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RAPID COMMUNICATION

In situ hydrothermal growth of ferric oxides on carbon cloth for low-cost and scalable high-energy-density supercapacitors ☆

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Abstract
Nowadays, supercapacitor devices employed in the practical application have been growing rapidly, ranging from consumer electronics and hybrid electric vehicles to industrial electric utilities. However, there are certain disadvantages in the supercapacitors, including low energy density and high production cost, which are still considered to be tremendous challenges in their developments. Herein, a new kind of high-energy-density symmetric supercapacitor, energy density of 11.0 mWh cm^{-3} and power density of 1543.7 mW cm^{-3}, has been designed using 2.0 M Li_2SO_4 aqueous solution as the electrolyte and carbon cloth (CC) with α-Fe_2O_3 nanoneedles grown on (CC/Fe_2O_3) as electrode materials. Furthermore, the fabrication of this kind of supercapacitor is low-cost, easily operational, environmentally friendly, practicable, and scalable, which indicates this method is feasible to fabricate cost-effective high-energy-density supercapacitors.

Introduction

Currently, supercapacitors (also called ultracapacitors, electrochemical capacitors) can achieve a much higher power delivery or uptake for shorter times than the conventional capacitors [1–3], but nevertheless, they still suffer from low energy density [4]. Therefore, one of the

☆Supporting information available. SEM images; nitrogen adsorption and desorption isotherms; EDS; XRD; galvanostatic charge-discharge curves; electrochemical impedance spectroscopy; cycling performance; *ex-situ* XRD analysis and Raman spectra.

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most crucial aspects in the development of supercapacitors is to enlarge their energy density meanwhile retaining their intrinsic high specific power [5,6]. In order to satisfy such pressing requirements, multicomponent capacitor materials combining pseudo-active species and high conductive substrate including active carbon [7,8], graphite [9], carbon nanotubes (CNTs) [10-12], graphene [13,14], and conducting polymers [15,16], have been explored [17]. Among these, several carbon-based nanocomposites, such as carbon/transition metal oxide [4,18-19], are mainly studied. Owing to its large specific capacitance, low cost, environmental friendliness, and natural abundance, Fe_2O_3 has been recognized as a desirable component for the electrode material of electrical capacitor [20,21]. Unfortunately, the working voltage is relatively small, and consequently limits the enhancements of energy density.

Lately, the energy density was further improved by extending the operating voltage utilizing the strategy of designing the asymmetric system by coupling different positive and negative electrode materials with well-separated potential windows to obtain a high operation voltage [15,17,18,22,23]. In fact, regardless of a higher energy density has thus been achieved, the stability of the supercapacitors remains a major problem [24]. Additionally, the preparation of two different electrode materials increases the cost of production and inhibits their widespread application.

More recently, symmetric supercapacitors with high reversible charge/discharge voltage have been achieved in the neutral electrolyte [24-27] because of the high overpotential of electrode materials for hydrogen/oxygen evolution [26]. These results demonstrate the prospect of neutral electrolyte for developing a high-voltage, long-cyclability supercapacitor system with high energy density [25]. However, the relevant electrode materials for this kind of supercapacitor are usually prepared by employing hazardous, awkward, time-consuming, or high-cost preparation processes, which impedes the large-scale applications. Therefore, it is essential to develop relatively simple, cost-effective, green, and scalable approaches.

Our strategy is to construct a new kind of high-performance supercapacitor by coupling the binder/additive-free electrode material of α-Fe_2O_3 grown on the low-cost highly conductive carbon cloth (CC/Fe_2O_3) [7,28] and the environment-friendly electrolyte of Li_2SO_4 aqueous solution. The electrical conductive substrate (4.102 $\Omega\,cm^{-2}$) can provide a three-dimensional (3D) porous conducting network to effectively assist charge transfer and ion transport within the composites [15]; meanwhile, a great amount of porous α-Fe_2O_3 well-arranged on the substrates ensures the high utilization of active materials [15]. Besides, the CC/Fe_2O_3 nanocomposite directly serves as a current collector, thereby avoiding the usage of conducting additives and polymer binders increasing the contact resistance of α-Fe_2O_3 and the current collector. Moreover, the aqueous medium electrolyte is relatively green, economical, and non-corrosive, which makes the supercapacitor assembling process much easier [25].

Herein, the as-constructed symmetrical supercapacitors with CC/Fe_2O_3 as the electrodes and 2.0 M aqueous solution Li_2SO_4 as the electrolyte show a high operational voltage window of 2.0 V, where the preparation of large-scale electrode material (14.50 × 31.00 cm^2) was executed *via* a simple, efficient, and low-energy cost hydrothermal route followed by a post annealing treatment. Meantime, a superior energy density of 11.0 mWh cm^{-3} was achieved, which is much higher than most of the previously reported carbon cloth-based asymmetric supercapacitors. The high specific capacitance (1.695 F cm^{-2}) and power density (1543.7 mW cm^{-3}) were also obtained. In addition, this kind of supercapacitor can be amplified from 1.50 cm^2 to 100.00 cm^2 without obvious areal capacitance loss, indicating that the fabrication of cheap, easily operational, environmentally friendly, scalable, and practicable supercapacitor is feasible.

Materials and methods

Materials

Carbon cloth (thickness: 0.20 mm) was purchased from Shanghai Hesen Electric Co., Ltd., China. All other chemicals were analytical grade and commercially available from Shanghai Chemical Reagent Co. Ltd. and used as received without any further purification.

Preparation of carbon cloth/Fe_2O_3

The carbon cloth/Fe_2O_3 (CC/Fe_2O_3) was prepared by a catalyst and surfactant-free hydrothermal method. Typically, 35.0 mmol $Fe(NO_3)_3 \cdot 9H_2O$ and 35.0 mmol Na_2SO_4 were dissolved into a mixture with 640.0 mL · H_2O. Then, a piece of carbon cloth (31.00 × 14.50 cm^2) cleaned by deionized water and ethanol was immersed in that mixed solution for 30 min. Next, they were transferred into one 800 mL of Teflon-lined stainless autoclave. Subsequently, the autoclave was sealed and heated in an electric oven at 120.0 °C for 6.0 h. Then, the as-prepared sample was collected, washed with deionized water and ethanol for several times, vacuum dried at 60 °C. At last, the composite was annealed in air at a relatively low temperature of 450.0 °C for 2.0 h with 2 °C min^{-1} heating rate. To study the effect of the amount of Fe_2O_3 on the supercapacitive performance, we adjusted the content of Fe_2O_3 in the nanocomposites by adding different amounts of Fe $(NO_3)_3 \cdot 9H_2O$ and Na_2SO_4 in the hydrothermal process. To easily discriminate these samples, the control samples with different amounts of Fe_2O_3 coating on the carbon cloth was denoted as CC/Fe_2O_3–x (x=1 and 2, standing for 26.25 and 43.75 mmol $Fe(NO_3)_3 \cdot 9\,H_2O/Na_2SO_4$ used in the synthesis).

Characterization

Scanning electron microscopy (SEM) images were obtained on a field emission scanning electron microanalyzer (Zeiss Supra 40) at an acceleration voltage of 5 kV. Transmission electron microscope (TEM) was operated on a Hitachi H7650 transmission electron microscope with CCD imaging system on an acceleration voltage of 120 kV. High-resolution transmission electron microscope (HRTEM) and Energy filter TEM (EFTEM) mappings were carried out on a JEM-ARM 200F Atomic Resolution Analytical Microscope. The powder X-ray diffraction (XRD) studies were performed on a Philips X'Pert Pro Super X-ray diffractometer equipped with graphite monochromatized Cu Kα radiation (λ=1.541841 Å). X-ray