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A hydroquinone redox electrolyte for polyaniline/SnO_2 supercapacitors

Yinhai Zhu, Enhui Liu*, Zhenyu Luo, Tiantian Hu, Tiantian Liu, Zengpeng Li, Qingling Zhao

Key Laboratory of Environmentally Friendly Chemistry and Applications of Ministry of Education, College of Chemistry, Xiangtan University, Hunan, 411105, P.R. China

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ABSTRACT

In order to achieve high specific capacitance of polyaniline/SnO_2 (PANI/SnO_2) supercapacitors, utilizing hydroquinone (HQ) as redox electrolyte for PANI/SnO_2 supercapacitors was reported. In this redox electrolyte, the specific capacitance was heightened by 356 F g^{-1}, reaching 857 F g^{-1} with a specific energy density of 116.6 Wh kg^{-1} at an applied current of 0.5 A g^{-1}. Long-term cycling experiments performed showed good stability with retention of the initial capacitance values of 81.2% after 2000 galvanostatic cycles. The remarkable results presented here illustrate that the HQ redox electrolyte was a facile and straight forward approach to improve the performances of PANI/SnO_2 supercapacitors.

1. Introduction

In recent years, electrochemical supercapacitors have been recognized as key energy efficiency devices for rapid energy storage and delivery due to their high power density, long life cycle, high efficiency, wide range of operating temperature, environmental friendliness, and safety [1–5]. With these advantages, supercapacitor have become very competitive for applications such as electric hybrid vehicles, digital communication devices such as mobile phones, digital cameras, electrical tools, pulse laser technique, uninterruptible power supplies, and storage of the energy generated by solar cells. However, several challenges such as low energy density, high cost, and high self-charge rate have limited its wider applications [6]. Regarding low energy density, one of the major limitations is induced by the low specific capacitance of the supercapacitor. Consequently, the development of high specific capacitance supercapacitor has become the focus of present study.

It is well known that electrode materials and the electrolyte used are particularly critical in determining the performance of supercapacitors. At the current state of technology, pseudocapacitance materials such as metal oxides and conducting polymers are the most practical materials for supercapacitor electrode. These materials have higher capacitive nature than carbon materials with electrical double-layer mechanism. Nowadays, great interests are shown by researches on the incorporation of conducting polymers and metal oxides to improve the energy stored in supercapacitors [7–10]. Among the metal oxides electrode materials, SnO_2 with the advantages of low cost, efficient semiconducting nature and environmental safety has been applied extensively [11–13]. The advantages of easy synthesis, cost-effective and good conductivity make polyaniline (PANI) become a unique and promising polymeric material with great potential applications in supercapacitors [14–17]. But it suffers from the poor electrochemical cyclebility. Currently many approaches have been taken to overcome these disadvantages through synthesizing composite material of PANI/SnO_2 [18–20]. Such a hybrid material can possess both the advantages of the two moieties.

Another factor that affects the performance of supercapacitors is the electrolytes used. To date, inorganic electrolytes as well as organic electrolyte solutions are used for assembly of supercapacitors greatly. However, these two kinds of conventional electrolytes are difficult to fulfill higher capacitance. Adding redox mediator such as, hydroquinone (HQ) [21], indigo carmine (IC) [22], p-phenylenediamine (PPD) [23] or methylene blue (MB) [24] into conventional electrolytes is a highly efficient and low cost alternative route to enhance supercapacitor capacitance because these redox mediator can bring enormous capacitive contributions and enhance energy densities for supercapacitor systems through the reversible Faradic reactions. To the best of our knowledge, until

* Corresponding author.
E-mail address: liuenhui99@sina.com.cn (E. Liu).

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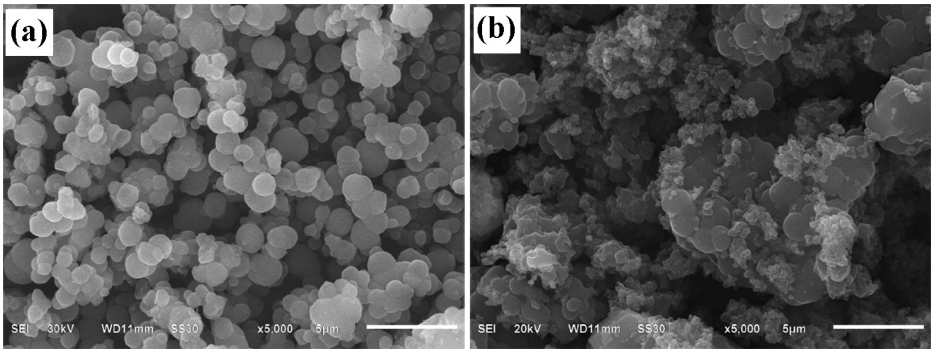

Fig. 1. SEM images of the as-prepared (a) SnO_2 and (b) PANI/SnO_2.

recently, redox electrolyte for PANI/SnO_2 supercapacitors has not yet been reported.

Herein, the redox mediator (HQ) is introduced directly into conventional H_2SO_4 aqueous electrolyte to form a redox electrolyte for PANI/SnO_2 supercapacitors. The quick redox processes happening in the electrolyte contribute additional pseudocapacitance to the supercapacitor system. Morphological and structural characterizations of the prepared samples were carried out using scanning electron microscope (SEM); power X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR). The electrochemical properties of the supercapacitor were investigated by cyclic voltammetry (CV), galvanostatic charge-discharge (GCD), and electrochemical impedance spectroscopy techniques (EIS).

2. Experimental

2.1. Electrode material

SnO_2 was synthesized based on the hydrothermal route. In a typical synthesis, 2 mmol oxalic acid and 2 mmol cetyltrimethyl ammonium bromide was dissolved in 50 ml deionized water, then, 2 mmol $SnCl_2{\cdot}2H_2O$ was added to this solution under constant stirring to get a milky solution. The pH of the resulting solution was adjusted to 9 using dilute $NH_3{\cdot}H_2O$. Then, the mixed solution was stirred for 2 h at room temperature. Finally the obtained milky solution was transferred into an 80 mL teflon-lined stainless steel autoclave. The autoclave was maintained at 150 °C for 10 h and then was cooled to room temperature. The final product was collected and washed with distilled water and absolute ethanol for several times, and then was dried in vacuum at 60 °C for 12 h.

The PANI/SnO_2 composites were prepared as follows: aniline was distilled under reduced pressure before use. 5 mmol oxalic acid was dissolved in 50 mL deionized water, Then, 0.5 mmol SnO_2 and 5 mmol aniline were dispersed in above solution and stirred for 30 min to facilitate aniline to adsorb on the SnO_2. Upon stirring, 5 mmol ammonium persulfate was separately dissolved in 50 mL deionized water and finally added to the above mixture, cooled to 0-5 °C, and then kept in a polymerization for 8 h. The resulting powders were filtered and washed successively with water until the filtrate was colorless, and then dried at 50 °C overnight under vacuum.

2.2. Electrolytes

All of the solutions were prepared using analytical grade reagents and used immediately after their preparation. 0.1 M or 0.4 M HQ dissolved in 1 M H_2SO_4 made up the redox electrolyte. 1 M solution of H_2SO_4, was also studied for comparative purposes.

2.3. The characterization of materials

Scanning electron microscope (SEM) measurements were performed on a JEOL JEM-3010 scanning electron microscope. X-ray diffraction patterns (XRD) were recorded on a D/MAX-3 C diffractometer with Cu Ka radiation (λ = 1.541 Å). The Fourier transform infrared spectra (FTIR) were recorded on a spectrometer (NEXUS870, Nicolet).

2.4. Electrode preparation and electrochemical characterization

The electrode was prepared by mixing 80 wt.% of PANI/SnO_2 powder with 10 wt.% acetylene black conductor and 10 wt.% polivinylidene fluoride emulsion to form slurry. The slurry was filled into a piece of stainless steel net with a geometric diameter of 11 mm. The mass of the single electrode active material was approximate 4 mg. All the electrodes were dried in a vacuum oven at 110 °C overnight before each experiment. Electrochemical testing for supercapacitor was performed on a CHI 660A electrochemical workstation system (CHI Inc., USA) under ambient conditions. CV, GCD, EIS, and cycle life test were carried out to assess the electrochemical properties of the devices. CV experiments were performed at varying scan rates. GCD was conducted with different current densities. EIS was performed on a fully discharged cell by sweeping frequencies from 100 kHz to 0.01 Hz at amplitude of 5 mV. The cycling performance was charged and discharged at a constant current density of 0.5 A g^{-1} on a Neware BTS cell test apparatus.

The capacitance (C, F g^{-1}), energy density (E, Wh kg^{-1}) and powe density (P, W kg^{-1}) of the electrode are calculated according to the following formulas [25,26]:

$$C = 2\frac{I \times \Delta t}{\Delta V \times m} \quad (1)$$

$$E = \frac{C\Delta V^2}{2} \times \frac{1000}{3600} \quad (2)$$

$$P = \frac{E}{\Delta t} \times 1000 \quad (3)$$

Here, I (A) is the discharge current, m(g) is the mass of active material, Δt (s) is the discharge time, ΔV (V) represents the voltage change during the corresponding discharge time.

3. Results and discussion

The morphologies of SnO_2 and the PANI/SnO_2 nanocomposite were investigated by SEM. The results are displayed in Figure 1. From Figure 1 (a), it is observed that the pure SnO_2 are well dispersed and are of spherical shape with uniform diameter lying in the range from 0.8 to 1.6 um. For PANI/SnO_2 nanocomposite, as