



# Solvothermal preparation of microspherical shaped cobalt–manganese oxide as electrode materials for supercapacitors



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## ABSTRACT

Microspherical shaped cobalt–manganese oxide (CMO) as electrode materials for supercapacitor is synthesized by solvothermal method. The microstructure and surface morphology of CMO are characterized by X-ray diffraction and scanning electron microscopy, respectively. Cyclic voltammetry and chronopotentiometry are employed for the characteristics of electrode process and the calculation of specific capacitance in KOH solution. It is shown that as prepared CMO with cobalt/manganese mole ratio of 1:2 has excellent specific capacitance of  $348.0 \text{ F g}^{-1}$  at current density of  $0.5 \text{ A g}^{-1}$ . In addition, long-term stability of the composites electrode is measured at current density of  $1.0 \text{ A g}^{-1}$ , and 58.6% of initial capacitance is retained after 500 cycles.

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## 1. Introduction

Supercapacitors, also known as electrochemical capacitors, have now been proved to be the most powerful candidates for next-generation energy storage devices due to their high power density, fast charge/discharge rate as well as better performance of cycle stability compared with conventional battery and electrolytic capacitor [1]. Generally, on the basis of the energy storage mechanism, supercapacitors can be classified into two categories, i.e., electrical double layer capacitor and pseudocapacitor [2]. In general, three kinds of electrode materials are used for the preparation of supercapacitors, including carbon materials, transition metal oxides and conducting polymers [3].

Progress towards supercapacitors technologies can benefit from the continuous development of a variety of different structure materials [4]. Among those electrode materials above, hydrous ruthenium dioxide stands out due to a number of desirable properties, such as high conductivity, high specific capacitance and good environmental stability. However, the high cost, rareness and toxic nature of  $\text{RuO}_2$  have limited its commercial attractiveness [5]. Therefore, cheaper metal oxides with various oxidation states and excellent electrochemical behaviors are intensively studied as alternative materials, including  $\text{NiO}$  [6],  $\text{MnO}_2$  [7],  $\text{Fe}_3\text{O}_4$  [8] and  $\text{Co}_3\text{O}_4$  [9], etc. Most attentions have been focused on hydrous

manganese oxide as a candidate for pseudocapacitor due to the low cost of raw materials and the fact that manganese is more environmentally friendly than any other transition metal oxide systems, thus it has attained a large variety of applications.

To bridge the performances gap between these materials, attempts at novel electrode design have been extensively made. Despite the numerous of publications, nearly all of them can be clarified into one general concept, that is, the use of pseudocapacitive materials conductive matrix hybrid nanostructures [10].

Recently, many two- or three-metal oxide composite materials, such as  $\text{CoMoO}_4$  [11] and  $\text{Co}_2\text{SnO}_4$  [12], have been synthesized with excellent electrochemical properties. Prasad et al. [13] deposited nanostructured and microporous nickel–manganese oxide (NMO) and cobalt–manganese oxide (CMO) onto stainless steel substrate by potentiodynamic method and found that the specific capacitances of NMO and CMO were much higher than that of any individual, indicating the possibility that electrochemical performances of metal oxide composites were superior to that of single metal–oxide materials.

In this paper, based on solvothermal preparation different from the literatures above, precursor composed of Co and Mn was prepared using urea as precipitator and hexadecyl trimethyl ammonium bromide (CTAB) as template. Then the precursor was calcined at temperature of  $400^\circ\text{C}$  to obtain microspherical shaped materials, exhibiting a higher specific capacitance ( $348 \text{ F g}^{-1}$  at current density of  $0.5 \text{ A g}^{-1}$ ) compared to the value reported by Gopal and Chang ( $78 \text{ F g}^{-1}$  [14] and  $180 \text{ F g}^{-1}$  [15], respectively).

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## 2. Experimental

### 2.1. Synthesis and characteristics of microstructured CMO

Cobalt acetate, manganous acetate, urea, CTAB and ethanol were analytically pure and used without further purification. All the chemicals were purchased from Chengdu Chemical Reagent Factory (Chengdu, China). Distilled water was used throughout the experiments.

In a typical procedure, 1.0 g CTAB and 2.0 g urea were dissolved in solution containing 10 mL ethanol and 20 mL distilled water and stirred with a magnetic stirrer for 10 min to form a homogeneous solution at room temperature. Subsequently, different mole ratios of cobalt acetate and manganous acetate with a total amount of 5 mmol were added to the above solutions, respectively. The solutions were transferred into teflon-lined stainless steel autoclaves with 50 mL capacity. The autoclaves were then loaded into an oven preheated to 140 °C for 12 h. After the reaction system cooled down to room temperature, the pink precipitate was collected and washed with distilled water and absolute ethanol until no  $\text{Br}^-$  was detected, then it was dried at 60 °C for 12 h in air, followed by calcination in a muffle furnace at a temperature of 400 °C.

As prepared samples with different mole ratios of cobalt acetate and manganous acetate (1:2, 1:1, 2:1) were marked as CMO-1, CMO-2 and CMO-3, respectively.

The morphologies of samples were investigated using a field emission scanning electron microscope (Ultra 55, Zesis Corporation). The mole ratio of Co and Mn contained in CMO-1 was analyzed with energy dispersive X-ray (EDX) detector (HORIBA, EMAX). The crystallographic structures were characterized by XRD (X' Pert PRO, Netherlands) with Cu  $\text{K}\alpha$  radiations ( $\lambda = 0.15406 \text{ nm}$ ) performed from 10° to 80° at a speed of 2° per minute.

### 2.2. Electrode fabrication and electrochemical measurements

The fabrication of working electrodes was carried out as follows: briefly, the electroactive materials, conductive carbon black and polytetrafluoroethylene (PTFE) were mixed in a mass ratio of 8:1:1 and dispersed in ethanol. The resulting composite was ultrasound for 30 min to form a sticky slurry, which was eventually pasted onto a nickel foam sized 1 cm × 2 cm, followed by drying at 80 °C under vacuum for 24 h.

2.0 M KOH solution was used as electrolyte in all experiments at room temperature. All electrochemical measurements were carried out by introducing a three-electrode test system using platinum sheet as counter electrode, as prepared composite electrode as working electrode and Hg/HgO electrode as reference electrode. Cyclic voltammetry (CV) and galvanostatic charge–discharge tests were performed between –0.5 and 0.5 V using PARSTAT 2273 electrochemical workstation (Princeton Applied Research, USA).

## 3. Results and discussion

Shown in Fig. 1 are the selected XRD patterns of CMO with different ratios of cobalt acetate and manganous acetate. It is shown that the samples presented similar XRD patterns with relatively broad XRD peaks, indicating the amorphous nature of CMO. Due to the poor crystallinity, the definite phase could hardly be ascertained from Fig. 1. All the three samples could be a series of amorphous CMO containing various valences of Mn and Co and their oxides [16].

It is found in the latter part of this work that the electrochemical performances of CMO-1 based electrode were much better than that of CMO-2 or CMO-3, so only the SEM images of CMO-1

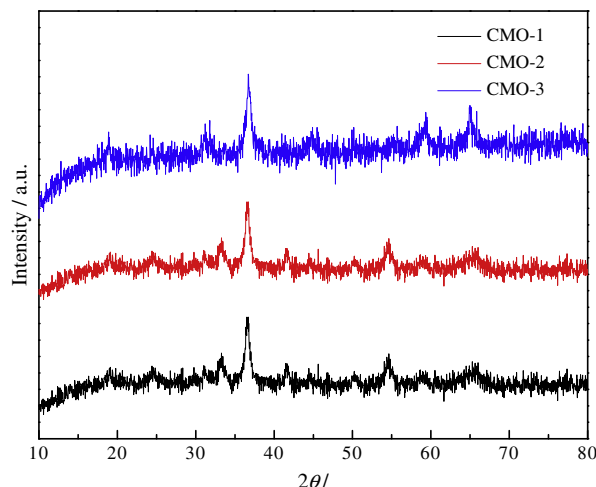


Fig. 1. XRD patterns of as-prepared CMO-1, CMO-2 and CMO-3.

are presented (Fig. 2). It is shown clearly in Fig. 2a and b that microsphere shaped CMO-1 particles with various sizes were asymmetrically ranged and there were many small particles uniformly scattering on the surface of microspheres like sea urchins. In addition, it is shown that CMO-1 particles tended to exist in the form of bigger particles with tiny trigonal planar structure covering on the surface. The mechanism for the formation of CMO-1 particle was probably as follows.  $\text{CO}_3^{2-}$  and  $\text{OH}^-$  resulted from the decomposition of urea at a high solvothermal temperature [17]. Furthermore, Mn and Co possessed different binding ability with  $\text{CO}_3^{2-}$  and  $\text{OH}^-$ , and emerged different nucleation and growth mechanism under the action of CTAB during the whole solvothermal procedure, which could explain the observed microspherical and sea urchins shapes.

Shown in Fig. 2c is a typical EDX wide-range spectrum of as prepared CMO-1. It was indicated that CMO-1 was consisted of Mn, Co and O without any other impurities in the composites, and the calculated atomic ratio of Co and Mn was practically consistent with the added amount of Co and Mn.

Shown in Fig. 3 are the typical CVs of different CMO electrodes in 2.0 M KOH electrolyte at scan rate of  $2 \text{ mV s}^{-1}$  (a) and CVs of CMO-2 at different scan rates (b). It was obvious that the surrounded CV area of CMO-1 was much larger than that of either CMO-2 or CMO-3, suggesting a higher specific capacitance. Compared to Mn oxides, the added Co oxides were less electroactive when the pseudocapacitance was concerned. But the added Co could suppress the anodic dissolution of the oxides and therefore improve the electrochemical reversibility. In addition, since the capacitance of Mn oxide was determined by a reversible, fast and continuous redox reaction between its trivalent and tetravalent states [18,19], reactions  $\text{Mn}_2\text{O}_3 + \text{Co}_2\text{O}_3 + 2\text{H}_2\text{O} \rightarrow 2\text{MnO}_2 + 2\text{Co(OH)}_2$  and  $\text{Mn}_2\text{O}_3 + 2\text{CoOOH} + \text{H}_2\text{O} \rightarrow 2\text{MnO}_2 + 2\text{Co(OH)}_2$  might probably happen and hinder the ideal pseudocapacitive reaction and thereby decrease the overall specific capacitance [15].

The galvanostatic charge–discharge behaviors of CMO-1, CMO-2 and CMO-3 composite electrodes were investigated by chronopotentiometry from –0.5 to 0.5 V at current density of  $1.0 \text{ A g}^{-1}$  in 2.0 M KOH solution and the corresponding results were shown in Fig. 4a. All the samples exhibited nonlinear charge/discharge behaviors with time. The specific capacitance was evaluated from the slope of the charge–discharge curves, according to the equation  $C = I\Delta t / (m\Delta V)$ , where  $I$  was the applied current,  $m$  was the mass of each electrode, and  $\Delta t / \Delta V$  was calculated from the discharge curve after the IR drop. The inclined parts indicated superimposed redox reactions, which was consistent with the cyclic voltammograms in

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