



Facile chemical synthesis of nanoporous layered δ -MnO₂ thin film for high-performance flexible electrochemical capacitors

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ABSTRACT

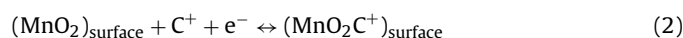
Layered δ -MnO₂ thin films with a three-dimensional nanostructure are successfully fabricated on stainless steel foil substrates for flexible electrochemical capacitors by a facile and effective chemical bath deposition technology from ethanol and potassium permanganate solution at 15 °C. The as-prepared thin films display nanoporous morphology and a water contact angle of 20°. Energy-dispersive X-ray spectroscopy, X-ray diffraction, and Fourier transform infrared spectroscopy analyses reveal that the thin films are composed of δ -MnO₂. Electrochemical data demonstrate that the δ -MnO₂ thin film electrodes can deliver a high special capacitance of 447 F/g at 2 mV/s, and provide a good capacitance retention ratio of 87% after 1000 continuous cycles at 10 mV/s in 0.5 M Na₂SO₄. Compressive and tensile bending tests show that the as-prepared electrodes can steadily work over a wide range of applied curvatures between -2.5 cm^{-1} (tension) and 2.5 cm^{-1} (compression). Only a small decrease in special capacitance (0.9% at a curvature of 2.5 cm^{-1} under compressive strain, or 1.2% at a curvature of -2.5 cm^{-1} under tensile strain) is observed even after bending for 200 cycles, indicating the excellent mechanical flexibility and electrochemical stability of the δ -MnO₂ thin film electrodes.

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1. Introduction

Electrochemical capacitors (ECs) representing an emerging class of energy-storage devices have gained a number of potential applications in electronic devices, hybrid electric vehicles, and backup energy sources because of their characteristics, such as high capacitance, long-cycle life, and fast charge/discharge rate [1–5]. Compared with the bulky, rigid and binder-enriched conventional capacitors, flexible ECs represent a new candidate for wearable and miniaturized energy-storage devices, not only have many more advantages such as thinness, portability, large area, and good flexibility, but have better electrochemical properties as well [6–13]. Meanwhile, their superior mechanical flexibility and binder-free characteristic can increase the probability of realizing large-area and fast roll-to-roll processes for industrial manufacturing. Moreover, flexible ECs assembled with solar cells, Li batteries, or fuel cells, can transform energy-conversion and energy-storage devices into entirely bendable ones [14–18]. Therefore, fabricating low cost, thin, lightweight, flexible and even roll-up ECs is clearly a worthwhile endeavor.

Manganese oxide has recently attracted a great amount of attention as a promising active electrode material for ECs because of its high theoretical capacity, low cost, and eco-friendly properties [19–23]. The charge storage mechanisms of manganese oxide can be described by the following reactions [24]



where $\text{C}^+ = \text{H}^+$, Li^+ , Na^+ and K^+ . Based on reaction (1), the layered δ -MnO₂ with a basal spacing of 0.71 nm would be better for the intercalation/deintercalation of H^+ or alkali metal cations into and out of the bulk of the active material than other crystallographic forms of manganese oxide, thus exhibiting promising properties in enhancing special capacitance [25–28]. Meanwhile, the limited use of MnO₂ at high charge/discharge rates is mainly due to the thick active layers of conventional bulk electrodes, as shown by reaction (2) [29,30]. After realizing that the practical applications of high-performance bendable ECs do not only need large capacitance and high-energy storage, but excellent mechanical flexibility and electrochemical stability as well, we fabricate δ -MnO₂ thin films directly on inexpensive stainless steel (SS) foils which act as electrodes. On one hand, the binder-free porous thin films have more active surfaces to accelerate the adsorption/desorption, as well as shorten the diffusion path length for ions into and out of the active layers, thus maximizing the use of MnO₂. On the

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other hand, the thin film electrodes make the capacitor prototypes thinner, smaller, portable, and even bendable. However, it will be limited that large-scale industrial production of δ -MnO₂ thin films use approaches such as the sol-gel method [31], electrostatic spray [32], hydrothermal synthesis [33,34], electrodeposition [35], and sonochemistry method [36], because these procedures are complicated, energy-consuming, and require harsh reaction conditions. In this study, δ -MnO₂ thin films have been synthesized by a facile and effective chemical bath deposition (CBD) technique at low temperature in one step. In situ growth of active thin films on the collect currents will both skip various steps involving in the fabrication of binder-enriched electrodes and decrease the contact resistance of the electrodes.

Many literatures about flexible ECs just only provide some optical images of the bent electrodes or even do not give any information under bending states [13,37,38], can not well demonstrate their potential application as bendable electronics. In addition, though the dependence on operating temperature for ECs is of substantial practical significance, there is limited related studies in the literature [39,40]. Therefore, in the present paper, bending tests and operating temperature tests are systemically investigated to clarify the mechanical flexibility and electrochemical stability of the as-prepared δ -MnO₂/SS electrodes.

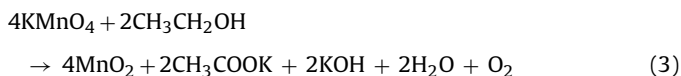
2. Experimental

2.1. Materials

Analytical grade potassium permanganate (KMnO₄, >99.5%), ethanol (>99.7%), and acetone (>99.7%) were used without further purification. SS foil substrates (100 μ m) were polished with different grits of emery paper (1000, 2000 and 3000) until a mirror finish was obtained. The substrates were then treated in an ultrasonic washer using acetone, ethanol, and de-ionized water for 10 min each and dried with purified nitrogen gas.

2.2. Fabrication of the δ -MnO₂/SS electrodes

The precursor solution for deposition of the δ -MnO₂ films was prepared by dissolving 9.0 mM KMnO₄ in 30 mL de-ionized water under magnetic stirring for 30 min. A piece of clean SS foil substrates masked with polyimide tape was vertically immersed into the solution. After adding 0.25 mL ethanol into the above solution, the heterogeneous reaction that occurred on the SS surface can be represented as follows:



The container was sealed and maintained at 15 °C. After 1 h, the as-prepared brown thin film electrode was fetched out, washed with de-ionized water, and then air-dried for 12 h.

2.3. Physical characterization of the δ -MnO₂ thin films

The bond between the δ -MnO₂ thin film and the SS substrate was achieved by a Scotch tape adhesion test. The weight of the δ -MnO₂ thin films was measured by a microbalance (MT5, Mettler-Toledo) with an accuracy of 0.01 mg. The surface morphology was examined by a field emission scanning electron microscope (FE-SEM) (JSM-6330F, JEOL, 15 kV). Elemental analysis was carried out by an energy dispersive X-ray (EDX) spectrometer (Inca Energy 350, Oxford). The crystallinity was analyzed through an X-ray diffractometer (XRD) (D-MAX 2200 VPC, Rigaku) using Cu K α radiation ($\lambda = 1.5405$ nm), with a working current of 30 mA and a voltage of 30 kV. The Fourier transform infrared (FT-IR) spectrum was obtained with a Fourier

transform mid-IR spectrometer (EQUINOX 55, Bruker) using the KBr pellet technique. Wettability was determined with a contact angle system (OCA-20, DataPhysics) at 25 °C.

2.4. Electrochemical characterization of the δ -MnO₂/SS electrodes

The electrochemical characteristics of the δ -MnO₂/SS electrodes were measured by a CHI660B electrochemical workshop (CH instruments, Inc.) with a standard three-electrode cell in 0.5 M Na₂SO₄ at 25 °C. A saturated calomel electrode (SCE) and a platinum foil (2.0 cm²) were used as the reference electrode and the counter electrode, respectively. The cyclic voltammetry (CV) measurements were carried out at scanning rates ranging from 2 mV/s to 10,000 mV/s over a range of 0–0.8 V (vs. SCE). The galvanostatic charge/discharge curves were measured at different currents. The electrochemical impedance spectroscopy (EIS) tests were performed with a superimposed 5 mV sinusoidal voltage over a frequency ranging of 0.01 Hz–100 kHz at an open circuit potential.

The special capacitance (C_{sp} , F/g) and interfacial capacitance (C_{in} , mF/cm²) of the δ -MnO₂ thin films can be calculated by Eqs. (4) and (5), respectively.

$$C_{sp} = \frac{Q}{m \times \Delta V} \quad (4)$$

$$C_{in} = \frac{Q}{S \times \Delta V} \quad (5)$$

where Q is the charge, ΔV is the potential window (V), m is the mass of the δ -MnO₂ thin film (g), and S is the apparent area of the working electrode (cm²).

The C_{sp} , energy density (D_e , Wh/kg), and powder density (D_p , W/kg) of the δ -MnO₂ thin films can also be calculated from the chronopotentiometric curves according to Eqs. (6)–(8).

$$s_{sp} = I \times \frac{\Delta t}{m \times \nabla V} \quad (6)$$

$$D_e = \frac{1}{2} C_{sp} \times \nabla V^2 \quad (7)$$

$$D_p = \frac{D_e}{\nabla t} \quad (8)$$

where I is the special current (A) and Δt is the discharge time that can be derived from the plot of galvanostatic charge/discharge cycling at a special current (s).

2.5. Bending tests of the δ -MnO₂/SS electrodes

The mechanical flexibility and electrochemical stability of the δ -MnO₂/SS electrodes were investigated through compressive and tensile bending tests at different curvatures and flexure counts. The flexible working electrode (2.5 cm $\times$ 3.0 cm) with a geometric surface area of 2.5 cm $\times$ 1.0 cm was bent around a series of standard columns and immersed into the electrolyte to test the effects of tensile strain and compressive strain on electrochemical properties at 25 °C. Curvatures were the inverse of the radii of the columns.

2.6. Temperature tests of the δ -MnO₂/SS electrodes

The thin film electrode was placed in a drying oven to evaluate the effect of the temperature on electrochemical performances by CV measurements under different operating conditions at 10 mV/s in 0.5 M Na₂SO₄.

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