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Three-dimensional crisscross porous manganese oxide/carbon composite networks for high performance supercapacitor electrodes

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ABSTRACT

Manganese oxide/carbon (MnO_x/C) composites have been successfully prepared via a high temperature heat treatment method followed by the electrochemical oxidation. The presence of carbon not only enhances the electronic conductivity of manganese oxides (MnO_x), but also provides more active sites for the transformation of manganese monoxide (MnO) during the galvanostatic charge–discharge process. Simultaneity, the interconnected porous structures of MnO_x/C samples are believed to provide a continuous channel for the diffusion of electrolyte ion and shorten the diffusion length of ions involved in the charge/discharge cycling processes. Consequently, these advantages endow the MnO_x/C electrode a better capacitance performance, a superior long-term cyclic stability and outstanding rate capability compared with pristine MnO_x. More importantly, the composites show a fascinating capacitance of 807 F g^{-1} at 1 A g^{-1}, which is much higher than the reported hydrous RuO_2 electrodes. It can be easily speculated that MnO_x/C composites will act as a promising electrode materials for designing high-performance supercapacitors.

1. Introduction

As an electrochemical energy storage cell, supercapacitors have attracted significant attentions, because of their higher power density and longer cycle life compared with lithium-batteries [1–4]. According to the charge storage mechanism, supercapacitors are classified as electric double layer capacitors and Faradaic capacitors. The capacitance of electric double layer capacitors comes from the pure electrostatic charge accumulation at the electrode/electrolyte interface, whereas the Faradaic capacitors are based on the reduction-oxidation (redox) reaction [5,6]. In most cases, pseudocapacitors exhibit a relatively high specific capacitance [7–9], which make them receive great interest recently.

MnO_x are currently considered as the most promising candidates for pseudocapacitors materials owing to its low cost, environmental compatibility, moreover, relatively high theoretical capacitance [10,11]. However, the capacitance of MnO_x could not be fully achieved in most cases because of its intrinsically poor electrical conductivity, which greatly impede their application in supercapacitors [12]. In order to overcome this shortcoming, binary composites of MnO_x with conductive materials included metal [13–15], metal oxides [16–18], conducting polymers [19,20], and carbonaceous materials [21–25] have been widely researched in recent years. In most cases, the combination of MnO_x with metal oxides or conducting polymers suffers from mechanical instability and poor cycle stability, although the specific capacitance is improved. For instance, CFP@ZnO@MnO_2 electrodes exhibited poor electrochemical stability for the 40% decrease in specific capacitance value over 3000 cycles. PEDOT–MnO_2 nanocomposites only remained 85% of its initial capacitance after 500 cycles [18,26]. Therefore, the components containing both MnO_x and metal oxides or conducting polymers may not be able to gratify demand of excellent electrochemical performance.

Conducting carbon materials possess porous structures, electrical conductivity and well mechanical stability. In such MnO_x/C composite electrodes, the additive carbon source effectively mitigates the low electric conductivity of manganese oxides and tailors a hierarchical pore structure, which in turn contributes to the outstanding performance of electrodes. Pan et al. successfully

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prepared a mesoporous MnO_2/C composite with surface area of 324 $m^2 g^{-1}$ and its specific capacitance was as high as 383 $F g^{-1}$ at 2 $mV s^{-1}$ [21]. The powdery carbon@MnO_2 hybrid nanospheres were synthesized with the specific capacitance of 252 $F g^{-1}$ at 2 $mV s^{-1}$, in which the core carbon sphere served as an electronical carrier [27]. It should be pointed out that the specific capacitance ranged between 200 $F g^{-1}$ and 400 $F g^{-1}$ in most works. The key to the not high specific capacitance may be attributed to rarely develop a three-dimensional "through-connected" porous MnO_x/C networks for continuous channels of electron and ion transport [28]. Of course, some of researchers have achieved much higher specific capacitance as the construct of three-dimensional compound materials. For example, the capacitance performances of ultralight and flexible MnO_2/carbon foam hybrids were achieved at 1270.5 $F g^{-1}$ with 3.4% weight percent of MnO_2 [29]. However, the low mass loading of MnO_2 materials limit its practical applications in the hybrid electric vehicle and fuel cell electric vehicle.

In this paper, we propose a simple strategy to synthesize the three–dimensional crisscross porous network of MnO_x/C composites for improving the capacitive performance of MnO_x. The carbons are well incorporated with MnO_x nanoflake architectures and form a penetrative porous structure. With the enhancement of electrical conductivity and the contribution of open texture, the produced MnO_x/C structures present a maximal specific capacitance about 807 $F g^{-1}$ with high mass-loading at a specific current density of 1 $A g^{-1}$, which can even be better than some reported RuO_2 electrodes [30,31].

2. Experimental

2.1. Synthesis of MnO_x/C composites

All reagents used in this work were analytical grade without further purification. The slurry containing $MnCO_3$ nanoparticles were prepared by mixing bulk $MnCO_3$ particles (10 g) with water (50 mL). Subsequently, Ascorbic acid (10 g) were dissolved in deionized water (50 mL), and mixed with the above-mentioned semisolid slurry of $MnCO_3$ nanoparticles under continuous stirring for about 2 h to obtain a transparent solution. In the next step, the Mn-containing aqueous was dried at 100 °C overnight in air atmosphere in preparation for Mn-containing intermediates. Then the intermediates were pyrolyzed at 700 °C for 6 h under flowing nitrogen gas to obtain the MnO/C composites. Finally, the MnO_x/C composites were synthesized by the conversion of MnO/C materials via the process of galvanostatic charge and discharge.

2.2. Structure characterization

The morphology of the obtained materials was characterized by scanning electron microscopy (SEM, S-4800 operated at 10 kV). Transmission electron microscopy (TEM) observations were obtained by using a JEM-2010 instrument. The X-ray diffraction (XRD) analysis was carried out with Rigakud/MAX-2500/pc X-ray diffractometer with Cu Kα radiation, λ = 1.54056 Å. The diffraction patterns were recorded from 10° to 80° at a scanning rate of 5° min^{-1}. To acquire the carbon weight of composite materials, thermal analysis of the precursors under air flow was characterized at a heating rate of 10 °C min^{-1} from room temperature to 800 °C (Pyris Diamond, PerkinElmer Thermal Analysis). Raman spectra were recorded at 5% and 100% power using a Renishaw in a Raman microscope instrument. The materials were characterized by X-ray photoelectron spectroscopy (XPS, Kratos XSAM-800 spectrometer with Al Kα). N_2 absorption/desorption measurements were conducted on a V-Sorb 2800P surface area and pore distribution analyzer instrument.

2.3. Electrochemical measurement

A conventional three-electrode configuration was employed to measure the electrochemical properties of the obtained materials, including cyclic voltammetry, constant current charge/discharge behavior and capacitance retention at 6 M KOH within potential window of -0.2 to 0.53 V *vs.* Hg/HgO. Electrochemical impedance spectra was measured on CHI 660 E electrochemical workstation, varying frequency from 0.01 to 100 000 Hz. The working electrode was fabricated by mixing the active material (MnO/C), acetylene black, and binder polytetrafluoroethylene with ethanol for viscous slurry in a mass ratio of 70:30:20 and then pressed the slurry on a piece of foamed nickel grid whose area is 1 × 1 cm^2 before drying at 80 °C for 12 h in air. The total loading mass of active materials in each working electrode is 2–4 mg. The specific capacitances of the

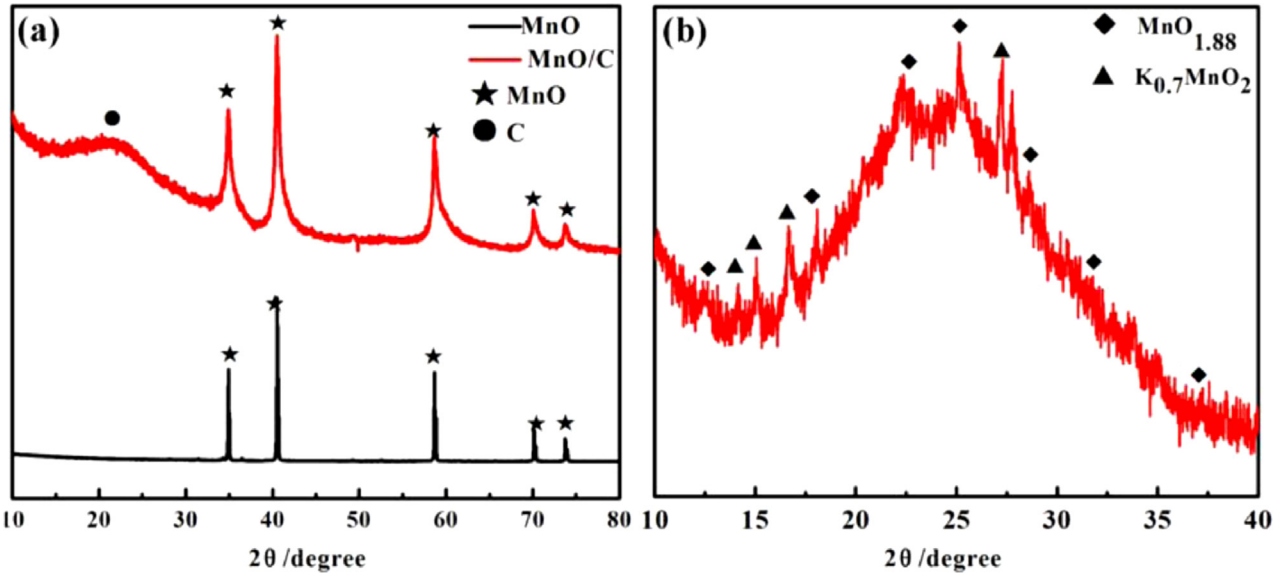

Fig. 1. XRD patterns of (a) pure MnO MnO/C composites and (b) MnO_x/C composites after 800 cycles.