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Preparation and Electrochemical Performance of Nano-Co_3O_4 Anode Materials from Spent Li-Ion Batteries for Lithium-Ion Batteries

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A hydrometallurgical process for the recovery of cobalt oxalate from spent lithium-ion batteries was used to recycle cobalt compound by using alkali leaching, reductive acid leaching and chemical deposition of cobalt oxalate. The recycled cobalt oxalate was used to synthesize nano-Co_3O_4 anode material by sol-gel method. The samples were characterized by thermal gravity analysis and differential thermal analysis (TGA/DTA), X-ray diffraction (XRD), scanning electron microscopy (SEM) and charge/discharge measurements. The influence of molar ratio of Co^{2+} to citric acid and calcination temperature on the structure and electrochemical performance of nano-Co_3O_4 was evaluated. As the molar ratio of Co^{2+} to citric acid is 1:1, the face-centered cubic (fcc) Co_3O_4 powder shows the discharge capacity of 760.9 mA h g^{-1}, the high coulombic efficiency of 99.7% in the first cycle at the current density of 125 mA g^{-1}, and the excellent cycling performance with the reversible capacity of 442.3 mA h g^{-1} after 20 cycles at the current density of 250 mA g^{-1}.

KEY WORDS: Spent lithium-ion batteries; Sol-gel method; Reductive acid leaching; Nanostructure cobalt oxide; Electrochemical behavior

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1. Introduction

Lithium-ion batteries (LIB) are dominantly used as electrochemical power sources in the mobile telephones, personal computers, video cameras and other modern-life appliances due to their favorable characteristics of lightweight and high energy density.

However, the spent LIB not only contains metals such as nickel, cobalt, copper, and lithium, but also produces large amounts of metal-containing hazardous waste. Therefore, the research of recycling technologies for spent LIB is attracting great attention, both for environmental protection and resource conservation.

Currently, $LiCoO_2$ is the most widely used active cathode material for lithium-ion secondary batteries. However, $LiNi_xMn_yCo_{1-x-y}O_2$ and $LiMn_2O_4$ cathode materials are gradually used to substitute for $LiCoO_2$ in order to improve the safety and electrochemical performance of lithium-ion batteries. This means that the active cathode materials in spent LIB contain cobalt, nickel, and manganese with variable concentrations, thus making chemical processes for recovery of the spent LIB more complex. In order to efficiently recover the valuable metals (Co, Ni, Mn and Li), various physical and chemical processes have been reported, involving crushing, dismantling, sieving, alkali leaching, acid leaching, solvent extraction, chemical precipitation and electrochemistry[1–4]. Cobalt and lithium are easily leached from spent lithium-ion batteries by using HNO_3[5], HCl[6] and H_2SO_4[7,8] as leaching agents. But generally, reducing agents like hydrogen peroxide (H_2O_2) is required to promote the dissolution of transition metal oxide cathode material. For the purification of Co(II) from the leach liquor, the separation methods such as chemical precipitation and electrolysis were proposed. However, the important drawback of the above methods is the low purity of the cobalt compounds.

Recently, nano-sized transition metal oxides such as NiO, CuO, Co_3O_4, Fe_2O_3 and Fe_3O_4 have been widely studied for alternative anode materials to replace graphite[9–15]. The core-shell nanostructure was used to improve the electrochemical performance of metal oxides[16]. This means that most the impurities from the spent LIB can be used to prepare the metal oxide anode material for lithium-ion batteries, which indicates that the recycled cobalt compounds can be directly used to synthesize cobalt oxide anode material. Among the candidates of transition metal oxides, cobalt oxide (Co_3O_4) has shown the highest capacity and best cycle performance. Many routes have been applied to synthesize Co_3O_4 powders with various morphologies, such as the flower-like sphere fabricated by means of a simple calcination process from α-phase cobalt

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hydroxide precursors[17], hollow Co_3O_4 spheres prepared with a electrostatic spray deposition (ESD) technique with a precursor suspension of cobalt alkoxide with a hollow structure[18], macroporous Co_3O_4 platelets with a microwave-assisted synthesis method[19], *etc*.

In this study, nano-sized Co_3O_4 powders have been synthesized by sol-gel method with recycled cobalt oxalate from spent LIB. The recycled cobalt oxalate was not further purified. The effects of synthesizing conditions on the powder characteristics were investigated and the charge−discharge behavior as an anode material was discussed.

2. Experimental

2.1. Materials and reagents

Spent LIBs used in different mobile phones were collected for this study, and they were dismantled through a manual procedure to remove both plastic and steel shells. Both the anode and cathode films were crushed in the range of 1−5 mm in size and then bathed in N-methyl pyrrolidinone (NMP) solvent at 100 °C for 6 h with high speed stirring. The mixed powder of active anode and cathode materials was effectively separated from copper and aluminum support substrates (which were recovered here in the metallic form), and dried at 120 °C for 24 h. The dried mixture powder was finally ground for 30 min to obtain a fine powder that was screened in sequential sieves with openings ranging from 10 to 500 μm.

2.2. Precipitation of cobalt oxalate

First, the mixture of active powder materials was leached with 2 mol L^{-1} NaOH solution to selectively dissolve aluminum. Then the filter residue was leached with 6 wt% H_2SO_4 and 1.5 wt% H_2O_2 at 60 °C for 3 h. The pH of leach liquor was adjusted to 5 with 2 mol L^{-1} NaOH solution in order to make the impurity ions form $Al(OH)_3$, MnOOH, $Cu(OH)_2$ and $Ni(OH)_2$ precipitation. Lastly, $(NH_4)_2C_2O_4$ saturation solution was added into the leach liquor containing Co^{2+} and the pH of mixed solution was adjusted to a pH value of 2 to form CoC_2O_4 precipitation. The CoC_2O_4 products were washed with deionized water for several times and dried at 100 °C for 24 h. The recycled CoC_2O_4 precipitation was used to synthesize nano-Co_3O_4 without being further purified.

2.3. Sample synthesis

The recycled CoC_2O_4 powder was first dissolved in 4 mol L^{-1} HNO_3 acid solution. This solution was mixed until homogeneous and citric acid was added while stirring, until the molar ratio of Co^{2+} to citric acid was up to the designed molar ratio (molar ratio, 1:0.4, 1:0.7, 1:1). Then the solution was heated to 70−80 °C until a gel formed. Lastly, the gel was transferred to an alumina boat and heated at 2 °C/min to 500−650 °C under air atmosphere and was decomposed at that temperature for 1 h to form Co_3O_4 products.

2.4. Sample characterization

Morphology of the fabricated sample was characterized by field emission scanning electron microscopy (SEM, FEI Quanta-200) operated at an acceleration voltage of 5 kV. Powder X-ray diffraction (XRD, Philips X'Pert MPD Diffractometer, Cu$K\alpha$ radiation) was used for phase identification. Scan rate of 4° min^{-1} and step size of 0.04° were applied to record the pattern. The operation voltage and current were 40 kV and 45 mA, respectively. Thermal gravity analysis (TGA) /differential thermal analysis (DT-2) data for decomposition and oxidation of cobalt citric acid gel precursors were obtained at a heating rate of 5 °C min^{-1} in air with a TGA/DTA50 thermal gravimetric analyzer (Shimadzu Corporation, Japan).

2.5. Electrochemical characterization

Electrochemical performances of the nano-Co_3O_4 particles were investigated with two-electrode coin-type cells (CR 2025). The working electrodes were prepared by a slurry coating procedure. The slurry consisted of 800 wt% Co_3O_4 powder, 10 wt% acetylene black and 10 wt% polyvinylidene fluoride (PVDF) dissolved in N-methyl pyrrolidinone (NMP), and was incorporated on copper foil with 12 mm in diameter. After being dried at 110 °C for 24 h in vacuum, the foil was pressed under a pressure of 20×10^6 Pa. The loading stress of Co_3O_4 is 10.81×10^{-2} kg m^{-2} Test cells were assembled in an argon-filled glove box with the metallic lithium foil as both the reference and counter electrodes, 1 mol L^{-1} $LiPF_6$ in ethylene carbonate (EC)- dimethylene carbonate (DMC)- ethyl methyl carbonate (EMC) (1:1:1 in volume) as the electrolyte, and a polypropylene (PP) micro-porous film (Celgard 2300) as the separator. The galvanostatic charge−discharge tests were conducted on a blue-key battery program-control test system (BK6061 Testing System, Guangzhou Blue-key Electronic Industry Co., Ltd) at a current density of 125 mA g^{-1} and 250 mA g^{-1} in the voltage range of 0.02−3.0 V (versus Li/Li^+) at room temperature (25 ± 1 °C). The electrochemical impedance spectroscopy (EIS) measurements of the cells were performed on an electrochemical workstation (CHI 660C) in the frequency range from 0.01 to 100 kHz.

3. Resultants and Discussion

3.1. Thermal analysis of cobalt citric acid gel precursor

The TGA/DTA measurement of cobalt citric acid gel precursor was carried out to find out suitable calcination temperature for the precursor and the results are shown in Fig. 1. The double peaks located at 160 °C and 200.5 °C on the DTA curve are

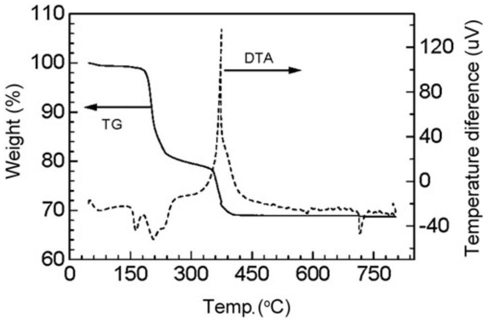

Fig. 1 TGA/DTA profiles of cobalt citric acid gel precursor at a heating rate of 5 °C min^{-1} in air.