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Polyaniline-modified activated carbon electrodes for capacitive deionisation

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HIGHLIGHTS

- The conductivity of AC/PANI was higher than that of the original AC.
- Higher specific capacitance of AC/PANI CV was found.
- Fast ion removal rate was observed.

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ABSTRACT

A composite of activated carbon particles (AC) and the conducting polymer polyaniline (PANI) was synthesised by in-situ polymerisation. The resultant composite was used as electrodes in the capacitive deionisation. The PANI presence was confirmed by Fourier transform infrared spectroscopy (FTIR). The morphology and porous structure were investigated by scanning electron microscopy (SEM) and N_2 adsorption–desorption measurement. Electrochemical behaviour was studied by a cyclic voltammetry (CV) test. The results showed that the electrodes made of the composite had an ion removal capacity of 3.15 mg/g, which was much higher than that of AC only electrodes (1.98 mg/g) at the initial concentration of around 250 mg/L. Moreover, a faster ion removal rate was found for the composite electrodes with an absorption rate constant of 0.67, more than twice as high as the original activated carbon electrodes (0.23). The combination of two materials reduced the number of micropores and increased conductivity. It was believed that PANI formed conducting chains that connected micro-AC particles together and blocked most of the micropores. Weak acid functional groups at the surface of AC acted as dopant for PANI to increase its conductivity. It was found that the ion electrosorption by AC/PANI composite follows the Langmuir adsorption model.

1. Introduction

Activated carbon particles (AC), in its broadest sense, is an amorphous carbon material with a high degree of porosity and an extended inter-particulate surface area as stacks of flat aromatic sheets in a random crosslink manner [1]. Due to its very high surface area and exceptional adsorption capability as well as its low cost, AC has become the most widely used porous material [2]. The use of AC as an electrode material in capacitive desalination dates back to the early 1960s when Caudle and Murphy [3,4] first introduced the technique of making porous carbon electrodes from AC in a flow-through mode desalination system, and more recently by Zou et al. [5]. The focus of study on electrode material for capacitive deionisation turned to other porous carbons [6,7] during the 1990s because of the low conductivity and unavailability of microporous capacity. Recently, novel carbon material much as ordered mesoporous carbon [8], carbon nanotubes [9], graphene [10] and composite of ordered mesoporous carbon and carbon nanotubes [11], composite of graphene and carbon nanotube [12], carbon nanotube/AC composite [13] as well as graphene/AC composite [14] were proved to be promising CDI electrode material. Candidates such as conducting polymer [15] and titania [16] were used as components to improve the capacitance and desalination performance of activated carbon powder. Composites of AC and conducting polymer maintain low costs and possess better electrical conducting property [17].

Among the conducting polymers, polyaniline (PANI) is one of the most highly researched substances because of its extraordinarily electronic optical properties, good processability, environmental stability and ease of synthesis [18]. It has been considered a candidate in microelectronic devices [19], chemical sensors [20,21], drug delivery [22], anticorrosion coatings [23] and energy storage systems [24]. It is in fact also the most frequently used conducting polymer incorporated with various carbon materials [25–27]. Composites of PANI and AC were reported to possess a conductivity of 1.53 S/cm at room temperature,

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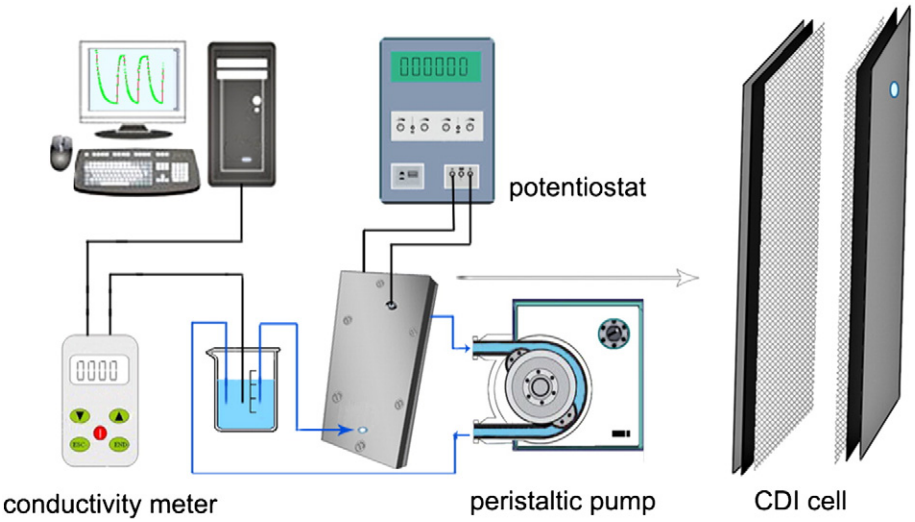

Fig. 1. Illustration of the CDI system.

which was even higher than that of pristine PANI [28]. Bleda-Martinez [29] synthesised an AC/PANI composite to use as an electrode material in a super capacitor. The resultant composite possessed higher specific capacitance than either the AC or PANI electrode alone, indicating that the combination of two components leads to an enhanced electrochemical property. Considering the low cost of bulk AC material, these results were encouraging for the potential application of AC/PANI composites.

In this study, we used an AC/PANI composite as electrode material in capacitive deionisation. To obtain better conductivity, in-situ polymerisation was employed to synthesise an AC/PANI composite. The composite was characterised by scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR). Electrical conductivity was studied by the four-point probe method. Electrochemical property was investigated through cyclic voltammetry (CV) measurement and electrochemical impedance spectra (EIS). The ion electrosorption isotherms were studied by fitting the Langmuir adsorption model.

2. Experimental

2.1. Materials

AC was supplied by Activated Carbon Technologies PTY Ltd. Aniline (AR grade), ammonium persulphate (APS), polytetrafluoroethylene (PTFE; 60% water solution), graphite powder (<20 μm) and ethanol were purchased from Aldrich Co., Ltd. Hydrochloric acid (HCl) was purchased from Merck Pty. Ltd. Deionised Milli-Q water (18.2 MΩ cm, Millipore Corporation, France) was used in all the experiments.

2.2. Synthesise AC/PANI composite

In-situ polymerisation procedures were carried out according to reported method [30]. Briefly, 0.45 g AC was dispersed in 80 mL 1-molar (M) HCl solution assisted by ultrasound for 30 min; 46 μL aniline monomer was dissolved in 10 mL 1 M HCl; 0.1141 g APS was also dissolved in 10 mL 1 M HCl. Then, aniline monomer solution was added to the AC suspension and ultrasonicated to allow the attachment of aniline to the surface of AC. Following that, APS solution was added to the mixture of AC and aniline as an oxidant to initiate polymerisation. The reaction solution was shaken vigorously for 10 s and left in ultrasound for 3 h at 0 degrees Celsius (°C). Finally, the reaction mixture was centrifuged and washed three times with deionised water to obtain an AC/PANI composite. Neat PANI samples were synthesised according to parallel procedure and used as a reference in the characterisation of the composites.

2.3. Characterisation

The morphology of the initial AC and the resulting AC/PANI composite were characterised by SEM (Philips XL20). The specific surface areas and pore size distributions were determined by N_2 adsorption–desorption method using a Belsorp system (BEL Japan, Inc.). Specific surface areas and mean pore diameter were calculated by Brunauer–Emmett–Teller (BET) method. FTIR (PerkinElmer Ltd. UK) was used to identify both components in the composite by the attenuated total reflectance (ATR) measurement mode at a resolution of 4 cm^{-1} with 32 scans.

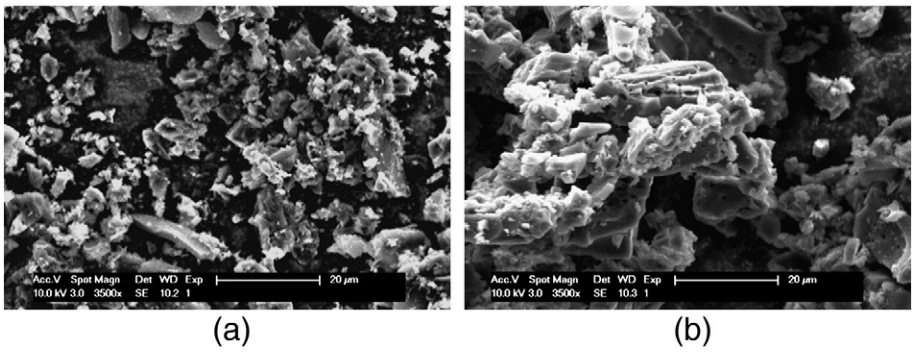

Fig. 2. SEM images of neat AC (a) and the AC/PANI composite (b).