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Facile synthesis and electrochemical performance of Co_2SnO_4/Co_3O_4 nanocomposite for lithium-ion batteries

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ABSTRACT

A novel dispersed structure Co_2SnO_4/Co_3O_4 composite has been successfully synthesized by a conventional co-precipitation method with certain amount of NaOH concentration. The obtained composite exhibits dispersed structure with small spherical nanocrystals adhering to the surface of large polyhedral particles, which has been studied as an anode material in lithium-ion battery. Galvanostatic charge–discharge and cyclic voltammetry has been conducted to measure the electrochemical properties of the material. The results show that Co_2SnO_4/Co_3O_4 composite demonstrates good reversible capacity of 702.5 mA h g^{-1} after 50 cycles at a current density of 100 mA h g^{-1}, much better than that of pure Co_3O_4 (375.1 mA h g^{-1}) and pure Co_2SnO_4 (194.1 mA h g^{-1}). This material also presents improved rate performance with capacity retention of 71.1% when the current ranges from 100 mA g^{-1} to 1000 mA g^{-1}. The excellent electrochemical performance of the as-prepared dispersed structure Co_2SnO_4/Co_3O_4 composite could be attributed to the good dispersibility of nanoparticles which can effectively alleviate the volume expansion and improve the conductivity, thus enhance the cycling stability.

1. Introduction

Lithium-ion batteries (LIBs) are considered to be the promising power source for portable electronic devices and electric vehicles due to their high energy density, long cycle life and environmental benignity [1–3]. It is well known that the extensive used commercial anode materials used for LIBs are graphite. However, graphite used as anode material exhibits a low theoretical specific capacity (372 mA h g^{-1}) and poor rate capability, which greatly limits its application on lithium-ion batteries. With the development of the increasing demand for higher energy densities LIBs, it is essential to find electrodes with high theoretical specific capacity, excellent cycling performance, and good rate capability. Compared with commercial graphite of 372 mA h g^{-1}, metal oxides which possess higher theoretical capacity (500–1000 mA h g^{-1}), such as SnO_2, Co_3O_4 and ZnO, have been widely studied as anode materials [4–6]. In recent years, some ternary stannates such as M_2SnO_4 (M = Mn, Co, Zn) possess higher theoretical capacity, which have shown good capability on cycling for using as anode materials [7–12]. Among them, Co_2SnO_4, where both Co and Sn are electrochemical active metals with respect to lithium, with the addition of its high theoretical capacity (1105.6 mA h g^{-1}), has attracted much attention [13–15]. Wang reported the synthesis of Co_2SnO_4 nanocrystals by a hydrothermal method, the electrochemical performance of Co_2SnO_4 nanocrystals were much better than that of bulk Co_2SnO_4 prepared by high temperature solid-state reaction [13]. Multiwalled carbon nanotubes (MWCNTs) are attractive materials in energy storage due to superior electrical conductivity and high activated surface area. Wang had found that the composite of Co_2SnO_4/MWCNTs as a reversible anode material exhibited a reversible specific capacity of 898.8 mA h g^{-1} after 50 cycles [14]. Carbon coating is also an effective way to enhance cycle ability and rate performance. Qi et al. synthesized a Co_2SnO_4@C core–shell nanostructure through a simple glucose hydrothermal and subsequent carbonization approach. The capacity of Co_2SnO_4@C-thick composite maintained at 474 mA h g^{-1} after 75 discharge/charge cycles with capacity retention of 60.4%. Uniform and continuous carbon buffering matrix improved cyclic performance compared to pure Co_2SnO_4 nanocrystals [15]. However, it should be noted that the relatively low capacity retention for Co_2SnO_4 is still exist, which has a negative impact on its potential application. Therefore, further

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improving the electrochemical performance, especially cycle stability, is very necessary.

Among the metal oxides, cobalt oxides (Co_3O_4, CoO) demonstrated better electrochemical properties in LIBs [9,11,12], have attracted a number of attentions on preparing composite of Co_3O_4 with other promising materials. For example, Luo had report the synthesis of hierarchical graphene-wrapped TiO_2@Co_3O_4 nanobelt arrays (G-TiO_2@Co_3O_4 NBs) as anode materials for LIB applications [16]. The results showed that the as-formed hierarchical G-TiO_2@Co_3O_4 NBs exhibited highly reversible capacity, excellent cyclability, and good rate capability as anode materials for LIBs. Xing had demonstrated a simple template-free method to prepare the SnO_2–Co_3O_4 core–shell nanoneedles arrays [17]. The as-formed SnO_2–Co_3O_4 core–shell nanoneedles arrays exhibited high reversible capacity, improved cycling stability and rate capability with respect to the SnO_2 nanostructures and bare Co_3O_4 nanoneedles arrays. Other materials composite with Co_3O_4, such as carbon-sphere/Co_3O_4 nanocomposites, Co_3O_4/NiO/C nanowire arrays, has also been reported [18,19]. These results mentioned above demonstrate that Co_3O_4 can well perform as carrier or matrix when used on lithium-ion battery materials.

In the present work, a novel Co_2SnO_4/Co_3O_4 composite has been prepared by a simple one-pot synthesis co-precipitation method. The Co_2SnO_4/Co_3O_4 composite exhibit dispersed structure with small bulk Co_3O_4 particles surrounded by Co_2SnO_4 nanoparticles. In the special structure, the Co_3O_4 bulk particles seem to take the role of supporting materials and electrochemical active materials. With the addition of the special dispersed structure, the agglomeration problem can be partially relieved. Compared with pure Co_2SnO_4 and pure Co_3O_4 which prepared by the same experimental procedure, the Co_2SnO_4/Co_3O_4 material exhibit higher lithium storage capacities and better cycling performance.

2. Experimental procedure

2.1. Preparation

The chemicals used in this study were analytical grade without further purification. Co_2SnO_4/Co_3O_4 composite was synthesized by a co-precipitation method. Firstly, 1.19 g $CoCl_2{\cdot}6H_2O$ and 0.875 g $SnCl_4{\cdot}5H_2O$ were respectively dissolved into 50 ml distilled water, and two solutions were mixed together at room temperature with magnetic stirring. Subsequently, 50 ml 4 M NaOH solution was dropped into the Sn–Co mixture solution under magnetic stirring. A dark blue precipitate was formed instantaneously. After being stirring 10 min, the precipitate was collected by centrifugation, washed with distilled water and ethanol thoroughly, and then dried in an electric oven at 120 °C for 12 h, thus the precursor of composite was prepared. Finally, the obtained precursor was calcined at 900 °C for 6 h to produce the Co_2SnO_4/Co_3O_4 composite.

For comparison, pure Co_2SnO_4 was also prepared by the same procedure, except that the NaOH concentration was controlled in 2 M. Pure Co_3O_4 was also prepared by the same procedure, except that $SnCl_4{\cdot}5H_2O$ was absent to this experiment.

2.2. Characterization

Crystallographic phases of prepared samples were characterized by X-ray diffraction (XRD, PANalytical X'Pert PRO) with Cu Kα radiation, the morphology and microstructure were investigated by field emission scanning electron microscopy (FESEM, ZEISS ULTRA 55) and transmission electron microscopy (TEM, JEM-2100HR).

2.3. Electrochemical measurements

The electrochemical performance was tested by using half-cells (CR2530) assembled in an argon-filled glove box. Working electrodes, with a composition of 60 wt.% active materials, 20 wt.% acetylene black, and 20 wt.% PVDF, were fabricated on the copper foil of 13 μm thickness and dried at 80 °C for 12 h under vacuum subsequently. The electrolyte was 1.0 M $LiPF_6$ in a mixture of ethylene carbonate, diethyl carbonate, and ethyl methyl carbonate (1:1:1 by volume, provided by Chei Industries Inc., South Korea). The separator was made of a Celgard 2400 film.

Galvanostatic discharge–charge measurement of the cells were carried out at a current density of 100 mA g^{-1} in the voltage range of 0.001–3.0 V (versus Li/Li^+) using a LAND-CT2001A instrument. Cyclic voltammetry measurements were performed using electrochemical workstation (Shanghai Chenhua Instrument Co.) at a scan rate of 0.1 mV/s in the range of 0.01–3.0 V.

3. Results and discussion

XRD pattern of the Co_2SnO_4/Co_3O_4 composite precursor is shown in Fig. 1. The precursor included cobalt hydroxide, hydrated Co/Sn hydroxide is a primary product before the final calcine synthesis. In the precursor formation process, alkaline concentration is effective for controlled growth of as-prepared metal oxides or compounds with phase composition, morphology and size [20,21]. The concentrated NaOH solution also results in the partial or complete dissolution of the constituent element (Sn) formed by the complexation. For the novel Co_2SnO_4/Co_3O_4 composite, the schematic representation of reaction is illustrated in Fig. 2b. When NaOH concentration is 2 M, the formation of Co_2SnO_4 will be easily happened without any impurity which has been reported by literature [22]. The complexation of precipitates including $Sn(OH)_4$ and $Co(OH)_2$ could absolutely form $Co_2SnO_4{\cdot}4H_2O$, which will translate into Co_2SnO_4 after calcinations. The synthetic process can be expressed by:

$$Co^{2+} + Sn^{4+} + 6OH^- \rightarrow Co(OH)_2 \downarrow + Sn(OH)_4 \downarrow$$

$$2Co(OH)_2 + Sn(OH)_4 \rightarrow Co_2SnO_4{\cdot}4H_2O$$

$$Co_2SnO_4{\cdot}4H_2O \rightarrow Co_2SnO_4 + 4H_2O \uparrow$$

However, when NaOH concentration increased to 4 M, the reaction process cannot be precisely expressed by chemical

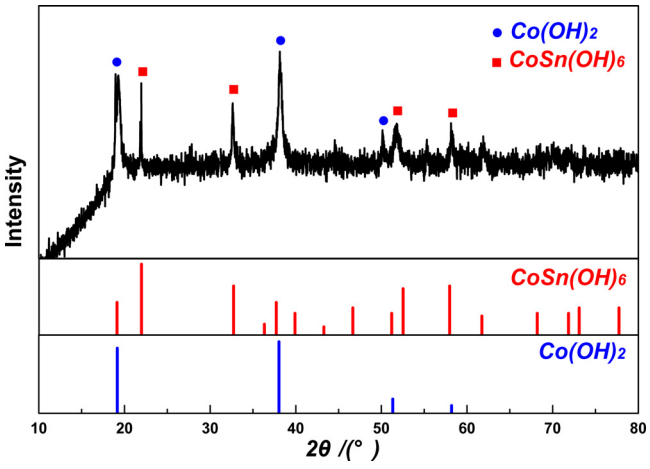

Fig. 1. XRD pattern of the Co_2SnO_4/Co_3O_4 nanocomposite precursor.