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Synthesis and characterization of spinel type $ZnCo_2O_4$ as a novel anode material for lithium ion batteries

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Since the introduction of lithium ion batteries with carbon as anode material in 1990 by Sony Energetics Inc., research has been undertaken to search for new anode materials to improve the energy density of practical cells. Idota *et al*. [1] have reported that tin-based amorphous oxides as new materials for lithium ion batteries exhibit high lithium storage capacity. Recently, some metal oxides and metal-based composite oxides, such as nickel oxides, cobalt oxides and copper oxides [2], and spinels as Mg_2SnO_4, Zn_2SnO_4 [3] were also studied as new anode materials. These materials showed much higher lithium storage capacity than carbon materials (theoretical maximum capacity of 372 mAh/g [4–6]), and were considered as possible candidates for next generation of anode materials.

Spinel-type $ZnCo_2O_4$ has long been used as pigments or dying materials, and also studied as catalysts for some reactions [7]. In this work, nano-sized $ZnCo_2O_4$ powder was obtained by the decomposition of the oxalate precursor, which was synthesized by the rheological phase reaction [8]. The result of electrochemical tests showed that the obtained $ZnCo_2O_4$ as an novel anode material was also feasible and demonstrated high energy density.

The oxalate precursor was prepared by the rheological phase reaction, $CoCO_3{\cdot}3Co(OH)_2{\cdot}xH_2O$, ZnO and $(COOH)_2{\cdot}2H_2O$ were ground and fully mixed in 1:2:6.1 mol ratio. The rheological body was obtained with a proper amount of deionized water and reacted at 60 °C for 5 h. After drying in an oven, it was pyrolyzed at 600 °C for 4 h in air, and then a black powder $ZnCo_2O_4$ was obtained. Thermogravimetry and differential thermal analysis (TG/DTA) of the precursor were performed by the Shimadzu DT-40 thermal analyzer at a heating rate of 10 °C/min in air. The X-ray diffraction (XRD) measurements of the sample were carried out by Shimadzu XRD-6000 diffractometer with Cu K_α radiation ($\lambda = 1.54056$ Å). Transmission electron microscope (TEM) image of the sample was observed on the Jeol JEM-100 CXII transmission electron microscope.

The discharge (inserting of lithium ions to the negative electrode) and charge (extracting of lithium ions) properties of the prepared sample were examined by a simulated cell system. The simulated cell was assembled in an Ar-filled glove box with both water and oxygen concentrations less than 5 ppm. The working electrode was prepared by pressing $ZnCo_2O_4$ powder, acetylene black and polytetrafluoroethylene (PTFE) binder (weight ratio of 80:15:5) onto a nickel gauze current collector. Lithium pellet of high purity was used for the counter electrode. The two electrodes were separated by a porous polypropylene film (Celgard 2400) and soaked in the electrolyte of 1 $molL^{-1}$ $LiPF_6$ (EC, DEC dissolved on 1:1 by volume). The cell was discharged and charged between 3.0 and 0.01 V vs. Li^+/Li at a constant current density of 100 mA/g.

The TG and DTA curves of the oxalate precursor are shown in Fig. 1. It indicates that the decomposition of the precursor proceeds in three steps. The weak endothermic peak on the DTA curve located at about 70 °C is due to the loss of lattice water and the excessive oxalic acid. The strong endothermic peak is corresponding to the decomposition of the oxalate. The sharp exothermic peak is caused by the oxidation reaction in air.

The XRD pattern of the prepared $ZnCo_2O_4$ is presented in Fig. 2. The peaks located at 18.99, 31.26, 36.84, 38.58, 44.81, 55.64, 59.33, 65.22, 74.15, 77.31 and 78.40 ° are characteristics of spinel-type $ZnCo_2O_4$, which are consistent with JCPDS 23-1390. The grain size is estimated to be about 100 nm according to the Sherrer formula, according to the observation of the TEM image (Fig. 3).

Fig. 4 shows the charge and discharge curves of $ZnCo_2O_4$/Li test cell at a constant current density of 100 mA/g. The initial discharge capacity is 1320 mAh/g with a large irreversible capacity about 612 mAh/g, which is due to the formation of solid electrolyte interface (SEI) and the irreversible reaction of lithium with oxygen atoms in the active material [9]. There are three potential plateaus located at 1.0 V (a), 0.7 V (b) and 0.4 V (c) in the process of the first discharge, and the capacity of the three plateaus is 615, 238 and 420 mAh/g, respectively. With the formation of a stable SEI, the plateau at 1.0 V is gradually disappeared but other plateaus still exist. The plateaus on the charge process emerge between 1.5 and 2.2 V, which is a little high for practical application, and doping with other transition metals can probably solve this problem.

Poizot *et al*. [2] have proposed that different from the tin oxides materials, the mechanism of the lithium storage in the cobalt oxide materials is due to the reversible oxidation and reduction of the cobalt oxides, coupled

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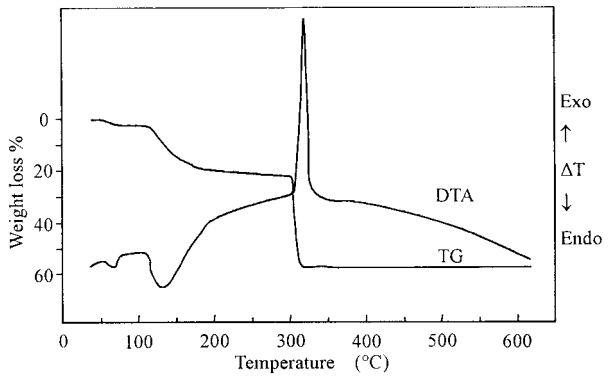

Figure 1 TG/DTA curves of the oxalate precursor.

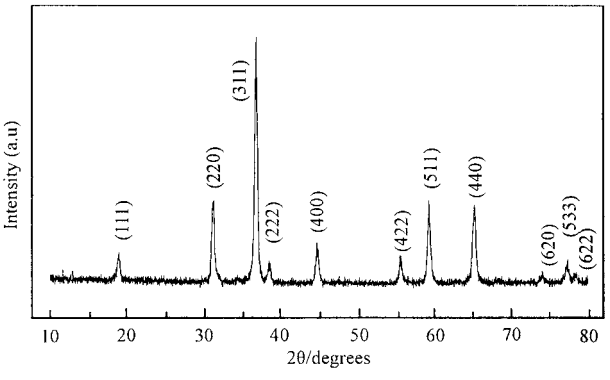

Figure 2 XRD pattern of $ZnCo_2O_4$.

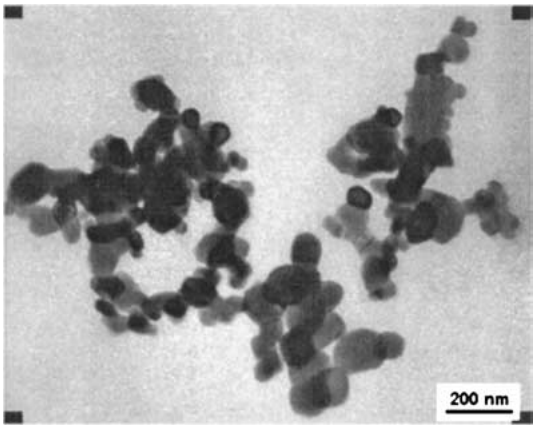

Figure 3 TEM image of $ZnCo_2O_4$.

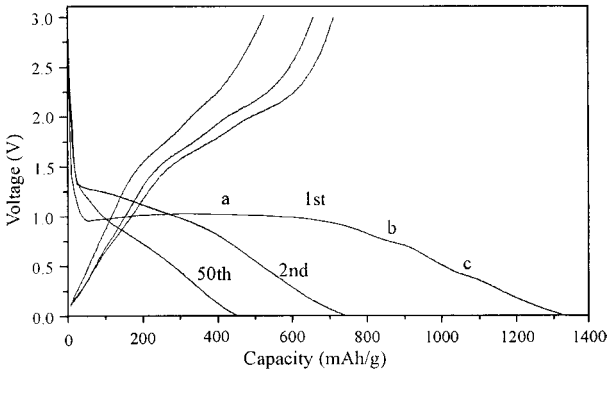

Figure 4 Charge and discharge curves of $ZnCo_2O_4$/Li test cell at a constant current density of 100 mA/g.

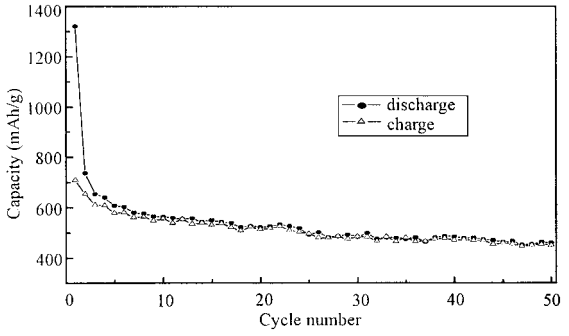

Figure 5 Cycle performance of $ZnCo_2O_4$ at current density of 100 mA/g.

with the formation and destruction of lithium oxides:

$$CoO + 2Li \leftrightarrow Li_2O + Co$$

But for the spinel-type $ZnCo_2O_4$, we consider that in the electrochemical process, nano-sized metal cobalt particles formed in the equation above have reacted with zinc and lithium and formed LiZn or Li_xZnCo alloys, which can insert and extract lithium ions reversibly, and further investigations are needed to confirm this speculation.

The cycle performance of nano-sized $ZnCo_2O_4$ within fifty cycles is shown in Fig. 5. As mentioned above, the irreversible capacity can be observed on the first cycle. After the first few cycles, the process of charge and discharge gradually become considerably stable, the efficiency of charge and discharge amounts to 95% in the following cycles, and the charge capacity retention from the tenth to fiftieth cycle is 80% with an average capacity fade of 0.5% per cycle.

With a view of our findings, spinel type $ZnCo_2O_4$ as anode materials for lithium ion batteries demonstrates a large reversible capacity and excellent cycleability. It has been reported that the electrochemical performance of tin-based anode materials and cobalt oxide materials [2, 10, 11] is very sensitive to their particle size. Smaller particle size probably cause better electrochemical performance of tin-based anode materials [1, 12]. But it is not the case for the cobalt oxides materials and there exists a proper range of particle size for better performance of $ZnCo_2O_4$, to which our future efforts should be directed.

Acknowledgment

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