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Study of new phases grown on $LiNbO_3$ coated $LiCoO_2$ cathode material with an enhanced electrochemical performance

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ABSTRACT

$LiNbO_3$, a fast ionic conductor, was chosen as the layer to coat commercial $LiCoO_2$ particles through a sol-gel method followed by heat treatment at various temperatures. As opposed to conventional coating materials, we first report new coating layer resulting from the reaction between coating material $LiNbO_3$ and bulk material $LiCoO_2$, is grown during annealing. The composition of formed new coating layer varies with the calcination temperature. Electrochemical properties of the coated material annealed at different temperatures indicated that the formed new coating layer had an effective enhancement of the cycle life, compared to a bare sample. 2 mol%–800 °C-coated sample has a discharge capacity of 175.2 mAh/g after 70 cycles with capacity retention of 97.1%, showing the best cycling stability. It can be speculated that the formed new coating layer of Co_3O_4 and Li_3NbO_4 has an effective improvement of the electrochemical performance.

1. Introduction

$LiCoO_2$ is one of the most important cathode materials because of its high energy density, high safety, and good electrochemical performance with charging voltage lower than 4.2 V. However, its capacity fades quickly when charging voltage is beyond 4.2 V. In order to obtain higher performance beyond 4.3 V, modification of $LiCoO_2$ has been developed by doping or coating.

A lot of surface coating materials have been employed to improve electrochemical performance of $LiCoO_2$, including TiO_2 [1,2], ZrO_2 [3–6], Co_3O_4 [7], Al_2O_3 [8–10], ZnO_2 [11–13], $AlPO_4$ [14], AlF_3 [15], and so on. They can effectively improve the chemical performance of the $LiCoO_2$. Up to now, several different mechanisms have been suggested for the improvement of the electrochemical stability of $LiCoO_2$: (1) formation of a solid solution layer on the surface to improve structural stability of $LiCoO_2$ [16]; (2) the coating layer can restrain the growth of the impedance and the dissolution of Co ions [17]; (3) the coating material can increase the conductivity between particles [18]; (4) the coating material can react with electrolyte and form some Lewis acids [19].

Many reports have shown that heat treatment is crucial to the electrochemical performance of coated materials [20,21]. Researchers usually put effort into the performance comparison of different coating amount at various heat treatment temperatures. There always exists a close relationship between the properties of coated materials and the annealing temperature, whereas, the reason behind this relationship did not cause concern. The formed coating materials are always simply recognized as the selected coating materials, due to the small amount of coating materials.

In fact, investigation of the coating layer is very important to clarify coating mechanism, for all the proposed mechanisms should be based on the formed coating layer rather than the selected coating layer. Additionally, the recognition of the composition of coating layer can help researchers to select the appropriate and effective coating materials. Recently, only a few works studied the coating layer and reported that new phases could be formed after coating. Yang et al. [22] reported a new hexagonal phase $LiTiO_2$ appeared on the surface of TiO_2-coated $LiNi_{0.8}Co_{0.2}O_2$. Cho et al. [23] found that an olivine $LiCoPO_4$ phase was grown on the coated $LiNi_{0.8}Co_{0.16}Al_{0.04}O_2$. It was suggested that the $Co_3(PO_4)_2$ coating material reacted with LiOH and Li_2CO_3 impurities on the cathode particle surface, during annealing to form $LiCoPO_4$ phase on the bulk surface. Unfortunately, these reports have not attracted enough attention.

It has been reported that $LiNbO_3$ is a good coating layer for $LiCoO_2$ in all solid-state lithium secondary batteries for it shows high ionic conductivity [24]. It can reduce the interfacial resistance and improve the high-rate capability of the solid-state systems.

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In this work, $LiNbO_3$ was employed to coat commercial $LiCoO_2$ for lithium ion batteries. The aim of this paper is to investigate the composition of coating layer at different sintered temperatures, and study the effect of composition of coating layer on electrochemical properties of coated materials, and then reveal the relationship between the annealing temperature and electrochemical property.

2. Experimental

Commercial $LiCoO_2$ (Hunan, China) with average particle size of 8–10 μm was used as pristine material. Niobium ethoxide (Nanjing, China) and Li_2CO_3 (Tianjin, China) were selected as the starting materials for the coating layer. $LiNbO_3$-coated $LiCoO_2$ materials were synthesized by the sol-gel method. Firstly, stoichiometric amounts of niobium ethoxide and citric acid were dissolved in ethanol, and then an amount of $LiCoO_2$ was added into the solution. The mixture was stirred for 12 h and a sol was formed. The sol was then heated at 70–80 °C with mechanically stirring. As the evaporation of ethanol proceeded further, the sol turned into a viscous transparent gel. The gel precursors were sintered at 600, 700, and 800 °C for 10 h, respectively, to get the final coated cathode materials.

Thermal decomposition behavior of the gel precursor was examined by differential scanning calorimetry (DSC) and thermal gravimetric (TG) analysis using a SETRAM SETSYS EVOLUTION16/18 at a heating rate of 10 °C/min in the air atmosphere. Structural analysis of the bare and the coated samples were carried out by X-ray powder diffraction (Japan Science D/MAX-TTR3). Microstructures of the coated particles were examined by Hitachi S-4800 scanning electron microscope.

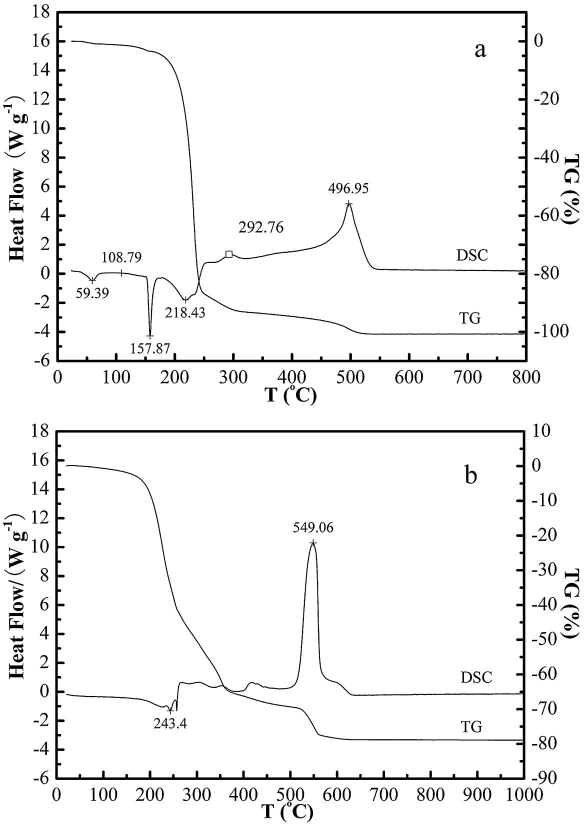

Fig. 1. TG-DSC curves of (a) citric acid; (b) the precursor of $LiNbO_3$: citric acid and niobium ethoxide.

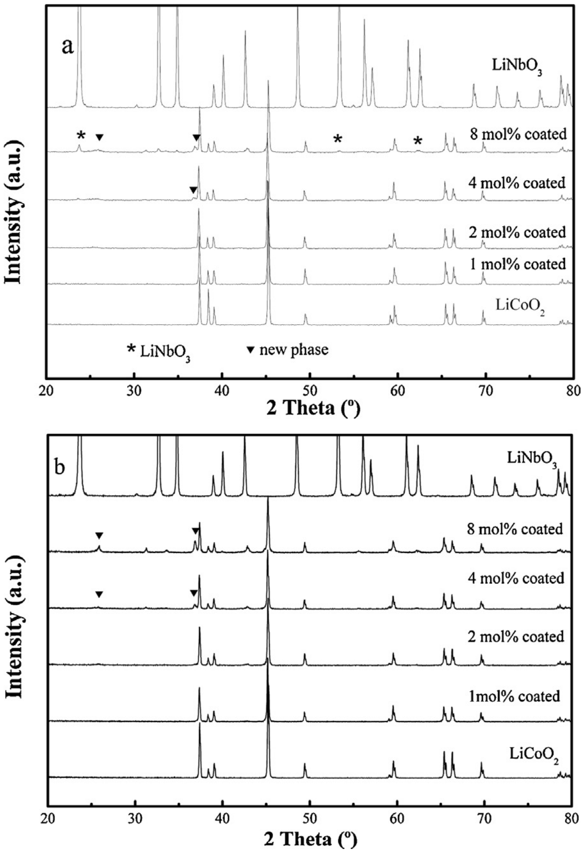

Fig. 2. XRD patterns of bare and $LiNbO_3$-coated materials (1, 2, 4, and 8 mol%) sintered at (a) 600 °C; (b) 700 °C; (c) 800 °C for 10 h.

A coin-cell (CR2032) was used to examine the electrochemical performance. The cathode consisted of 83 wt% active materials, 10 wt% acetylene black (AB) conductor, and 7 wt% polyvinylidene fluoride (PVDF) binder. The mixed slurry was uniformly spread on a thin aluminum foil, followed by drying at 120 °C for 2 h. The electrode was roll-pressed and then cut into pieces. The electrodes were dried in a vacuum oven at 120 °C for 8 h. Half-cells were then assembled with the bare or coated $LiCoO_2$ as the working electrode, lithium metal foil as the counter electrode, $LiPF_6$(1M)–EC + DEC + EMC (1:1:1 by volume) as the electrolyte, and a polypropylene-based film as the separator. All the cells were charged and discharged between 3.0–4.5 V at 45 or 80 mA/g by means of a CT2001A Land.

3. Results and discussion

Fig. 1a is the TG-DSC curves of citric acid, indicating that the citric acid totally decompose before 550 °C. The TG-DSC curves of precursor of $LiNbO_3$ (citric acid and niobium ethoxide) have an obvious exothermic peak at 549 °C, and there are no thermal peaks and weight loss after 550 °C, indicating that $LiNbO_3$ is formed at around 550 °C. So the sintering temperatures of 600, 700, and 800 °C are selected to get the coated cathode materials.

Fig. 2 shows the XRD patterns of coated samples (the mol ratio of $LiNbO_3$ to coated material is 1, 2, 4, and 8%, respectively) which were sintered at 600, 700, and 800 °C for 10 h, respectively. It can be seen that the peaks for coating material are not observed in the patterns until the ratio of coating material is up to 4 mol%, because the relatively low content of coating material is difficult to be detected by XRD technique. When the coating material increases to