Ionics
DOI 10.1007/s11581-008-0227-y

Synthesis and characterization of $ZnCo_2O_4$ nanomaterial for symmetric supercapacitor applications

K. Karthikeyan · D. Kalpana · N. G. Renganathan

Received: 29 May 2007 / Revised: 8 April 2008 / Accepted: 11 April 2008

Abstract $ZnCo_2O_4$ nanomaterial was prepared by co-precipitation method and characterized by X-ray diffraction (XRD), scanning electron microscope (SEM), transmission electron microscopy (TEM), cyclic voltammetry (CV), and galvanostatic charge–discharge tests at various current densities. It is shown that the crystal structure and surface morphology play an important role in the enhancement of the specific capacitance. The TEM results clearly indicate that the prepared material shows aggregated particles. The particle size powder was about 50 nm, and SEM pictures indicate a porous morphology. The electrochemical behavior of $ZnCo_2O_4$ was characterized by mixing equal proportion of carbon nanofoam (CNF). From CV, it is concluded that the combination of redox and pseudo-capacitance increases the specific capacitance up to 77 F g^{-1} at 5 mV s^{-1} scan rate. The $ZnCo_2O_4$-based supercapacitor cell has good cyclic stability and high coulombic efficiency.

Keywords Supercapacitor · Zinc oxide · Carbon nanofoam · Specific capacitance

Introduction

With increasing demand for alternative energy sources, electrochemical capacitors with high power densities compared to batteries and high energy density compared to dielectric capacitors are in big demand. They have several advantages like long cycle life, short charge–discharge time and safety. Practical applications are seen for electric vehicles and as memory back up for computers [1, 2].

The basic electrode material used for electrochemical capacitors are (1) Carbon (aerogel, nanofoam, nanotube, etc.) [3] (2) Metal oxides (RuO_2, IrO_2) [4], and (3) Conducting polymers [5]. Among the metal oxides, oxide of Ru exhibit very high specific capacitance, but its wide acceptance is reduced due to high cost. Hence, a cheap material with equivalent performance is required. Transition metal oxides [6, 7] have been considered as promising materials for supercapacitors.

$ZnCo_2O_4$ is a spinel, where Zn ions occupy the tetrahedral sites in the cubic spinel structure, and the trivalent Co ions occupy the octahedral sites. When nano-size particles of $ZnCo_2O_4$ are electrochemically discharged, it will occupy the three-dimensional network carbon within the electrode to participate in the formation of electrochemical double layer. Energy is stored in these porous electrodes by accumulation of ionic charge in the double layer at the electrode–electrolyte interface.

To our knowledge, there is no report, so far, on the application of $ZnCo_2O_4$ for supercapacitor. Recently, Kalpana et al. have prepared ZnO nanoparticles by the sol–gel method and used this material for supercapacitor applications [8].

In the present study, we have prepared $ZnCo_2O_4$ by co-precipitation because of its high purity, atomic level homogeneous mixing of the constituent metal ions, and good control of stoichiometry [9].

K. Karthikeyan · D. Kalpana (✉) · N. G. Renganathan
Central Electrochemical Research Institute,
Karaikudi 630 006, India
e-mail: dkalps@rediffmail.com

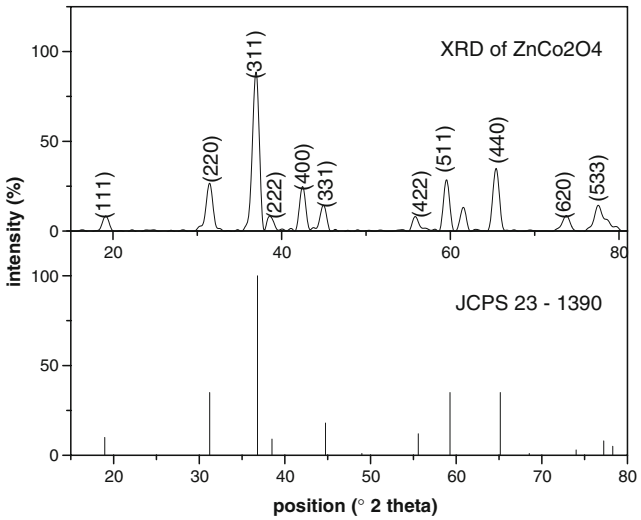

Fig. 1 XRD pattern of $ZnCo_2O_4$ nanoparticle

Experimental

Synthesis and fabrication of $ZnCo_2O_4$

Stoichiometric quantities of $ZnCl_2$ and $CoCl_2$ were dissolved in triple distilled water. A 6-M KOH solution was added slowly at a rate of five drops with an interval of 15 min into the solution. The solution was constantly stirred well at 80 °C until the precipitate was formed. Then, it was filtered and washed with distilled water followed by ethanol. The precursor was kept in an oven at 200 °C for 3 h. Electrodes for the symmetric electrochemical capacitor were prepared by mixing an equal proportion of $ZnCo_2O_4$ and carbon nanofoam of 1,500 m^2g^{-1} surface area bonded with N-methyl pyrolidine. The slurry was pasted on the stainless steel current collector of 1 cm^2 geometrical area and dried in an oven at 200 °C for 30 min and slowly cooled down to room temperature. The cell was fabricated by sandwiching the electrodes between a polypropylene separator using 6 M KOH as electrolyte. For cyclic voltammetry (CV), an Electrochemical Analyzer (BAS 100B, USA) was used. The crystalline structure of $ZnCo_2O_4$ nanoparticles was examined by XRD with CuKα radiation (λ=1.54056 Å). The morphology of the samples was investigated by a scanning electron microscope (HITACHI, S-3000H). The impedance properties of the cells were measured by a PARSTAT 2263, USA. The charge–discharge cycling properties of the cells were evaluated by using Won-A-Tech Battery Cycler (WBCS 3000).

Results and discussions

X-ray analysis

X-ray powder diffraction analysis was performed using CuKα radiation (λ=1.5405 Å) at a scanning rate of 2^0 min^{-1}, and the XRD pattern was identified by comparison with the JCPD standard. The crystalline size D_c, was determined by using the Scherrer equation,

$$D_c = 0.9\lambda/(\mathrm{B}\ \cos\theta)$$

where, λ is the corrected wavelength of the X-radiation, B the full width at half-maximum corrected for instrumental broadening, and θ is the Bragg angle of the diffraction peak. The mean grain size of as prepared $ZnCo_2O_4$ was 50 nm.

Figure 1 shows the XRD pattern of $ZnCo_2O_4$ powder. The peaks are shaped, well-defined, and reveal the formation of the cubic spinel structure. The XRD patterns exhibited the characteristic peaks at 2θ=31.45, 36.96, 45.00, 55.65, and 77.49° of the spinel type $ZnCo_2O_4$ (JCPS 23-1390).

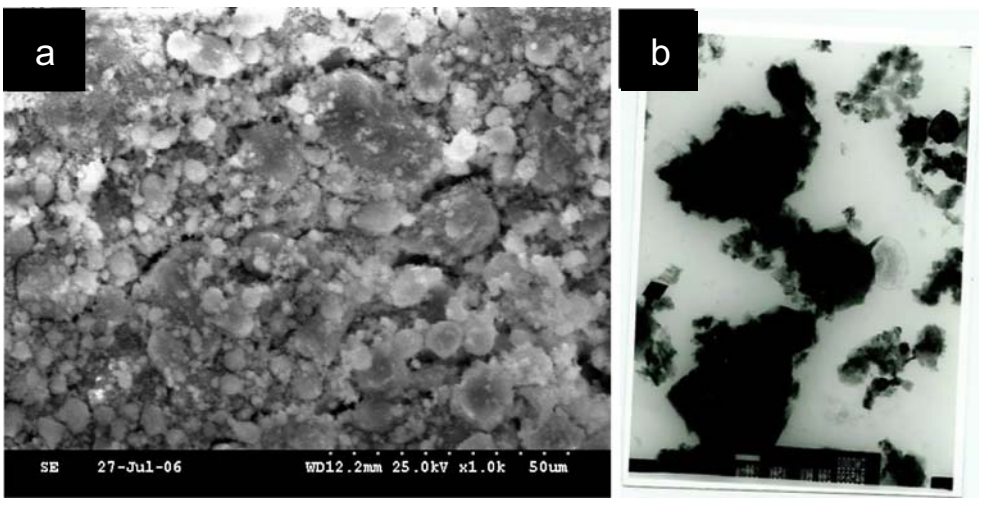

Fig. 2 SEM and TEM photograph of $ZnCo_2O_4$ nanoparticle. **a** SEM and **b** TEM

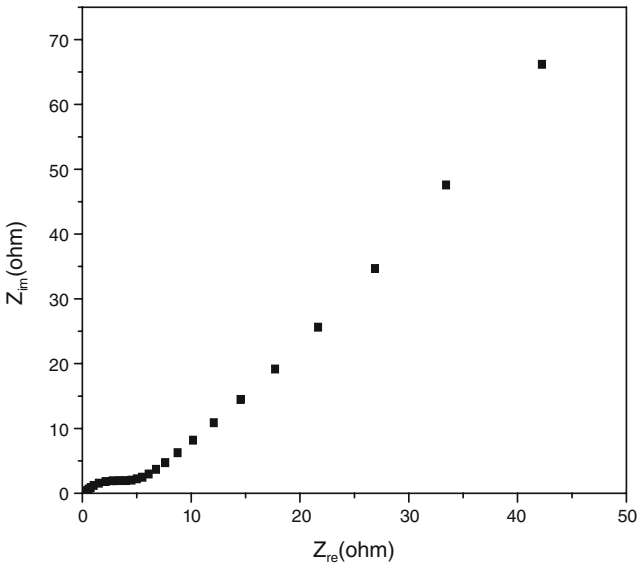

Fig. 3 Nyquist plot of $ZnCo_2O_4$/CNF-based supercapacitor cell

SEM analysis

Figure 2 shows the SEM and TEM images of $ZnCo_2O_4$. Nano-size particles with spherical shape reveal that the co-precipitation method enables to form well crystalline $ZnCo_2O_4$ powder. The TEM result clearly indicates that the prepared material has aggregated particles consisting of average particle size of 40–50 nm. The $ZnCo_2O_4$ powder are smooth, porous with submicron crystallite formation, which will contribute to higher capacitance and low impedance.

Table 1 Specific capacitance of $ZnCo_2O_4$/CNF based supercapacitor cell at various scan rates

Scan rate (mV/s)	Specific capacitance of $ZnCo_4O_2$/CNF (F/g)
5	77
10	64
20	48
50	42

Electrochemical impedance analysis

Figure 3 shows the electrochemical impedance results of the $ZnCo_2O_4$ nanomaterial. As shown in the figure, there are two distinct regions depending on the frequency range. The complex plane plot consists of a small semicircle at high frequencies with a transition to a linear part at low frequencies corresponding to a capacitive behavior. The electrolyte solution resistance of 0.2 Ω is determined from the intersecting point of the semicircle with the real axis. The intermediate frequency region is the 45° line, which is characteristic of diffusion into the electrode. The more close to the vertical spike the higher will be the supercapacitive behavior. The charge transfer resistance R_{ct} of the electrode was estimated to about 4.6 Ω from the point of intercept with the real axis in the high frequency range. It is obvious that $ZnCo_2O_4$ with the carbon nanofoam enhanced the conductivity by reducing the internal resistance.

Electrochemical analysis

Figure 4 shows the CV results of the $ZnCo_2O_4$/CNF composite electrode recorded at 5, 10, 20, and 50 mV s^{-1}

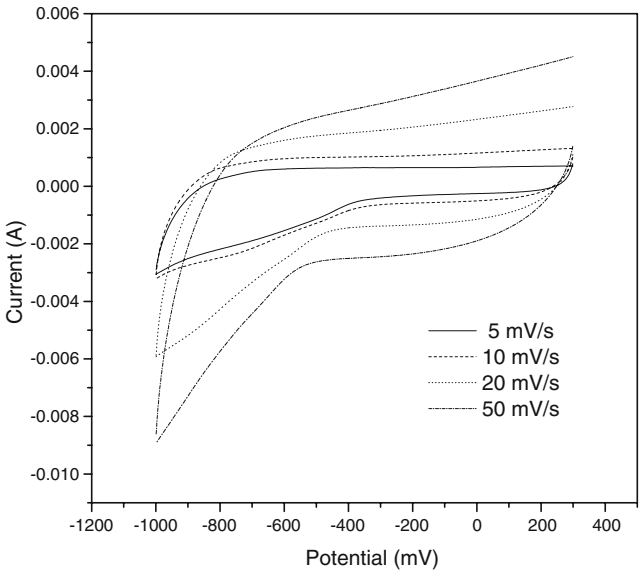

Fig. 4 Cyclic voltammogram of $ZnCo_2O_4$/CNF-based supercapacitor cell at various scan rates

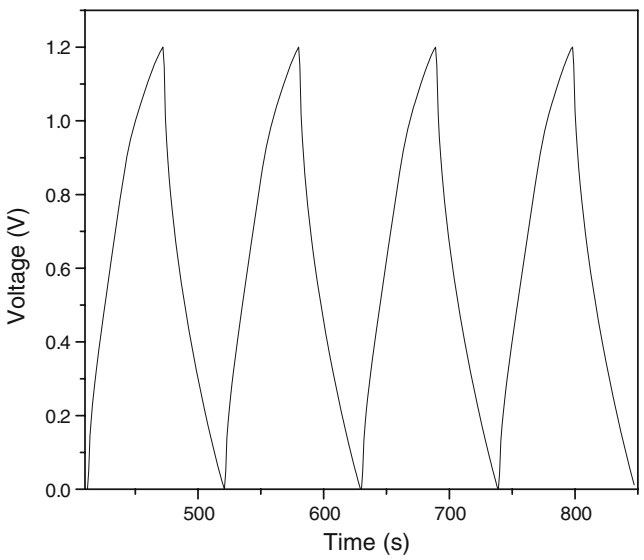

Fig. 5 Charge–discharge profile of $ZnCo_2O_4$/CNF composite-based supercapacitor cell at 2 mA/cm^2

scan rates. This composite electrode-based supercapacitor cell shows a rectangular-like shape in the cyclic voltammogram. This reveals that the compound stores the electrochemical charge as described by electrical double. The response current increases linearly with the increase of scan rate. These composite electrodes have good power characteristics of 1,200 W kg^{-1} because of the conductivity and dispersion of voids and carbon nanofoam. The pores of these composites allows the alkaline electrolyte to penetrate deeply into the composite matrix. The specific capacitance was calculated by using the equation,

$$C = i/s$$

where, i—the average current, s—the scan rate. From the CV results, a specific capacitance of 77 F g^{-1} was obtained for the $ZnCo_2O_4$/CNF-based supercapacitor cell. This larger capacitance arises from the uniform mixture of zinc cobaltate with the carbon nanofoam, which increased effectively the active sites on the oxide particles. The combination of redox and pseudocapacitance increases the power characteristics of $ZnCo_2O_4$ yielding a value as high as 77 F g^{-1} at 5 mV s^{-1} scan rate. Table 1 shows the relationship between the scan rate and specific capacitance.

Galvanostatic charge–discharge characteristics

Figure 5 shows the galvanostatic charge–discharge curves of $ZnCo_2O_4$/CNF composite electrodes in 6 M KOH at 2 mA cm^{-2} current density. The discharge curves are symmetric as expected. The cycle life of this capacitor is more than 100,000 cycles. The internal resistance of the supercapacitors was determined from the steep rise in the potential of the charge–discharge plot using the relation:

$$R = V/i$$

where i is the charging current, and V is the magnitude of the vertical rise/drop of potential during charging and discharging. $ZnCo_2O_4$/CNF composite electrodes gave a uniform charge–discharge with an internal resistance (IR) of 175 Ω up to 1,000 cycles. IR was even found to decrease (2 Ω) after 100,000 cycles. It should be noted that the IR was minimum due to the low electronic conductivity of the oxides. The voltage varies linearly with time between 0 and 1.2 V. This result indicates that the $ZnCo_2O_4$/CNF composite electrode can be used as an electrochemical capacitor with an extended operating voltage of 1.2 V. The coulombic efficiency η of the capacitor cell was calculated from the galvanostatic charge–discharge experiments as follows.

$$\eta = (\Delta t_D/\Delta t_C) \times 100\%$$

where Δt_D and Δt_C are the times of charging and discharging, respectively. It can be seen that the system has an efficiency greater then 98% even after 100,000 cycles.

Conclusion

The $ZnCo_2O_4$/CNF was introduced for the first time as electrode material for supercapacitors. It shows high specific capacitance and low impedance when compared to pure metal oxide nanocomposites. The introduction of CNF in metal oxide increased the specific capacitance by reducing the internal resistance of the electrode. A specific capacitance of 77 F g^{-1} was obtained for $ZnCo_2O_4$/CNF-based supercapacitors. Also, long cycle life, high couloumbic efficiency with minimum IR drop was observed.

References

1. Conway BE (1959) Electrochemical supercapacitors: Scientific fundamentals and Technological Applications. Klumer Academic Plenum Publishers, New York
2. Conway BE (1991) J Electrochem Soc 138:1539
3. Arulepp M, Leis J, Lätt M, Miller F, Rumma K, Lust E, Burke AF (2006) J Power Sources 162:1460
4. Chi-Chang Hu, Ming-Jue Liu, Kuo-Hsin Chang (2007) J Power Sources 163:1126
5. Hu CC, Chen WC (2000) J Electrochem Acta 49:3469
6. Zheng JP, Jow TR (1995) J Electrochem Soc 142:6
7. Srinivasan V, Weidner JW (1997) J Electrochem Soc 144:210
8. Kalpana D, Omkumar KS, Suresh Kumar S (2006) J Electrochem Acta 157:621
9. Tianshi Z, Hiing P, Jiancheng Z, Lingbing K (1999) Mater Chem Phys 61:1992