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Tartaric acid-assisted sol–gel synthesis of $LiNi_{0.5}Co_{0.5-x}Ti_xO_2$ ($0 \leqslant x \leqslant 0.5$) as cathode materials for lithium-ion batteries

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ABSTRACT

A series of $LiNi_{0.5}Co_{0.5-x}Ti_xO_2$ ($0 \leq x \leq 0.5$) are prepared by a tartaric acid-assisted sol–gel technique. The phase formation process is observed by TG–DTA. It is found that the target product appears at a temperature higher than 400 °C and completes to phase formation at 700 °C. The crystal structure and morphology are characterized by XRD, SEM and Raman spectroscopy. XRD patterns show that the as-prepared sample transforms from hexagonal structure into cubic structure with the increase of Ti content in $LiNi_{0.5}Co_{0.5-x}Ti_xO_2$. Raman spectra also demonstrate the successive substitution of Ti for Co in the structure with band blue-shift phenomenon. SEM images confirm that the as-prepared sample exhibits narrow and regular particles with the size between 0.5 and 1.5 μm. The apparent particle size of sample starts to decrease with $x \leq 0.1$, and the gradually increases by introducing Ti dopant with higher content ($x \geq 0.15$). The electrochemical behavior of the sample displays different characteristics after Ti substitution. It is found that the initial working potential increases with the increase of Ti doping content. As a result, the initial lithium storage capacity for trace Ti-doped sample is higher than that delivered by the pristine one. The decrease of reversible capacity for high degree Ti-doped sample is ascribed to the electrochemical inactivity of the cubic compound in the sample. Therefore, trace Ti doping is beneficial to achieve promising cathode material for lithium-ion batteries.

1. Introduction

Since the lithium-ion batteries were commercially issued by Sony Corporation, high capacity lithium-ion batteries have aroused great interest all over the world in the past 20 years. In the whole battery, cathode materials always show lower specific capacity (120–160 mA h g^{-1}) than that of anode materials (320–350 mA h g^{-1}). Moreover, the improvement of cathode materials fails to follow the demand of electronic devices. For instance, although $LiCoO_2$ has been used as commercial cathode material since 1991, its electrochemical properties have made very little progress in the past 20 years. Thus, it is important to pay more attention to develop novel capacity cathode materials for high capacity lithium-ion batteries. Among the candidate cathode materials, lithium nickel oxide, $LiNiO_2$, is a promising high capacity cathode material for lithium-ion batteries. As well-known, the practical capacity of $LiNiO_2$-based layered cathode materials, especially for $LiNi_{1-x}Co_xO_2$, is always higher than that of commercial $LiCoO_2$ [1–4]. However, $LiNi_{1-x}Co_xO_2$ layered cathode materials show poor cycle calendar life due to the structural and thermal instabilities.

In recent years, many oxides, phosphates and fluorides, such as Al_2O_3 [5], ZrO_2 [6], La_2O_3 [7], CeO_2 [8], TiO_2 [9], $AlPO_4^-$ [10], $Co_3(PO_4)_2^-$ [10], AlF_3 [11], have been applied to coat the particle surface to improve the structural and thermal stabilities of $LiNi_{1-x}Co_xO_2$ layered materials. Unfortunately, surface decoration is not an effective method to improve the intrinsic characteristics of active materials. Although the coated compounds show some improvements in electrochemical properties, these samples always experience the breakdown of microstructure for repeated volume evolutions after long-term cycles [11–13]. Because the coating layer can only suppress the whole particle expansion/shrinkage but can not avoid the phase transitions. To make intrinsic progress with structural and thermal stabilities, various metal elements, such as Al [14,15], Ca [16], Ce [17], Ga [18], Mg [19], Mn [20], Sn [21], Sr [22], Ti [23], Y [24], Zn [25], Zr [26], were used to dope and improve the electrochemical properties of $LiNi_{1-x}Co_xO_2$ layered cathode materials. It is thought that small amounts of additional metal ions doped into the $LiNi_{1-x}Co_xO_2$ lattice can

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stabilize the layered structure and improve electrochemical cycle behavior. For instance, Kalyani et al. reported that the partial substitution of Co for Al in $LiNi_{0.7}Al_{0.3-x}Co_xO_2$ can result in the stabilization of Ni^{3+}, the disappearance of cation mixing and the enhancement of 2D-layered structure [15].

Due to strong Ti–O bond in the structure, tetravalent titanium (Ti^{4+}) becomes a popular doping metal element to enhance electrochemical properties of various cathode materials [27–30]. For $LiNiO_2$-based layered structure materials, $LiNi_{0.7}Ti_{0.1}Co_{0.2}O_2$ [23], $LiNi_{0.7}Co_{0.2}Ti_{0.05}Zn_{0.05}O_2$ [31], $LiNi_{0.85}Co_{0.05}Ti_{0.05}Mg_{0.05}O_2$ [32], $LiNi_{0.5}Ti_{0.5}O_2$ [33] have been reported as excellent cathode materials with improved cycling performance and enhanced thermal stability after Ti doping. However, it is difficult to find the studies about the $LiNiO_2$-based layered compounds with full series of Ti doping. Most reports focus on the studies about single ratio and small amounts of additional metal ions doping [31–33]. As well-known, it is an important route to find the proper composition of compound with excellent structural and thermal stabilities by studying the structural evolutions in the full-scale doping.

In this paper, we report a full series of $LiNi_{0.5}Co_{0.5-x}Ti_xO_2$ ($0 \leq x \leq 0.5$) with different Co/Ti ratios prepared by tartaric acid-assisted sol–gel technique. The structural evolutions and electrochemical behaviors of these compounds are described and compared in detail by using various physical and chemical analytical techniques. It is expected that the advanced cathode material for lithium-ion batteries can be found through a thorough investigation of $LiNiO_2$-based layered compounds.

2. Experimental

2.1. Sample and electrode preparation

In the experiment, $LiNi_{0.5}Co_{0.5-x}Ti_xO_2$ ($0 \leq x \leq 0.5$) samples were prepared by a tartaric acid-assisted sol–gel technique using stoichiometric amounts of lithium acetate dihydrate, nickel acetate tetrahydrate, cobaltous acetate tetrahydrate, tetrabutyl titanate and tartaric acid as the starting materials. Firstly, tartaric acid was dissolved in distilled water and stirred for 30 min. Secondly, lithium acetate dihydrate, nickel acetate tetrahydrate and cobaltous acetate tetrahydrate were added into the tartaric acid solution and mixed for 2 h. After that, an ethanol solution of tetrabutyl titanate was added into the former mixed solution under constant stirring. The resulting solution was then stirred for 2 h to obtain a sol. To yield a gel, the sol was aged at 80 °C for 6 h. The resulting gel was dried at 120 °C for 48 h to achieve the precursor. The precursor was ground and preheated at 400 °C for 4 h to decompose the acetate and eliminate the water. After cooling down to room temperature, the obtaining specimen was ground again and calcined at 800 °C for 10 h under a stream of pure oxygen to achieve the final product.

The preparation of electrode and battery for electrochemical characterization can be found elsewhere [34]. The active electrode is comprised of active material (80 wt.%), acetylene black (AB, 12 wt.%) and polyvinylidene fluoride (PVDF, 8 wt.%). During the electrode preparation, N-methylpyrrolidone (NMP) was used as a solvent to obtain the slurry for film casting. After NMP was completely removed, the film was cut into disks with a diameter of 15 mm. For repeated cycling, the CR2016 type coin cells were assembled by using the active material film as working electrode, Whatman glass fiber filter as separator, lithium metal disk as counter electrode and 1 mol L^{-1} $LiPF_6$ dissolved in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1, v/v) as electrolyte in Ar-filled glove box (Etelux, China).

2.2. Physical and chemical characterization

Galvanostatic charge/discharge cycles were collected on multichannel Land Battery Test System (Wuhan Jinnuo, China). All CR2016 type coin cells were charged and discharged between 2.0 V and 4.3 V at a constant current of 30 mA g^{-1}. The electrochemical impedance spectroscopy (EIS) was measured by a CHI 660D (Shanghai Chenhua, China) electrochemical working station over a frequency range from 0.01 Hz to 100 kHz at a potentiostatic signal amplitude of 5 mV.

Thermogravimetry and differential thermal analysis (TG/DTA) was performed on a Seiko EXSTAR 6000 TG/DTA 6300 thermal analyzer at a heating rate of 5 °C min^{-1} from room temperature to 900 °C. The X-ray diffraction (XRD) patterns for the samples were carried out with Bruker AXS D8 FOCUS X-ray Diffractometer using nickel-filtered Cu Kα radiation (λ = 1.5408 Å). The surface morphology and apparent particle size were observed by using a Hitachi S4800 scanning electron microscopy (SEM). Raman spectra were collected on a Renishaw RM-1000 confocal microscope Raman spectrometer from 100 to 1500 cm^{-1}.

3. Results and discussion

Fig. 1 shows the TG–DTA curves of the precursor for $LiNi_{0.5}Co_{0.5-x}Ti_xO_2$ (x = 0.10) samples. The TG curve shows a step-wise weight loss in the temperature ranges from 30 to 100 °C, 100 to 200 °C, 200 to 245 °C, and 245 to 400 °C. The initial two steps correspond to four endothermal peaks at 85, 102, 164 and 181 °C, which are associated with the loss of absorbing and structural water in the reagents of the mixed precursor. Another exothermal peak located at 205 °C can be attributed to the thermal decomposition of acetate group as described by Hon et al. [35]. The last intensive exothermal peak observed at 372 °C is probably contributed to the combustion of tartaric acid and the preliminary formation of $LiNi_{0.5}Co_{0.5-x}Ti_xO_2$ compounds. In a typical tartaric acid-assisted sol–gel process, the tartaric acid used as a chelating agent can release a large amount of heat during combustion and improve the crystallization reaction. Above 400 °C, there is almost no weight loss observed in the TG curve, indicating that water and most organic groups have been removed. At 800 °C, the objective samples, $LiNi_{0.5}Co_{0.5-x}Ti_xO_2$ compounds, can form after 10 h calcination as confirmed by XRD results.

The XRD patterns of $LiNi_{0.5}Co_{0.5-x}Ti_xO_2$ ($0 \leqslant x \leqslant 0.5$) samples are shown in Fig. 2a–d. Synthesized by a tartaric acid-assisted sol–gel technique, the pristine $LiNi_{0.5}Co_{0.5}O_2$ displays a typical hexagonal layered structure (space group R-3m, No.166) with the diffraction peaks of (003), (101), (006), (102), (104), (105), (107), (108),

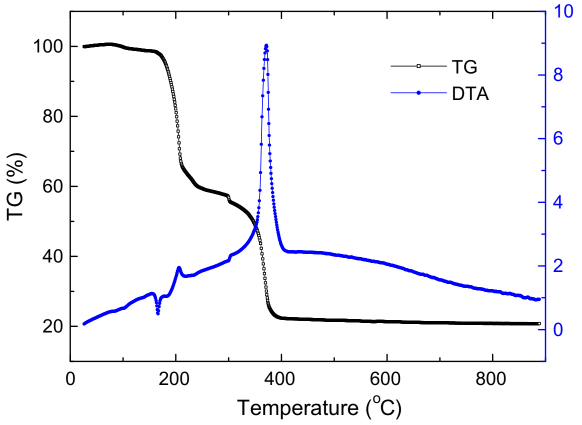

Fig. 1. TG–DTA curves of the precursor for $LiNi_{0.5}Co_{0.5-x}Ti_xO_2$ (x = 0.1) preparation.