



HYDROTHERMAL SYNTHESIS OF SPHERE-LIKE ZINC COBALTITE FOR ENERGY STORAGE DEVICES

B. Saleha Begum

Department of Instrumentation, Sri Venkateswara University, Tirupati – 517502, India.

ABSTRACT The electrochemical performance of zinc cobaltite-based nano/micromaterial depends on its shape and morphology. Here we report on the electrochemical performance of zinc cobaltite (ZnCo_2O_4) material synthesized via a facile hydrothermal method. The synthesized material was characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) analysis. It was found to be a single-phase zinc cobaltite material with a cubic spinel crystal structure. The electrochemical performance of the synthesized zinc cobaltite microstructure material was evaluated by cyclic voltammetry, cyclic chronopotentiometry and electrochemical impedance spectroscopy. The zinc cobaltite microspheres material displayed a high specific capacitance of 600.37 F g^{-1} at a current density of 1 A g^{-1} . Such electrochemical performance may qualify the zinc cobaltite microspheres material as a potential electroactive material in supercapacitors.

KEYWORDS : Hydrothermal; ZnCo_2O_4 ; microsphere; specific capacitance

1. INTRODUCTION

Supercapacitors, also known as electrochemical capacitors, have been considered as some of the most promising energy storage devices because of their many advantages, including high power density, faster charge and discharge processes, and longer lifespan, and hold great potential as power sources for applications in electric vehicles and hybrid electric vehicles [1]. Mixed transition metal oxides, typically binary metal oxides with two different metal cations, have received a lot of interest recently on account of their promising roles in many energy related fields [2]. Recently, binary ZnCo_2O_4 has been widely investigated as a high-performance electrode material for energy storage (including lithium-ion batteries and supercapacitors) due to its low cost, environmentally benign nature, natural abundance and high theoretical capacitance. Moreover, ZnCo_2O_4 possesses much better electrical conductivity and higher redox activity compared to nickel oxide and cobalt oxide, which originate from the co-existence of the Zn and Co species [3]. Herein, we present a two-step facile strategy involving a hydrothermal method and subsequent thermal annealing treatment to fabricate ZnCo_2O_4 microspheres. When evaluated as electrode materials for supercapacitors, the ZnCo_2O_4 microspheres show a high specific capacity of 600.37 F g^{-1} at 1 A g^{-1} , as well as good cycle stability.

2. Experimental

2.1 Synthesis of ZnCo_2O_4 microspheres

All chemical reagents were of analytical purity and were used without further purification. In a typical procedure, 20 mmol of $\text{Co}(\text{Ac})_2 \cdot 4\text{H}_2\text{O}$, 10 mmol of $\text{Zn}(\text{Ac})_2 \cdot 4\text{H}_2\text{O}$, 0.5g of urea and 0.8g of CTAB were dissolved in a 70 mL of DI water by constant stirring, and the mixture was stirred to form a pink solution. Then, the solution was transferred to a Teflon-lined stainless-steel autoclave and heated at 150°C for 4 h. After naturally cooling down to room temperature, the resulting precipitates were collected by centrifugation, washed several times with absolute ethanol and dried at 80°C in an oven. To obtain ZnCo_2O_4 microspheres, the precipitates were calcined at 400°C for 4 h.

2.2 characterization

The powder X-ray diffraction (XRD, PANalytical X'Pert Pro) patterns of the prepared samples were recorded using $\text{Cu K}\alpha$ radiation ($\lambda=1.540 \text{ \AA}$) at a voltage of 40 kV and a current of 30 mA. The morphology of the samples was analyzed by field emission electron microscopy (FE-SEM, S-4800, Hitachi, Japan). Electrochemical measurements were conducted at room temperature using a typical three-electrode system, where an Ag/AgCl electrode was used as the reference electrode and platinum wire as the counter electrode. For all experiments, KOH (6M) was used as the active electrolyte. Cyclic voltammetry (CV), galvanostatic charge-discharge cycling (CD), and electrochemical impedance spectroscopy (EIS) were used to examine the electrochemical performance of the samples using a commercial instrument CHI 760E, CH Instruments, USA. The specific capacitance (C) was determined using the CD curves according to the following equation [4]:

$$C_s = \frac{2I \int V dt}{m(V_2 - V_1)}$$

where CS is the specific capacitance of the electrode (F g^{-1}); I is the discharge current (A); m is the mass of the active material (g); $\int V dt$ is the area under the discharge curve and $(V_2 - V_1)$ is the voltage window (V).

3. RESULTS AND DISCUSSION

The crystalline phase and purity of the as-synthesized sample was determined by powder XRD, as shown in Figure 1a. All the XRD peaks matched well with the standard AB_2O_4 type pattern of the cubic spinel structure (JCPDS No: 23-1390) [5]. All the characteristic peaks at 19.03° , 31.18° , 36.78° , 38.60° , 44.66° , 55.57° , 59.20° , 65.27° , 74.11° , and 77.11° 2θ were assigned to the (111), (220), (311), (222), (400), (422), (511), (440), (620), and (533) planes of cubic spinel ZnCo_2O_4 , respectively. The XRD peaks were quite intense and sharp, indicating good crystallinity of the as-prepared ZnCo_2O_4 sample. In addition, no other XRD peaks were detected, confirming the absence of any contaminants and/or impurities. The morphology of the ZnCo_2O_4 products were carefully observed by means of SEM. The typical SEM images of the pure ZnCo_2O_4 products (Figure 1b) show that they are composed of microspheres with irregular diameters, very rough surface and comprised small nanoparticles.

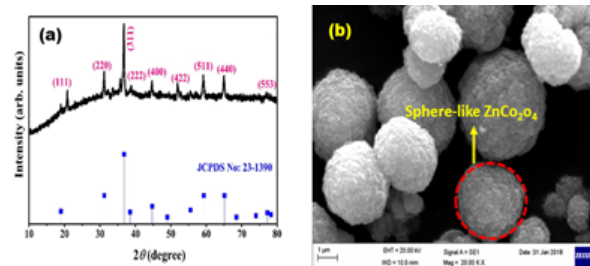


Figure 1. XRD pattern (a) and SEM image (b) for ZnCo_2O_4

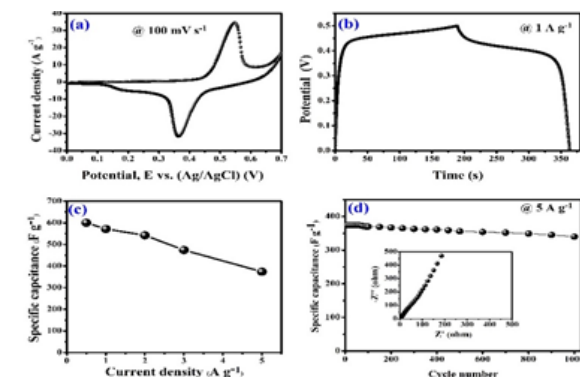


Figure 2. Electrochemical performance of ZnCo_2O_4 microspheres (a) CV (b) CD (c) Current density Vs. Specific capacitance (d) Cyclic performance and Nyquist plot (inset)

CV and CD were carried out to evaluate the electrochemical performance of porous ZnCo_2O_4 microstructures as a supercapacitor electrode material in a three-electrode system using a 6 M aqueous KOH solution as the electrolyte. Figure 2a shows the typical CV curves of the ZnCo_2O_4 microstructures at 100 mV s^{-1} over the potential window of 0 to 0.7 V (vs. Ag/AgCl). The entire CV curves do not have a rectangular shape, inferring a pseudocapacitance (exhibits a pair of

well-defined redox peaks) other than the electrochemical double-layer capacitance [6]. To further evaluate the potential applications of the ZnCo_2O_4 microstructures as an electrode material for electrochemical supercapacitors, CD measurements were carried out between 0 and 0.5 V at current density of 1 A g^{-1} (Figure 2b). The specific capacitance of the ZnCo_2O_4 microspheres electrode were estimated to be 600.37, 571.56, 542.41, 474, and 374.16 F g^{-1} at current densities of 0.5, 1, 2, 3 and 5 A g^{-1} , respectively, as shown in Figure 2c. The long-term cycle performance and stability are of great importance for practical applications of electrochemical supercapacitors [7]. The cycling performance of the ZnCo_2O_4 microspheres was examined by CD at a current density of 5 A g^{-1} for 1000 cycles over the potential region of 0 to 0.5 V. The capacitance of the ZnCo_2O_4 microspheres retained more than 90%, even after 1000 cycles, indicating good electrochemical cycling stability. To understand the outstanding electrochemical performance of the ZnCo_2O_4 microspheres, EIS measurements were further carried out. Inset of the Figure 2d exhibits the Nyquist plots of the ZnCo_2O_4 microspheres and exhibits a lower internal and charge-transfer resistance [8]. All of the results indicated the good electrochemical activity of the ZnCo_2O_4 microspheres electrode for energy storage.

4. CONCLUSIONS

- Zinc cobaltite microspheres material was synthesized by an economically facile hydrothermal process.
- The synthesized material displayed excellent electrochemical performance, which favoured electrolyte ion transport.
- It exhibits a high specific capacitance of 600.37 F g^{-1} at 1 A g^{-1} , a remarkable long-term cycling stability (90% of the maximum capacitance is retained after 1000 cycles at 5 A g^{-1})
- The synthesized zinc cobaltite microspheres material may prove to be promising electroactive material for applications in supercapacitors.

5. REFERENCES

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