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Applicable tolerance evaluations of ion-doped carbon nanotube/polypyrrole electrode under adverse solution conditions for capacitive deionization process

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ABSTRACT

In the capacitive deionization (CDI) process, the composites of carbon nanotube/polypyrrole (CNT/PPy) doped with chloride (Cl^-) and dodecyl benzene sulfonate (DBS^-) were respectively made into two types of coating electrode (CNT/PPy-Cl and CNT/PPy-DBS) to evaluate the applicable tolerance of the electrodes under different solution conditions. The effects of the solution conditions, including pH and temperature, on the ion-doped CNT/PPy electrodes were typically investigated in terms of the electrochemical characteristic, the ion adsorption performance and the stability. The results indicated that the appropriate solution conditions of ion-doped CNT/PPy electrodes were with the solution pH 6–9 and the solution temperature 5–25 °C, under which the ion adsorption performance could be at least 75.0% that in the optimum solution conditions (pH = 7, T = 15 °C). For the two electrodes, the poor solution tolerance in the strong acidic and alkaline solution can be ascribed to the interaction of hydrogen ions or hydroxide ions with the electrode structure which affects the conjugate effect between the doped ions and the PPy chains or accelerates the oxidation reactions on the electrode surface. The decrement of the electrode performance with increasing solution temperature from 15 °C to 55 °C mainly arises from the hydrophilic-hydrophobic transition on the surface of electrodes. The research results lay a good foundation for the practical application of CNT/PPy electrodes under different solution conditions.

1. Introduction

With the rapid development of the economy and the increment of water pollution, the fresh water scarcity has accelerated the development of separation technologies to transform seawater into fresh water [1,2]. Capacitive deionization (CDI) technology, as a great potential deionization alternative, has gained considerable attention due to the advantages of efficient energy use, low operational costs, eco-friendliness and high recovery rate [3,4]. In CDI, the removal of salt ions from aqueous solution is largely based on electric double layer (EDL) theory, which associates with charge separation to store and release large quantities of ions on the surface of electrodes [5]. Specifically, during the adsorption process, counter-ions are transported from the feed solution and stored in the electrical double layer region by imposing an applied potential, thus creating a purified stream with the diminished ion concentration. Once the electrodes are saturated, regeneration of the electrodes can be achieved by interrupting or reversing the applied potential to release the previously stored ions back into the bulk solution.

Based on the ion storage mechanism in the adsorption/desorption processes, the desalting performance for the CDI cell largely depends on the electrode materials. Significant efforts have been made with respect to the research of electrode materials, focusing particularly on exploring composite electrode materials [6–9]. Carbon material and conducting polymer as two promising electrode materials can be combined to prepare the composite electrode material. Compared with single electrode material, the composite can effectively enhance the ion adsorption capacity through the synergetic effect that perfectly integrates the excellent electrical conductivity, high surface area and suitable pore size of carbon material, as well as the high specific capacitance, good electron affinity and environmental compatibility of conducting polymer [10,11].

In the composite electrode materials, the ion-doped polypyrrole (PPy) and Carbon nanotubes (CNTs) are respectively considered as the desirable conducting polymer and carbon material [12]. As the typical composites, carbon nanotube/polypyrrole (CNT/PPy) doped with

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DBS^- and Cl^- respectively have been successfully made into two types of composite electrode (CNT/PPy-DBS and CNT/PPy-Cl) for the CDI cell in our research team. The types of dopants make CNT/PPy composite electrode have different ion exchange characteristics, which can promote the co-ions to leave the electrode region in the charging process and avoids the re-adsorption of ions in the discharging process [13]. The CNT/PPy-Cl shows the anion exchange characteristic in that a positive vacancy on the PPy chain is produced due to Cl^- de-doped easily from the electrode. For the CNT/PPy-DBS electrode, the electronegativity of DBS^- itself contributes to adsorb cations in the charging process due to bulky DBS^- de-doped difficultly from the polymer chain. Further investigation has indicated that the optimal configuration of the CDI cell should be with the CNT/PPy-Cl electrode as anode and the CNT/PPy-DBS electrode as cathode (Cell Cl-DBS) and its saturated adsorption capacity is about two times that of the opposite cell configuration (Cell DBS-Cl) [14]. These researches lay the foundation for the follow-up study on the application of the CNT/PPy electrodes.

In attempts to further improve the performance and broaden the application of the CDI cell, numerous studies have been contributed on the design of novel CDI systems, the optimization of the operating parameters and the selective removal of ions [15–20]. With the increasing development of the CDI technology, it is not only applied to the desalination of brackish water and purification of drinking water, but also promisingly expanded for treating the industrial effluents from chemical, pharmaceutical, electroplating, printing and dyeing, etc. [21,22]. The CDI technology used to treat the industrial effluents can avoid generating a large amount of sludge and high cost in comparison with the traditional method (e.g. chemical precipitation) [23].

Using CDI technology, Yuan et al. [24] and Mohan et al. [25] investigated the effect of solution pH on the removal of Cr (VI) from electroplating wastewater and the results demonstrated that the removal efficiencies of Cr (VI) were all over 98% under the acidic condition. Avraham et al. [26] found that it was possible to remove boron from boric acid solution by a simple CDI process where boric acidic could be dissociated to form borate ions on the negative electrode due to the local base near the surface of the polarizing electrodes. Obviously, when treating the industrial effluents, the electrodes of the CDI cell need to be immersed in different solution environments that are usually adverse solution conditions for the electrode. Currently, researches have been only conducted about the effects of operating conditions on the ion removal efficiency in the CDI process. However, few studies focus on evaluating the performance of the CDI electrodes in the adverse solution conditions, namely solution tolerance of the electrodes, which may significantly influence the stability of the electrodes and the CDI system. Therefore, the applicable tolerance of the electrode under different solution conditions becomes a challenge for the time being.

In this paper, the composites of CNT/PPy doped with Cl^- and DBS^- were prepared respectively and made into two types of electrodes (CNT/PPy-Cl and CNT/PPy-DBS) for the CDI process. An experimental Cell Cl-DBS was assembled by configuring the CNT/PPy-Cl electrode as anode and the CNT/PPy-DBS electrode as cathode. Based on the Cell Cl-DBS, applicable tolerance of the novel composite electrodes was investigated and evaluated in terms of the electrochemical characteristic, the ion adsorption performance and the stability under different solution pH and temperature conditions. In addition, the long-term cyclic desalination stability of the Cell Cl-DBS was also tested and analyzed under the optimum solution conditions.

2. Experimental

2.1. Synthesis of the ion-doped CNT/PPy materials

To prepare the CNT/PPy-DBS composite, the chemical oxidation method was used and the strategy is shown in Scheme 1. 0.2 g CNTs were suspended by ultrasonication in 40 mL ethanol for 30 min; then 0.7 mL purified pyrrole monomer under N_2 atmosphere, 0.15 g sodium dodecyl benzene sulfonate (SDBS) as the dopant and 2.28 g oxidant $(NH_4)_2S_2O_8$ were added into the suspending solution in sequence and reacted in the ice-water bath for 12 h. Finally, the precipitate was filtered and washed thoroughly with deionized water and the ethanol in sequence to get the CNT/PPy-DBS composite, followed by a drying process under vacuum at 60 °C. The CNT/PPy-Cl composite was synthesized via the same route except that the SDBS powder was replaced by the 1 M HCl solution. The inserted TEM images in Scheme 1 showed the morphology of CNTs, CNT/PPy-DBS and CNT/PPy-Cl. Compared with CNTs, the ion-doped CNT/PPy composites still maintained nanowire morphology and their average diameter all increased obviously. Moreover, the difference in the external diameter for both CNT/PPy-DBS and CNT/PPy-Cl composites might be due to the different radiuses of the doped ions.

2.2. Fabrication of the ion-doped CNT/PPy electrode

Briefly, to prepare the CNT/PPy-DBS electrode, the electrode slurry was made by mixing CNT/PPy-DBS, polyvinylidene fluoride and graphite powder at the weight ratio of 8:1:1. The N-methyl-2-pyrrolidone was used as the solvent. The obtained slurry was then cast onto a graphite paper and finally dried to remove the organic solvent. The CNT/PPy-Cl electrode was fabricated with the same procedure. The dimension of the experimental electrodes was about 25 mm × 45 mm for the electrochemical measurements and 80 mm × 100 mm for the ion adsorption performance tests.

2.3. Resistivity measurement

Resistivity (as reversed indication of electrical conductivity) of the CNT, CNT/PPy-Cl and CNT/PPy-DBS electrodes was measured by a four-point probe meter and listed in Table 1. The resistivity of the CNT electrode was 0.08 Ω cm, exhibiting excellent electrical conductivity. While the resistivity of the CNT/PPy-Cl and CNT/PPy-DBS electrodes was 0.25 Ω cm and 0.34 Ω cm respectively, which were a little higher than the resistivity of the CNT electrode. So the ion-doped CNT/PPy composite electrodes still remained higher electrical conductivity and could reasonably be used as electrodes. The resistivity of the CNT/PPy-DBS electrode was slightly higher than that of the CNT/PPy-Cl electrode, which can be ascribed to the long chain structure of DBS^-.

2.4. The electrochemical measurements

The electrochemical performance of the ion-doped CNT/PPy electrodes under different solution conditions was analyzed with the cyclic voltammetry (CV) tests. The feed solution was 1 M NaCl solution, and pH of the solution was adjusted by adding appropriate doses of 1 M HCl and 1 M NaOH. The solution temperature was controlled by using a water bath. The CV measurements were performed by a three-electrode system that the CNT/PPy-DBS electrode or CNT/PPy-Cl electrode, platinum electrode and standard calomel electrode (SCE) were used as the working, the counter and the reference electrode, respectively. CV tests were measured at a scan rate of 0.005 V/s in the voltage range of −0.4 to 0.8 V. The specific capacitance (C_m, F/g) of the electrode was calculated by the following equation [27]

$$C_m = \frac{\int_{E_1}^{E_2} i(E)dE}{2mv(E2-E1)} \quad (1)$$

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

The potential of zero charge (E_{PZC}) of the ion-doped CNT/PPy electrodes at different solution pH condition was measured by the differential capacitance tests. In the tests, the frequency and the RMS