The electrocapacitive properties of polyaniline/VXC-72 composite electrodes

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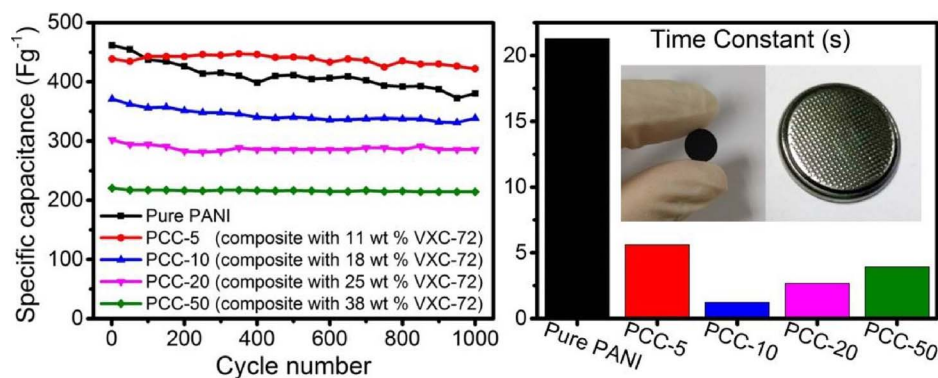
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While polyaniline holds a great promise as an electrode material for pseudocapacitors, its poor stability against charge/discharge hinders its practical applications. In this work, polymerization of aniline was conducted in the presence of commercial carbon black VXC-72 to prepare polyaniline/VXC-72 composite electrodes. Results showed that the stability of the polyaniline/VXC-72 composite electrode was drastically improved with over 90% capacitance retention after 10,000 cycles at a current density of $2 \, A \, g^{-1}$. It was found that VXC-72 particles played an important part in the chemical oxidative polymerisation process – they served not only as nucleation sites on which polymerization underwent to form polyaniline but also determined the morphology of the resultant solid product. The polyaniline/VXC-72 composite electrode materials with different contents of VXC-72 exhibited different morphologies and electrocapacitive performances. This research provides guidelines for designing polyaniline-carbon black composite electrode materials with an excellent stability against cycling, high capacitance, and low cost.

1. Introduction

Supercapacitors (SCs) are electrochemical energy storage devices that bridge conventional capacitors and batteries [1]. SCs store energy via two mechanisms, namely the electric double layer (EDL) mechanism due to charge adsorption at the electrode/electrolyte interface and the pseudocapacitive mechanism due to faradaic redox reactions at the electrode surface [1–4]. Porous materials that can conduct electron such as activated carbon are commonly used as the electrode for fabricating EDL capacitors while transition metal oxides and conducting polymers are the common choice for fabricating pseudocapacitors [5–7].

Polyaniline has been studied for electrocapacitive energy storage due to its high capacitance [8,9]. Polyaniline electrode materials with specific capacitances in the range of $140 - 1700 \, F \, g^{-1}$ have been reported [2,3]. However, pure polyaniline exhibits a poor stability against cycling due to significant change in structure conformation during the fast charge/discharge process [9,10]. To solve this problem, various solid materials have been used to stabilise polyaniline to make composite electrodes with improved electrocapacitive performance [9–19]. For examples, polyaniline grown on expanded graphite showed a specific capacitance as high as $1665 \, F \, g^{-1}$ at a current density of $1 \, A \, g^{-1}$ with a capacitance retention of 87% after 2000 cycles at a scan rate of $100 \, mV \, s^{-1}$ measured using a three-electrode system [15]. Polyaniline-graphene nanoribbon composites exhibited a specific capacitance of $340 \, F \, g^{-1}$ with 90% capacitance retention over 4200 cycles [16]. Polyaniline thin films coated on three-dimensional ordered macroporous carbon exhibited a specific capacitance of $1490 \, F \, g^{-1}$ at the current density of $0.5 \, A \, g^{-1}$ with 85% capacitance retention after 1000 cycles at $1.5 \, A \, g^{-1}$ [10].

In this work, Cabot carbon black VXC-72 was used to prepare polyaniline-based composite electrodes. Experimental results showed that in the presence of a small amount of VXC-72, the electrochemical stability of polyaniline was significantly improved while its capacitance was largely maintained. The charge transfer resistance of the composite based supercapacitors decreases first and then increase with the continuous increase of VXC-72 in the composites.

2. Experimental section

2.1. Materials and regents

The chemicals, including aniline, ammonium persulfate (APS), hydrochloric acid (HCl) and sulphuric acid (H_2SO_4) were of analytical grade (Sinopharm chemical Reagent Company) and used without further purification. Cabot carbon black VXC-72 was purchased from Cabot Corporation. Ultrapure water was used in the preparation of samples and electrochemical measurements.

2.2. Synthesis of polyaniline/VXC-72 composites

Polyaniline/VXC-72 composite samples were prepared using the *in-situ* chemical oxidative polymerization method [20]. X mg of VXC-72 (X was varied from 5 to 50) was added to 50 mL of $1 \, mol \, L^{-1}$ HCl solution under sonication for 30 min. Subsequently, 0.1 mL of aniline was added to the above mixture, followed by placing in an ice bath under stirring. 0.25 g of APS dissolved in 10 mL of $1 \, mol \, L^{-1}$ HCl was added drop wise to the mixture using a peristaltic pump at $3 \, mL \, h^{-1}$. Finally, the precipitate was collected by centrifugation, washed with ultrapure water and ethanol several times, and dried in a vacuum oven at 60 °C for 10 h. The samples thus obtained are designated as PCC-X. For comparison purpose, a pure polyaniline was also synthesized using the method as described above except for without adding VXC-72.

2.3. Characterization

X-ray diffraction (XRD) patterns were collected on a Rigaku Ultima IV with Cu-Kα radiation (λ = 0.154 nm). Raman spectra were collected using a Renishaw inVia Plus Micro-Raman spectroscopy equipped with a 50 mW DPSS laser at 532 nm. Thermogravimetric analysis (TGA) was performed with a Mettler Toledo TGA-2 thermal gravimetric analyzer under an air atmosphere with a heating rate of $10 \, ^{\circ}C \, min^{-1}$. The morphologies of the samples were examined by using a JEOL JSM-7800F scanning electron microscope (SEM) and a JEOL JEM-2100 plus transmission electron microscope (TEM). Fourier transformation infrared (FTIR) measurements were carried out with a Nicolet iS5 FTIR spectrophotometer using the KBr method.

2.4. Electrochemical measurements

The electrodes were prepared by mixing 5 wt% PTFE, 10 wt% acetylene carbon black and 85 wt% active material and pressed onto a stainless mesh current collector. Then, the electrode was dried in a vacuum oven at 60 °C for 10 h. The mass (m) of active material on the single electrode sheet is ∼ 2 mg. All the electrochemical measurements were carried out with a symmetric two-electrode configuration with $0.5 \, mol \, L^{-1} \, H_2SO_4$ as the electrolyte. The voltage range of cyclic voltammetry (CV) and galvanostatic charge-discharge (GCD) measurements was 0–0.7 V. The electrochemical impedance spectra (EIS) were measured in the frequency range from 0.01 Hz to 100 kHz with the AC voltage amplitude 5 mV versus open-circuit voltage. All the electrochemical measurements were performed by a CHI760E electrochemical workstation (CH Instrument, USA) at room temperature.

3. Results and discussion

Symmetric SCs based on pure polyaniline and polyaniline/VXC-72 composites (PCC-X) were assembled and tested using different electrochemical techniques. Fig. 1 and S1 show the CV curves of the SCs measured at different scanning rates ranging from 5 to $100 \, mV \, s^{-1}$ in $0.5 \, mol \, L^{-1} \, H_2SO_4$ electrolyte. The CV curves of the PCC-X-based SCs (denoted hereinafter as SC-PCC-X) all displayed two pairs of redox peaks, especially at low scan rates. The first pair of redox peaks (O_1/R_1) were due to redox transformations between a semiconducting state (leucoemeraldine form) and a conducting state (emeraldine form) of polyaniline, and the second pair of redox peaks (O_2/R_2) was very weak, ascribed to the Faradaic transformation between the emeraldine form and the pernigraniline form [18,21–23]. The CV curves were almost in rectangular shape at scan rates of 10 and $20 \, mV \, s^{-1}$, in which one or two pair of redox peaks appeared. With increasing scan rates, the oxidation peak shifted to the high-voltage region, and the reduction peak shifted to the low-voltage region. The diffusion of electrolyte ions determines the rate of oxidation of polyaniline. As the scan rate was increased, the rapid potential change enabled little kinetic-controlled Faradaic reactions, and the polarization of polyaniline became quite severe, leading to the increase of electrolyte resistance inside the porous electrode [10,24,25]. These caused the peak shifting, broadening or disappearing with the increase of the scan rate. On the other hand, it is seen that the change of the CV curves became less and less affected by increasing the VXC-72 content in the composite electrodes with increasing the scan rate, implying that the presence of VXC-72 in the composite materials favoured the rate performance, which is an important property of SC electrode materials.

The potential differences ($\triangle E$) between the oxidation and reduction peaks, representing the reversibility of redox reactions, were different among the SC-PCC-X cells [26]. The values were 100 mV for SC-PCC-5, 89 mV for SC-PCC-10, 71 mV for SC-PCC-20 and 70 mV for SC-PCC-50, while it was 158 mV for SC-PANI. These observations indicate that the reversibility of the redox peaks of the PCC-X electrodes is higher than that of pure PANI electrode and the reversibility improvement is