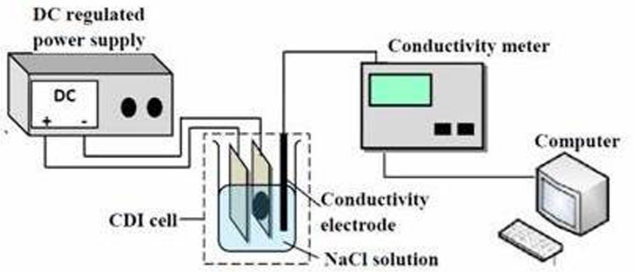

Fig. 2. Schematic diagram of the CDI desalinating system.

content. It indicates that the excessive addition of PVDF will cut down the portion of the active material and weaken the electrode performance in that PVDF without conductivity coats the active material leading to reduction in the ion adsorption sites and the transfer speed of ions and electrons inside the electrode [22]. Conversely, when the mass ratio of PPy/CNT and PVDF rises from 9:1 to 15:1, the specific capacitance of the electrode prepared with less PVDF decreases because poor contact between the active material and current collector will block the transfer of ions and electrons in the electrode. Thus, the specific mass capacitance of the PPy/CNT electrode at the optimal mass ratio of 9:1 for PPy/CNT and PVDF reached maximal value of 57.8 F/g.

In order to evaluate the effect of the proportion of PPy/CNT and PVDF on desalination performance of the PPy/CNT composite electrodes, the desalination tests of the assembled CDI cells were performed at a working voltage of 1.4 V in NaCl solution of 500 mg/L. Considering being doped with small anions, the PPy/CNT composite electrode was specially used as the anode to fully display its pseudocapacitance and an asymmetric cell system using the graphene nanoribbons electrode as the cathode was adopted to carry out the desalination tests [23]. Fig. 4 gives the saturated adsorbing curves of the PPy/CNT electrodes prepared with different mass ratio of PPy/CNT and PVDF. It can be seen that the solution conductivity in the five curves exhibits abrupt decrease followed by a more gradual decrease, to finally reach a plateau which indicates that most charge storage sites are utilized during the early phase of the deionization process and the rate slows approaching saturation around 2,000 s. According to Eq. (4), the specific mass adsorption capacity of the prepared electrodes are calculated and listed in Table 1. As can be seen from Table 1, the electrode for the mass ratio of PPy/CNT and PVDF of 9:1 has the highest specific mass adsorption capacity, followed by 12:1, 3:1, 15:1 and 6:1. Based on the results of the electrochemical tests and desalination tests, the mass ratio of PPy/CNT and PVDF of 9:1 is considered optimal to be employed in the following experiments.

The mass ratio of PVDF and conductive graphite powder from 1:3 to 3:1 was investigated. Fig. 5 shows the CV curves of the PPy/CNT electrodes fabricated with different mass ratio of PVDF and graphite powder. Obviously, the area of the closed CV curves for the mass ratio of PVDF and graphite powder of 1:2 is larger than that of the remaining mass ratio of PVDF and graphite powder within the scope of investigation. The appropriate amount of graphite powder as conductive agent can minimize the negative effect of the insulation of PVDF on the electrode performance. While the high content of graphite powder results in cutting back the effective specific surface area of the electrode because the lubrication of graphite powder promotes the

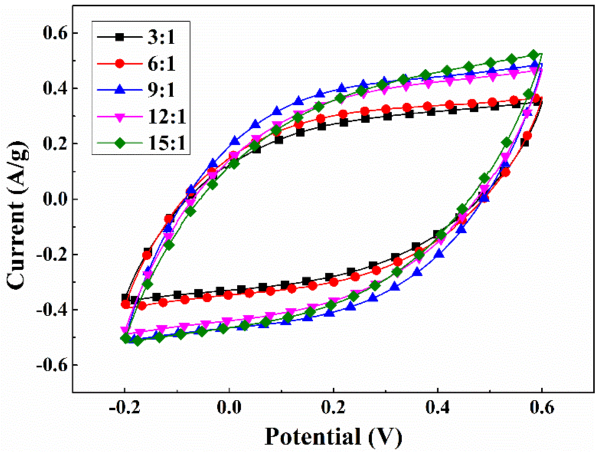

Fig. 3. CV curves of the PPy/CNT electrodes fabricated with different mass ratio of PPy/CNT and PVDF at the scanning rate of 5 mV/s in 1 M NaCl solution.

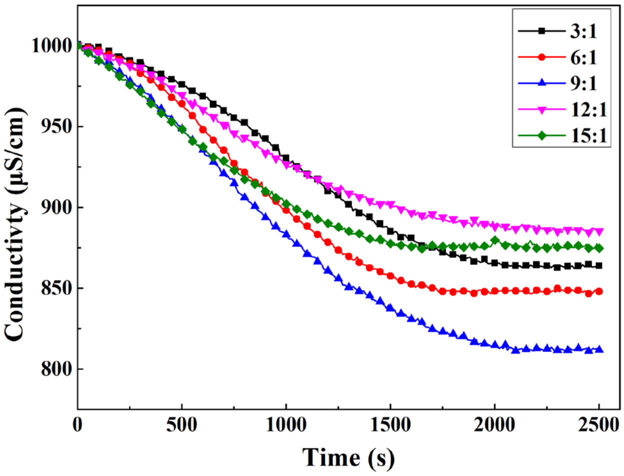

Fig. 4. Saturated adsorption curves of the PPy/CNT electrodes fabricated with different mass ratio of PPy/CNT and PVDF at a working voltage of 1.4 V.

Table 1
Specific mass capacitance and specific mass adsorption capacity of the PPy/CNT electrodes fabricated with different mass ratio of PPy/CNT and PVDF

Mass ratio of PPy/CNT and PVDF	Mass of PPy/CNT electrode active material (g)	Specific mass capacitance (F/g)	Specific mass adsorption capacity (mg/g)
3:1	0.0822	39.9	17.0
6:1	0.0993	43.6	15.6
9:1	0.0824	57.8	23.3
12:1	0.0910	51.5	17.1
15:1	0.0812	52.3	15.8

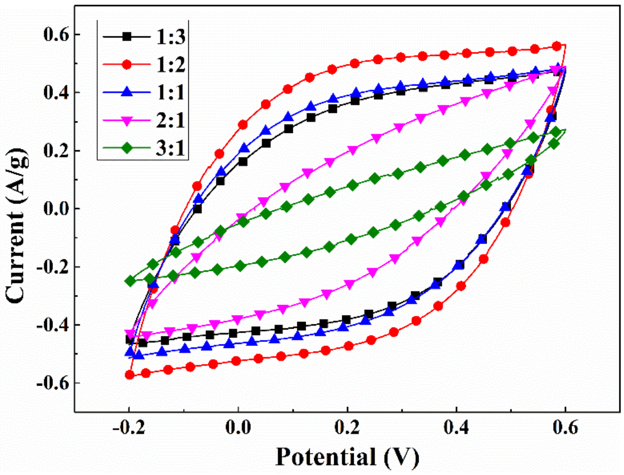

Fig. 5. CV curves of the PPy/CNT electrodes fabricated with different mass ratio of PVDF and graphite powder at the scanning rate of 5 mV/s in 1 M NaCl solution.

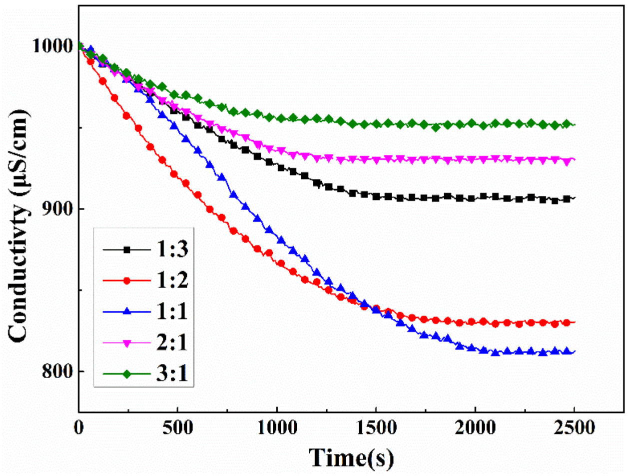

Fig. 6. Saturated adsorption curves of the PPy/CNT electrodes fabricated with different mass ratio of PVDF and conductive graphite powder at a working voltage of 1.4 V in NaCl solution.

relative shift of the electrode material mixture and making the electrode harden in the fabrication process. Since the CV curves are processed based on the current density, the area of the closed CV curves is representative of the specific mass capacitance. Therefore, the specific mass capacitance of the PPy/CNT composite electrode fabricated with the mass ratio of PVDF and graphite powder of 1:2 reaches maximal value of 72.1 F/g. Moreover, it can be observed from Fig. 6 that the declining trend of saturated adsorption curves at different mass ratio of PVDF and graphite powder is similar with that of saturated adsorption curves at different mass ratio of PPy/CNT and PVDF. According to calculations, the electrode for the mass ratio of PVDF and graphite powder of 1:2 has the highest specific mass adsorption capacity (26.8 mg/g), followed by 1:1 (23.3 mg/g), 1:3 (15.7 mg/g), 2:1 (9.9 mg/g) and 3:1 (6.1 mg/g). In conclusion, the optimum mass ratio of PPy/CNT, PVDF and conductive graphite powder is 9:1:2, and its specific mass capacitance and specific mass adsorption capacity can reach 72.1 F/g and 26.8 mg/g, respectively.

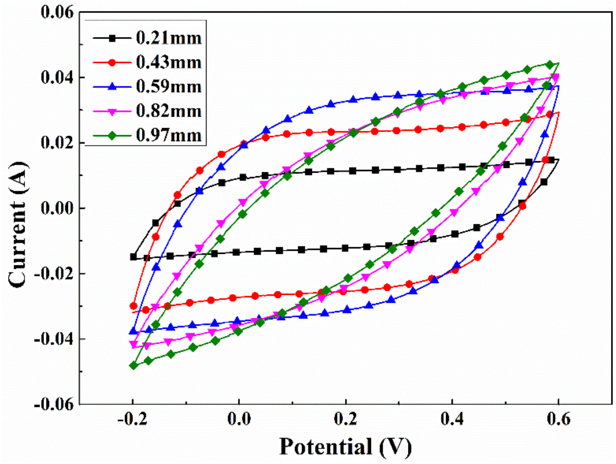

Fig. 7. CV curves of the electrodes with different thickness at the scanning rate of 5 mV/s in 1 M NaCl solution.

3.2. The thickness of the PPy/CNT electrode

The thickness of electrode is an important parameter for the PPy/CNT composite electrode fabricated by the compression moulding method. In the experiment, the PPy/CNT electrode with different thickness from 0.2 to 1.0 mm was prepared and investigated. The CV behaviors of the PPy/CNT electrodes as a function of the electrode thickness are clearly presented in Fig. 7. The difference of shape and area of the closed CV curves reveal that the capacitance of the PPy/CNT electrodes depends on the electrode thickness. For the thickness of the PPy/CNT electrode of 0.2 mm, the shape of the CV curve is nearly rectangular under the test conditions, while the shape becomes gradually distorted as the increase of the electrode thickness, suggesting that the thinner thickness of the PPy/CNT electrode contributes to improve the electrode performance. This can be attributed to the fact that the electrode thickness affect the speed of the ion transfer and the utilization of electrode material. For the thicker electrode, ion penetration is retarded due to a longer pathway inside the electrode which leads to dreadful utilization of the inner electrode material of the electrode. However, the PPy/CNT electrode with smaller thickness has less mass density, which is beneficial to the ion transfer inside the electrode. In Fig. 8, the specific mass capacitance and the specific area capacitance of the PPy/CNT electrodes with different thickness are calculated by Eqs. (1) and (2), respectively. The specific mass capacitance increases from 25.5 to 93.3 F/g as the thickness of electrode declines from 1.0 to 0.2 mm. While the specific area capacitance rises at first and then declines with the increase of the electrode thickness and the specific area capacitance of the electrode with thickness of 0.6 mm reaches maximal value of 5.30 F/cm^2. When the mass of the electrode material in the unit area has obvious difference for various electrodes, the specific mass capacitance can only evaluate the utilization of the electrode material, while the specific area capacitance, defined as the total capacitance per unit area, can reflect the overall capacitance performance of the electrode. Based on the specific mass capacitance, the thinner thickness of the PPy/CNT electrode is beneficial to the utilization of

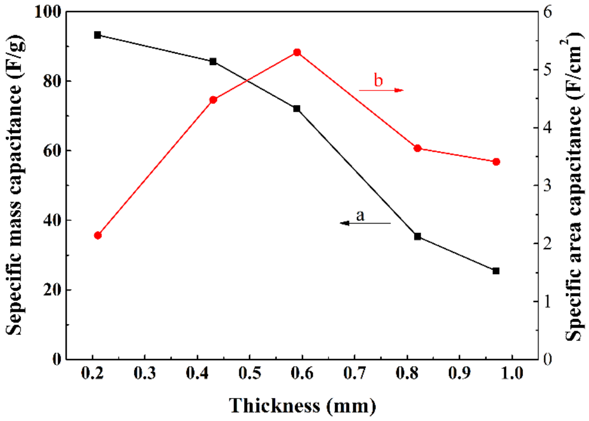

Fig. 8. The specific mass capacitance and the specific area capacitance of the electrodes with different thickness.

the electrode material. Nevertheless, the specific area capacitance of the electrode with the small electrode thickness is low due to the lack of the active material.

In addition, the desalting performance is also investigated for the CDI cell assembled by the prepared electrodes with different thickness. To the best of our knowledge, the deionization capacity has a good linear relationship to the charge capacity evaluated from the capacitance of the electrode [24]. Just as described in Fig. 9, the change of the specific area adsorption capacity is in accordance with that of the specific area capacitance in Fig. 8. The electrode with the thickness of 0.6 mm has the highest specific area adsorption capacity (1.97 mg/cm^2) calculated by Eq. (5). As a result, the electrode thickness of 0.6 mm is considered as the optimal thickness under the experimental conditions. The specific area capacitance and the specific area adsorption capacity reach up to 5.30 F/cm^2 and 1.97 mg/cm^2, and its corresponding specific mass capacitance and specific mass adsorption capacity are 72.1 F/g and 26.8 mg/g.

3.3. The moulding pressure of the PPy/CNT electrode

The mechanical strength for the PPy/CNT composite electrode is closely related to the moulding pressure in the process of tabletting, which directly affects the stability of the PPy/CNT electrode. Before studying the effect of the moulding pressure on the mechanical strength for the PPy/CNT composite electrode, the field-emission scanning electron microscope (FE-SEM) and transmission electron microscopy (TEM) images of CNT (Figs. 10(a) and (c)) and PPy/CNT (Figs. 10(b) and (d)) are measured to characterize the structure of electrode materials after applying the moulding pressure of 25 MPa. From Figs. 10(a) and (b), it can be seen that the CNT and the PPy/CNT materials still remain tubular structure after applying high pressure. And compared with the CNT, the structure of the PPy/CNT composite becomes tighter, which can relieve the PPy chains peeled from the surface of the electrode during doping/de-doping process. Furthermore, the internal structure of the CNT and PPy/CNT materials are presented in TEM images as shown in Figs. 10(c) and (d) indicating that the internal structure is not destroyed in the high pressure and the diameter of the PPy/CNT composite is larger than that of the CNT material. Thus, the pressure cannot cause disruption in the structure of the tubes for the CNT and PPy/CNT materials.

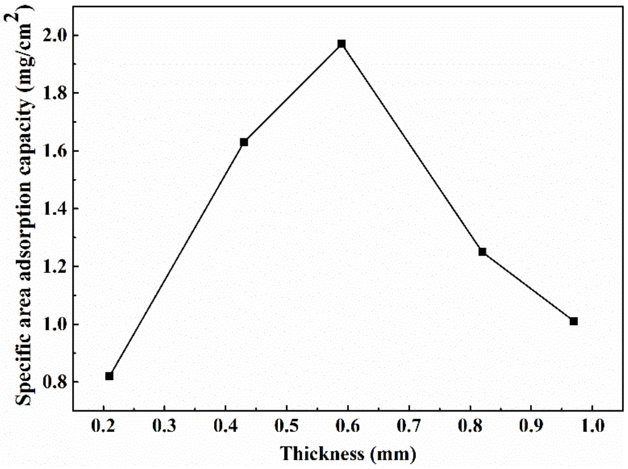

Fig. 9. The change of specific area adsorption capacity of electrodes with different thickness.

In order to evaluate the mechanical strength of the PPy/CNT electrodes fabricated at different moulding pressure, the flexural strength tests of the PPy/CNT electrodes are implemented by the electron universal testing machine at the optimum mass ratio of PPy/CNT, PVDF and graphite powder of 9:1:2 and the same electrode mass. Fig. 11 gives the change of the thickness and bending strength for the PPy/CNT electrodes at the moulding pressure from 5 to 25 MPa. As can be seen from Fig. 11, the electrode thickness declines whereas the mechanical strength increases with the increase of the moulding pressure, illustrating that the firmer electrode material pressed and the increase of the electrode density contribute to enhance the mechanical strength of the PPy/CNT electrodes. In principle, the greater moulding pressure promotes the better mechanical strength for the PPy/CNT electrodes. However, the change of the mechanical strength is not obvious when the moulding pressure is more than 10 Mpa. Also due to the decline of the electrode thickness, the specific surface area of the electrode decreases under the greater moulding pressure. Therefore, the moulding pressure of 10 MPa is considered as the ideal moulding pressure of the PPy/CNT electrode.

4. Conclusions

In this paper, a compression moulding method was adopted for the fabrication of the novel PPy/CNT electrode and a typical optimization on the major preparation parameters was conducted. Based on electrochemical tests and desalination tests, the parameters including the mass ratio of PPy/CNT, PVDF and graphite powder and the thickness of electrode have essential effect on the performance of the PPy/CNT electrode. The PPy/CNT, PVDF and graphite powder play different role in the composite electrode and only these components at the optimum mass ratio of 9:1:2, can their synergistic effect improve obviously the performance of the PPy/CNT electrode. Furthermore, the thinner thickness of the PPy/CNT electrode is beneficial to the utilization of the electrode material. Nevertheless, the specific

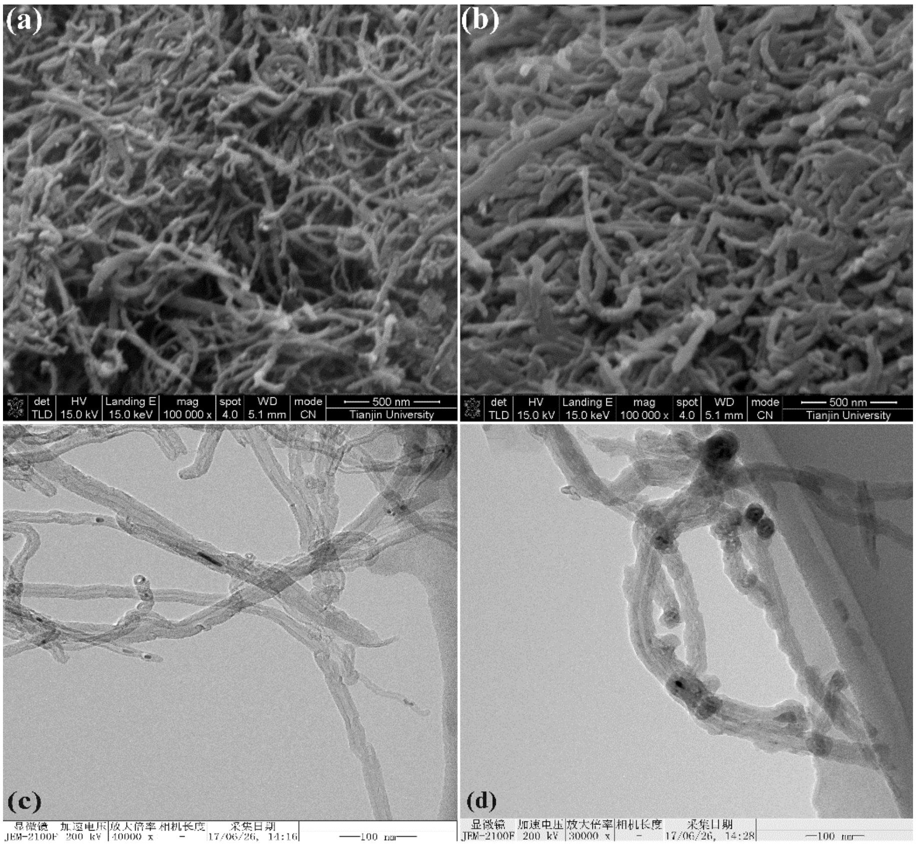

Fig. 10. FE-SEM and TEM images of CNT (a, c) and PPy/CNT (b, d) after applying the moulding pressure of 25 MPa.

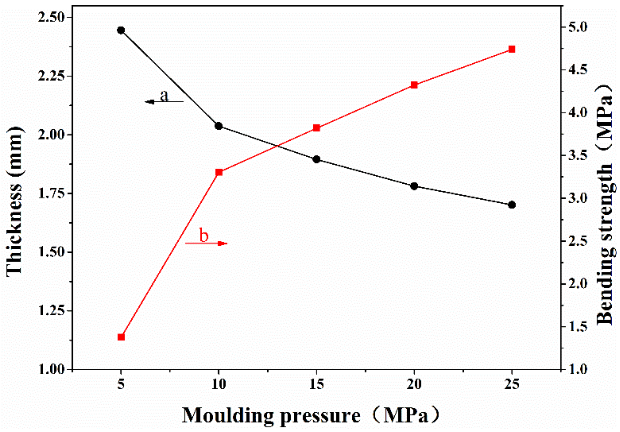

Fig. 11. The change of thickness (a) and bending strength (b) of electrodes fabricated by different moulding pressure.

area capacitance with thin thickness is low due to the reduction of the active material content. So the performance of the PPy/CNT electrode obtains the maximum value, when the thickness of electrode is 0.6 mm. Moreover, the mechanical strength of the PPy/CNT electrodes was measured by the flexural strength test using the electron universal testing machine to evaluate the best moulding pressure under the experimental conditions. The moulding pressure of 10 MPa is considered as the ideal moulding pressure of the PPy/CNT electrode. Therefore, the PPy/CNT composite electrode fabricated by the compression moulding method at the optimum conditions has the highest specific area capacitance of 5.30 F/cm^2 and specific area adsorption capacity of 1.97 mg/cm^2, and its corresponding specific mass capacitance and specific mass adsorption capacity are 72.1 F/g and 26.8 mg/g.

Acknowledgments

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