



Enhancing high-rate capability of MnO₂ film electrodeposited on carbon fibers via hydrothermal treatment



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ABSTRACT

MnO₂ films electrodeposited on carbon fibers were subjected to hydrothermal treatment in deionized water and a K₂SO₄ solution. The effects of hydrothermal treatment on the structures and capacitive properties of the films were systematically evaluated. Compared to the as-deposited and K₂SO₄-treated films, the water-treated film exhibits a much lower capacitance at 2 mV s⁻¹ due to the phase transformation from ramsdellite to manganite during the hydrothermal treatment. The K₂SO₄-treated film maintains the ramsdellite structure although the average oxidation state of Mn in the film is decreased to some extent. At the charge-discharge current density of 1C, the K₂SO₄-treated and as-deposited films show specific capacitances of 281.9 and 274.7 F g⁻¹, respectively. But the K₂SO₄-treated film displays a capacitance of 135 F g⁻¹ at 15C and a good high-rate capability which is more than 3 times as high as that of the as-deposited one. These results and the related kinetic analysis suggest that the suitable ratio of Mn⁴⁺ to Mn³⁺ plays an important role in determination of the high-rate capability of the film.

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1. Introduction

In response to the fast growing power and energy demands for electrical vehicles and next-generation portable electronics, development of environmentally friendly and lightweight energy storage devices has become increasingly urgent. Supercapacitors, also known as electrochemical capacitors, with high power and reasonably high energy densities, currently fill the gap between batteries and conventional solid state and electrolytic capacitors [1]. Based on the charge storage mechanism, supercapacitors are categorized as electrochemical double layer capacitors (EDLCs) and pseudocapacitors. Pseudocapacitors, in which electron storage mechanism involves reversible Faradic reaction, are generally expected to have higher capacitance than double-layer capacitors, wherein the capacitance arises from electrostatic separation at the electrode-electrolyte interface. However, the rate capability of pseudocapacitors is usually inferior to that of EDLCs and need further improvement [2,3]. To overcome these limitations, considerable efforts have been devoted to development of new electrode materials for pseudocapacitors.

Among these materials, MnO₂ has been considered to be one of the most attractive candidates due to its environmentally benign, good electrochemical performance in neutral electrolyte, as well as low cost of raw materials [4,5]. However, the densely packed structure and poor electrical conductivity is perceived to restrict the practical capacitance and rate capability of MnO₂. As an important strategy to improve the performance of MnO₂, nanostructuring provides more accessible surface areas for energy storage and facilitates ion and electron transport [6–10]. To date, much effort has been devoted to preparing MnO₂ with different nanostructures, so as to enhance the specific capacitance and power delivery capability [11–16].

To improve the electrical conductivity, great effort has been made to integrate MnO₂ on different carbon supports. Various carbonaceous materials, such as exfoliated graphite [17–19], carbon nanotubes (CNTs) [20–22], mesoporous carbon [23–25] and carbon foam [26], have been used to prepare composites by different approaches. The carbon materials in these MnO₂ composites can provide good conductive paths and help to effectively utilize the redox property of MnO₂, which in turn enhances the electrochemical performance of the electrodes. Considering the fact that powdery carbon/MnO₂ materials need to be mixed with a polymeric binder to form electrodes, and this possibly introduces unnecessary charge-transfer barriers among the active materials, a great deal of research work has been

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conducted to develop flexible, binder-free carbon/MnO₂ electrodes [27,28]. In most cases, carbon materials with different nanostructures were used as the backbone on which a MnO₂ film was coated by electrochemical deposition. Generally, the MnO₂ film showed a high specific capacitance and high-rate capability when the deposited MnO₂ film was thin enough, but these capacitive properties decreased with increasing the thickness of the film. Therefore, it is still necessary to improve the intrinsic performance of MnO₂ films based on a profound understanding of the complex charge storage mechanisms related to insertion/deinsertion and reaction of ions in the films.

In this study, MnO₂ films were electrochemically deposited on porous carbon fiber paper (CFP) slabs, and as active materials of binder-free electrodes, were firstly subjected to hydrothermal treatment in water and a potassium sulphate solution. The effects of hydrothermal treatment on the crystal structures, manganese valence and electrochemical performance of the films were explored in detail.

2. Experimental

All the reagents were analytical grade and used directly without further purification. Prior to deposition, rectangular carbon fiber paper (CPF) slabs (1 × 3 cm²) were ultrasonically cleaned in acetone, deionized water and ethanol sequentially for 15 min each, then dried and used as the carbon substrates. The electrochemical deposition of MnO₂ was carried out with a galvanostatic method in an aqueous solution containing 0.5 M

Na₂SO₄ and 0.2 M MnSO₄ at room temperature. The deposition process was monitored using a CHI660 B electrochemical workstation (Shanghai Chenhua Instrument Co.) connected with the CFP slab and a titanium plate counter electrode. After 5 minutes of deposition, the obtained MnO₂@CFP slab was taken out of the electrolyte, soaked and washed with deionized water and dried.

The MnO₂@CFP slab was put into a Teflon-lined stainless steel autoclave filled with deionized water or a 0.2 M K₂SO₄, then the autoclave was sealed and maintained at 150 °C for 10 h. After the autoclave cooled to room temperature, the slab was carefully washed with deionized water, and dried at 50 °C under vacuum. The weight of the oxide films was determined by the weight difference between the CFP and the obtained composite slab, as measured using a microbalance (Ohaus DV215CD) with an accuracy of 10 μg.

The surface morphologies and chemical composition of the oxide films were examined with a scanning electron microscope (JEOL JSM-6060LA) and its auxiliary X-ray energy dispersive spectroscope (EDS). X-ray diffraction (XRD) analyses were performed using a Rigaku-TTRIII with graphite-monochromatized high-intensity Cu Kα radiation to explore the crystal structures of the films. The oxidation states of manganese in the oxide films were determined by X-ray photoelectron spectroscopy (XPS), which were carried out using a monochromatic Al Kα source (PE = 1600 eV) on a Kratos Axis Ultra DLD instrument, with a 300–700 μm spot size. The dwell time was set to 200 ms with three sweeps and a step size of 1 eV (0.1 eV for regional scans). The XPS spectra were analyzed and fitted using Avantage software. The C 1s

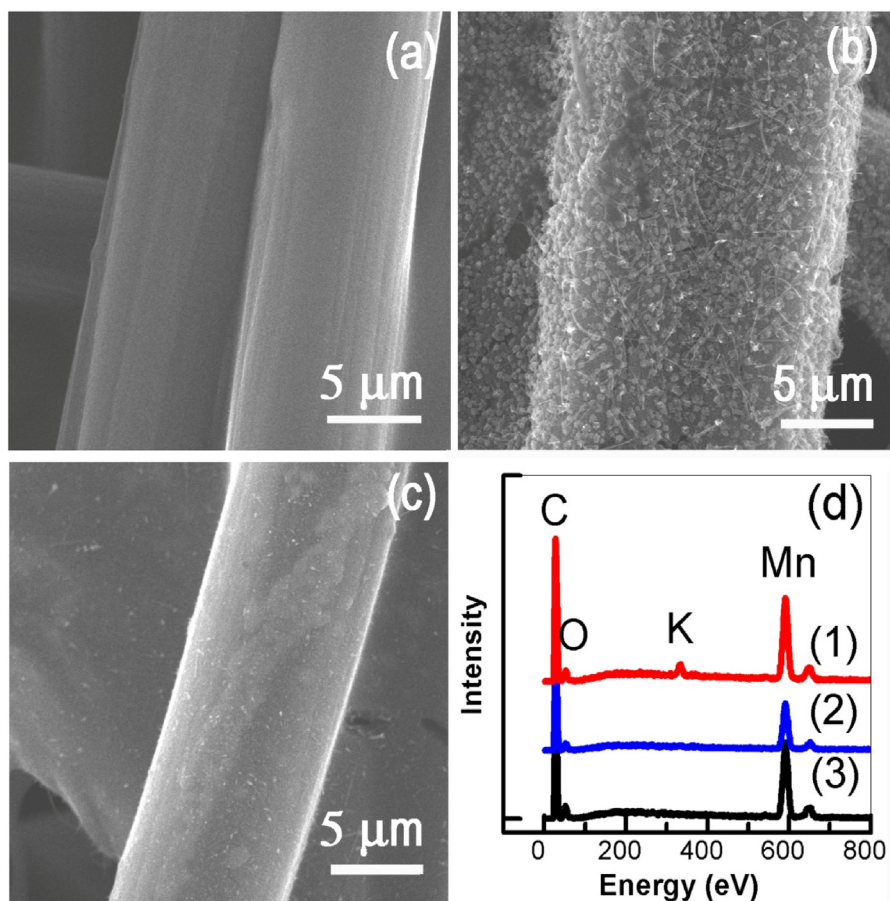


Fig. 1. SEM images of the (a) as-deposited, (b) water-treated and (c) K₂SO₄-treated films; (d) EDS spectra of the (1) K₂SO₄-treated, (2) water-treated and (3) as-deposited films.

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