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Bismuth oxide coated amorphous manganese dioxide for electrochemical capacitors

Xiaofeng Li[*], Linsen Zhang, Huichao Dong, Tongchi Xia, Zhigang Huang

Henan Provincial Key Laboratory of Surface & Interface Science, Zhengzhou University of Light Industry, Zhengzhou 450001, China

A B S T R A C T

With $MnSO_4$, NaOH and $K_2S_2O_8$ as the raw materials, the amorphous and δ-type manganese dioxide (MnO_2) is separately prepared by using different chemical precipitation-oxidation methods. The results of charge−discharge and electrochemical impedance spectroscopy (EIS) tests show that (i) the specific capacitance of the amorphous MnO_2 reaches to 301.2 F g^{-1} at a current density of 200 mA g^{-1} and its capacitance retention rate after 2000 cycles is 97%, which is obviously higher than 250.8 F g^{-1} and 71% of the δ-type one, respectively; (ii) good electrochemical capacitance properties of the amorphous MnO_2 should be contributed to easy insertion/extraction of ions within the material; (iii) when 5 wt% Bi_2O_3 is coated on the amorphous MnO_2, its specific capacitance increases to 352.8 F g^{-1} and the capacitance retention rate is 90% after 2000 cycles.

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1. Introduction

Electrochemical capacitors (ECs) also known as supercapacitors or ultracapacitors, have high power and energy density, very long cycle life, short charge time, high safety and efficiency, and they have become alternative energy storage systems for wild applications, such as auxiliary power sources in electric vehicles, memory back-up systems for computers, portable electronic devices, and so on.

The most widely used electrode materials for ECs are carbon [1,2], conducting polymers [3,4] and transition-metal oxides [5−9]. Until now, one of the best electrode materials for ECs is ruthenium oxide (RuO_2) [5]. However, RuO_2 has the inherent disadvantage of being both expensive and toxic, which has limited its commercial use. On the other hand, owing to its high theoretical specific capacitance (1370 F g^{-1}), low cost, environment friendliness and natural abundance, MnO_2 is considered as one of the promising electrode materials for next generation ECs. However, its poor electric conductivity ($10^{-5} \sim 10^{-6}$ S cm^{-1}) and low utilization for charge storage hinders the achievement of such high theoretical capacitance [10,11].

Generally, there are two mechanisms being proposed for the charge storage in MnO_2 [12−15]. The first one is the insertion/

extraction of protons (H^+) or alkali cations (Li^+, Na^+, K^+) within the materials.

$$MnO_2 + Na^+ + e \leftrightarrow MnOONa \qquad (1)$$

The second one is the adsorption/desorption of protons or alkali cations on the surface of MnO_2.

$$(MnO_2)_{surface} + Na^+ + e \leftrightarrow \left(MnO_2 - Na^+\right)_{surface} \qquad (2)$$
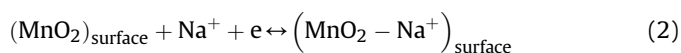
In order to improve its specific capacitance, many researchers have focused on the preparation of MnO_2 with special structure and high surface area [16−19]. Nam et al. prepared flower-like and nanowire structured MnO_2 by a sonochemical method, and the obtained material had a maximum specific capacitance of 300 F g^{-1} in 1 mol L^{-1} $NaSO_4$ solution at a scan rate of 5 mV s^{-1} by cyclic voltammetry [16]. γ-MnO_2 nanocrystalline particles were prepared by Dias et al. through a hybrid method with polyol-made Mn_3O_4 as the precursor, and the synthesized material exhibited a specific capacitance of 125.1 F g^{-1} at a mass loading of 0.98 mg cm^{-2} [17]. Ghimbeu et al. prepared porous λ-MnO_2 with an ordered and interconnected pore structure, and the obtained materials exhibited a surface area up to 150 m^2 g^{-1} and capacitance of 120 F g^{-1} at a current density of 1 A g^{-1} [18]. MnO_2 was electrodeposited from an aqueous acidic solution of $MnSO_4$ with the ionic surfactant sodium lauryl sulphate by Suhasini, and it possessed greater porosity and higher specific capacitance (314 F g^{-1}) than the one obtained in the

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absence of the surfactant (252 F g^{-1}) [19].

On the same time, other researchers have studied the electrochemical properties of MnO$_2$ with the doped or coated additives [20—23]. Nano-nest like amorphous MnO$_2$ with the doping of Fe was potentiostatically synthesized by Dubal et al., and their results showed that the addition of Fe improved the conductivity of MnO$_2$ by reducing its charge transfer resistance, and the maximum specific capacitance achieved for 2 at% Fe: MnO$_2$ was 273 F g^{-1} [20]. Wang et al. prepared mesoporous MnO$_2$ with the doping of cobalt through a pulse electrodeposition method, and a specific capacitance of 354 F g^{-1} was obtained in 6 mol L^{-1} KOH solutions when the molar ratio of Mn to Co was 200:10 [21]. Bahloul et al. revealed that the specific capacitance of λ-MnO$_2$ with a polypyrrole coating increased from 73.7 F g^{-1} to 141.6 F g^{-1}, and the improvement was due to not only the higher electronic conductivity of the polymer but also an increase of the BET surface area of MnO$_2$ [22]. Li et al. prepared the polypyrrole/manganese dioxide/carbon nanotubes (PPy/MnO$_2$/CNTs) composite with a tube-in-tube nanostructure through an in situ chemical oxidation polymerization method, and its specific capacitance was up to 402.7 F g^{-1} at a current density of 1 A g^{-1} [23].

In this paper, the amorphous and δ-type MnO$_2$ was separately prepared by using different chemical precipitation-oxidation methods with MnSO$_4$, NaOH and K$_2$S$_2$O$_8$ as the raw materials. Then, bismuth oxide (Bi$_2$O$_3$) was coated on the surface of the amorphous MnO$_2$. The bismuth compounds have been used as the additives for the rechargeable MnO$_2$ electrodes in the alkaline secondary batteries, as the doping of bismuth to MnO$_2$ could increase its discharge capacity and improve its cycle-ability [24,25], but they have been seldom used in the MnO$_2$ capacitors. Here Bi$_2$O$_3$ modified MnO$_2$ was prepared and its capacitance properties were studied in detail.

2. Experimental

MnO$_2$ was prepared as the following reaction,

$$MnSO_4 + K_2S_2O_8 + 4NaOH \rightarrow MnO_2 + K_2SO_4 + 2Na_2SO_4 + 2H_2O \quad (3)$$
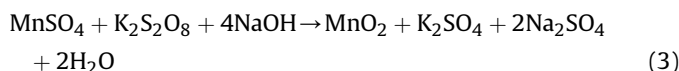
Two processes were used for the preparation of MnO$_2$. In process A, a 0.5 mol L^{-1} NaOH solution was dropwise added into a 0.1 mol L^{-1} mixed solution of MnSO$_4$ and K$_2$S$_2$O$_8$ at 25 °C in stirring, and the reaction was kept for 0.5 h after the dropping finished. In process B, a 0.1 mol L^{-1} MnSO$_4$ solution was dropwise added into a 0.5 mol L^{-1} NaOH solution at 25 °C in stirring, then a stoichiometric amount of K$_2$S$_2$O$_8$ powder was added into the reactor and the oxidation reaction was kept for 10 h, finally the obtained black powder was aged in the pregnant solution at 25 °C for 10 h. Both in process A and B, the mol ratio of Mn^{2+} to OH$^-$ in the reaction solutions was controlled at 1:4 (named separately A1 and B1), 1:5 (A2 and B2) and 1:6 (A3 and B3), respectively. The obtained black powder was washed repeatedly with distilled water, filtered, and finally dried at 100 °C for use.

The as-prepared MnO$_2$ was coated with Bi$_2$O$_3$ as the following reaction,

$$2Bi(NO_3)_3 + 6NaOH \rightarrow Bi_2O_3 + 6NaNO_3 + 3H_2O \quad (4)$$
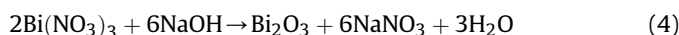
Bi(NO$_3$)$_3$•5H$_2$O was dissolved in a few dilute nitric acid, and 2 g as-prepared MnO$_2$ powder was immersed in a NaOH solution, then the Bi(NO$_3$)$_3$ solution was dropwise added into the NaOH solution at 25 °C in stirring. The reaction was kept for 2 h, and the obtained powder was washed repeatedly with distilled water, filtered, and finally dried at 100 °C for use.

The powder X-ray diffraction (XRD; Bruker, D8 Advance) was used to analyze the phase structure of the as-prepared MnO$_2$. Its morphology and surface composition was tested by using scanning electron microscopy (SEM; JOE, JSM-6490) and energy dispersive spectroscopy (EDS). Thermo-gravimetric and different thermal analysis (TG-DTA; Perkin Elmer, Diamond TG/DTA) was determined at a heating rate of 10 °C min^{-1} under the air atmosphere. Fourier transform infrared (FT-IR; Thermo Nicolet, Nicolet 5700) spectra were recorded with the standard KBr pellet method.

The electrochemical properties of the as-prepared MnO$_2$ were investigated in a simulated symmetric capacitor containing a 7 mol L^{-1} KOH solution at 25 °C. The pasted MnO$_2$ positive electrodes were made by filling a nickel foam substrate (1.5 cm × 1.5 cm) with a mixture of 5 wt.% polytetrafluoroethylene (PTFE) binder, 15 wt.% acetylene black and 80 wt.% MnO$_2$. The obtained electrodes were dried at 60 °C and pressed at a 20 MPa pressure to a thickness of 0.5 mm. The loading of the active materials (MnO$_2$) on the electrodes was about 35 mg cm^{-2}.

The galvanostatic charge—discharge tests were performed on the capacitors under different current densities between a voltage range of 0 V—1.0 V. The specific capacitance of the electrode was calculated as the following equation:

$$C = \frac{2I\Delta t}{m\Delta V} \quad (5)$$

where *I* is the discharge current (A), *Δt* is the total discharge time (s), *m* is the mass of the electroactive material (g), *ΔV* is the voltage drop during discharging (V) and *C* is the specific capacitance (F g^{-1}).

The electrochemical impedance spectroscopy (EIS) tests of the MnO$_2$ electrodes were performed using a Solartron Electrochemical Interface model SI1287 with a platinum electrode as the counter electrode. A Hg/HgO/7 mol l^{-1} KOH reference electrode was used with a Luggin capillary in the region of the working electrode.

3. Results and discussion

Fig. 1 shows the XRD patterns of the as-prepared MnO$_2$ by process A and B, respectively. As shown in Fig. 1, when the materials were prepared through process A, MnO$_2$ with an amorphous structure is obtained: the diffraction peaks of the materials are quite broad and their density is quite weak, which indicates a small degree of crystallization. On the contrary, when the materials were
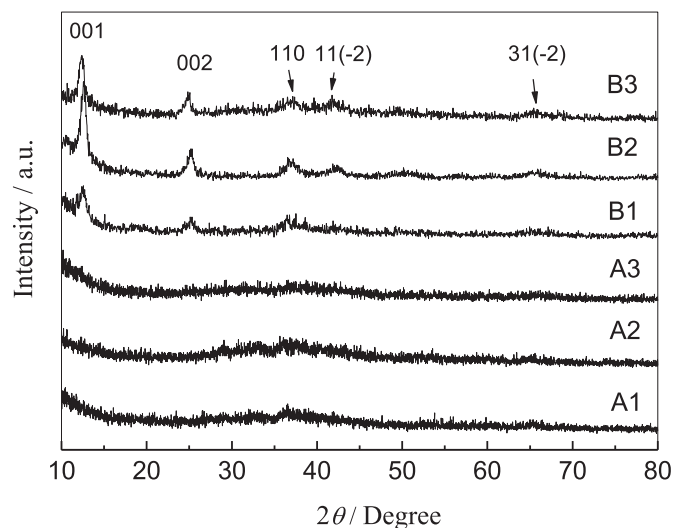

Fig. 1. XRD patterns of MnO$_2$ powder prepared separately by process A and process B.