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Preparation of nano-TiO_2/activated carbon composite and its electrochemical characteristics in non-aqueous electrolyte

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ABSTRACT

The composite of nano-TiO_2/activated carbon (ACT) was prepared by hydrolytic precipitation of TiO_2 from $TiCl_4$ in a mixed aqueous solution containing activated carbon and followed by calcination at 450 °C. The physical characteristics of the activated carbon and ACT composite have been studied by X-ray diffraction (XRD), scanning electron microscopy (SEM), X-ray photoelectronic spectroscopy (XPS) and nitrogen adsorption–desorption measurements at 77 K. Three electrode systems with lithium metal as reference electrode were assembled to study the electrochemical performance of ACT composite and the activated carbon. It is found from galvanostatic charge–discharge tests that the mass specific capacitance and the area specific capacitance of ACT composite in the electrolyte of 1 M $LiPF_6$–ethylene carbonate (EC)/diethyl carbonate (DEC)/dimethyl carbonate (DMC) increase by 20% and 50%, respectively compared to the pure activated carbon on average. The a.c. impedance spectra show that the ACT composite electrode has higher interfacial electron transfer resistance (R_t) but lower equivalent series resistance (R_s) than the pure activated carbon electrode has. Therefore ACT composite is a promising electrode active material for electrochemical capacitors.

1. Introduction

Activated carbon (AC) has many favorable characteristics, such as high specific surface area, good chemical stability, high conductivity, benign to environment, rich source in nature and low cost, so mostly it is the first choice as electrode materials for electrochemical capacitors [1–5]. The low energy density of electrochemical capacitors based on activated carbon is the main drawback compared to batteries, especially in aqueous electrolytes with relatively low decomposition voltages (theoretically only 1.23 V). Therefore non-aqueous electrolytes with the larger decomposition voltages (3–5 V) which are available for the higher operating voltages (U), are often used in the electrochemical capacitors to enhance the energy density ($E = 1/2\,CU^2$) [6]. However, the specific capacitance (C) of activated carbon in non-aqueous electrolytes is lower than that in the aqueous electrolyte because of the limitation of electrolyte ions size [6,7], which makes against further enhancement of the energy density for the electrochemical capacitors. In order to increase the specific capacitance of activated carbon in the non-aqueous electrolytes, one of the most important methods is that pseudocapacitance metal oxides ($LiFePO_4$, $LiMn_2O_4$, $LiCoO_2$ and so on) [8–10] are used to dope activated carbon. But the electrochemical resistance also increases a lot, which goes against the high power characteristic of electrochemical capacitors.

Therefore, in order to enhance the specific capacitance and avoid the resistance boosting much of activated carbon in the non-aqueous electrolytes, we employed a nano-metal oxide without electrochemical activity or without electrochemical activity in the range of working potentials to dope activated carbon for nano-metal oxide/AC composite. On the basis of our previous work [11], we prepared nano-TiO_2/activated carbon composite (ACT) via in-site chemical synthesis and utilized three electrode systems to study the capacitance property of ACT composite in non-aqueous electrolyte accurately. Meanwhile, the resistance property of ACT composite was studied by electrochemical impedance spectroscopy compared to pure activated carbon.

2. Experimental

2.1. ACT composite material preparation

In present work, nano-TiO_2/activated carbon composite was prepared by in situ chemical precipitation method. The sample was synthesized by following procedures: 0.75 mL $TiCl_4$ was slowly dipped into 10 mL ethanol solution, followed by the addition of 150 mL water and mechanical stirring. Then 4.2 g commercial activated carbon was added into the homogeneous $TiCl_4$ ethanol–water solution, which was

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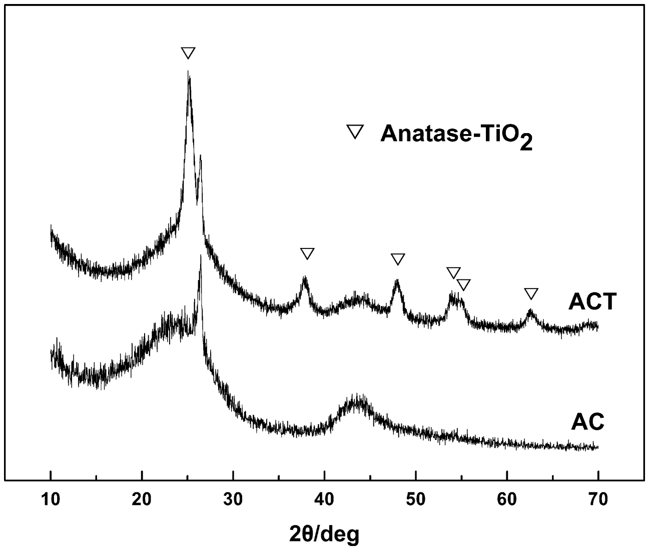

Fig. 1. The XRD patterns of AC and ACT composite.

continuously stirred for 12 h at room temperature. The mixture was heated at 90 °C for 2 h, cooled to room temperature and filtered. The solid material was heated to 450 °C from room temperature within 1 h and kept for 4 h in the air to give the composite that is noted as ACT.

2.2. Materials characterization

The microstructures of samples (AC and ACT composite) were examined by the Philips X'pert powder X-ray diffraction (XRD) with Cu Kα1 radiation. The surface morphologies of the samples were characterized by environmental scanning electron microscopy (SEM) instrument, JEOL JSM-6700F. The physical and chemical properties of surface species (C, O) in the samples were studied by the X-ray photoelectronic spectroscopy (XPS), VG ESCALAB MK II. Mg Kα (1253.6 eV) radiation was utilized as the X-ray source. And the spectra were deconvoluted according to Gaussian function on a Shirley-type background. The measurements of specific surface area and pore structure of the samples were carried out on an AUTOSORP ZXF-6 instrument by N_2 adsorption–desorption at 77 K. The specific surface area was taken from N_2 adsorption using Brunauer–Emmett–Teller (BET) equation. Pore volume was determined by the cumulative adsorption, and the pore size distribution was calculated from the adsorption isotherm with the BJH method.

2.3. Preparation of testing systems and electrochemical measurements

A uniform slurry consisting of 74 wt.% active material (AC or ACT), 14 wt.% acetylene black and 6 wt.% graphite as electronic conductors, 6 wt.% LA132 (from Indigo, China) as a binder and some water was pasted onto an aluminum foil. The sheet was cut into discs of 10 mm in diameter after the coated materials were dried under an infrared lamp, and then the discs were continually dried in a vacuum oven at 85 °C for 4 h.

The prepared electrode discs of ACT and AC (as working electrodes), AC electrodes (as counter electrodes), lithium metal (as reference electrode) and polypropylene (PP) film (Celgard 2400, as separator) were utilized to assemble ACT–AC and AC–AC three electrode cells, and the electrolyte of 1 M $LiPF_6$–ethylene carbonate (EC)/diethyl carbonate (DEC)/dimethyl carbonate (DMC) (1:1:1, w/w) mixture solution was added. All the cells were assembled in glovebox filled argon with humidity lower than 0.5%. The Neware Battery Testing System was employed to perform galvanostatic charge–discharge at a current of 0.25 mA cm^{-2} between 2.4 and 4.3 V versus Li^+/Li. Electrochemical impedance spectroscopy (EIS) measurements were carried out with a Solartron 1255B frequency response analyzer combined with a Solartron 1287 electrochemical interface, and the measurements were conducted over a frequency range from 1 MHz to 0.1 Hz with 5 mV rms amplitude.

3. Results and discussions

3.1. Physical characteristics

From the X-ray diffraction patterns of the activated carbon and ACT composite (shown in Fig. 1), it is found that the structure of activated carbon in ACT composite has no obvious change, and the diffraction peaks (▽) show the anatase of TiO_2 contained in ACT composite according to the JCPDS 21-1272. The crystallite size of TiO_2 is determined by means of the Scherrer equation expressed as follows:

$$d = \frac{0.9\lambda}{\beta \cos \theta} \tag{1}$$

where d is the crystallite size, λ is the X-ray wavelength (1.5406 Å), θ is the Bragg diffraction angle, and β is the full width at the half maximum of the diffraction peak. The crystallite size of TiO_2 is about 11.4 nm calculated from Eq. (1) for [1 0 1] direction.

Fig. 2 shows the scanning electron microscopy images of the activated carbon (a) and ACT composite (b). It can be seen from the images that a lot of nano-TiO_2 particles (proved by XRD) are deposited on the surface of activated carbon in ACT composite, and the size of nano-TiO_2 particles is about 12 nm on average which is close to the result calculated from XRD. It is also found that the nano-TiO_2 particles have the better distribution. In the process of ACT composite preparation, the stable homogeneous $TiCL_4$ ethanol–water solution is prepared initially. When the activated carbon is added, the ions of Ti^{4+} can evenly diffuse into the surface of activated carbon. Thus the nano-TiO_2 particles can uniformly precipitate on the surface of activated carbon as mixed solution is heated. But it is difficult to disperse metal oxides particles on the surface of activated carbon uniformly by mechanical mixing [11].

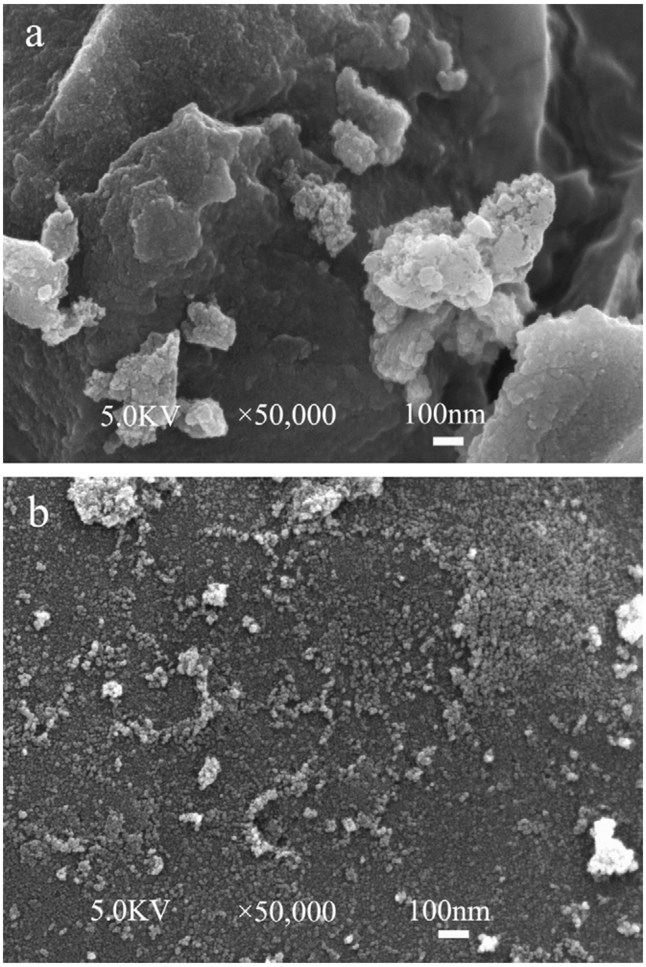

Fig. 2. The SEM images of AC (a) and ACT composite (b).