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The structural mechanism of the improved electrochemical performances resulted from sintering atmosphere for $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ cathode material

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ABSTRACT

The influence of preparing atmosphere on structure and the resultant electrochemical performances of $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ cathode material has been investigated in detail. The electrochemical performance measurements show that $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ cathode material can present significantly improved discharge capacities, good rate capability and excellent cycling stability simply by adjusting oxygen content in preparing atmosphere about 40 vol.%. Based on the results of rietveld refinements of the XRD data analyzed using Maud 2.14 software, the improved electrochemical performances could be ascribed to the well ordered layered structure and much lower degree of cation mixing in its structure. When the oxygen content increase to 40 vol.%, only 0.006 mol per formula unit of Ni are incorporated into the lithium layers (0.083 mol per formula unit for 10 vol.% oxygen content). Moreover, the highest ratio of $I(003)/I(104)$ (1.6025) in XRD pattern also approves the reduced cation mixing and well ordered layered structure of the composition. The revealed conclusions will help effectively create design strategies for large-scale synthesizing the cathode material for advanced lithium ion batteries.

1. Introduction

The low thermal stability, high cost and toxicity of $LiCoO_2$ shifts the research efforts toward the searching for alternative cathode materials for commercial lithium ion batteries. Layered $LiNi_xCo_{1-x-y}Mn_yO_2$ $(x + y \leqslant 1)$ composites [1–12] are more attractive because they can take advantage of good electronic conductive of $LiCoO_2$, high reversible capacity of $LiNiO_2$ and well thermal stability of $LiMn_2O_4$ through the synergic effect of cobalt, nickel and manganese [7,9,10]. Among these materials, $LiNi_{0.5}Mn_{0.3}Co_{0.2}O_2$ is expected to be a promising cathode material due to its high available capacity, low cost, and good thermal stability. Nevertheless, the cycling stability and actual capacity of the material could be and also need to be improved to meet the increasing requirements of today's digital products on lithium rechargeable battery.

Conventional solid-state sintering method using co-precipitation obtained $Ni_xCo_{1-x-y}Mn_y(OH)_2$ or $Ni_xCo_{1-x-y}Mn_yCO_3$ precursors as raw materials is the most promising route to realize the large-scale production of $LiNi_{1-x-y}Co_xMn_yO_2$ cathode [6,7,9–11]. Usually, two methods are adopted to improve the rate capability and cycling stability of these cathode materials when this synthesis route is used. One is coating the surface of final $LiNi_{1-x-y}Co_xMn_yO_2$ production [11–13], the other is doping [14] with appropriate metallic element into $Ni_xCo_{1-x-y}Mn_y(OH)_2$ or $Ni_xCo_{1-x-y}Mn_yCO_3$ precursors during the co-precipitation process. However, these modification methods will result in the reduction of charge/discharge capacity [13,14] and are also complicated and will bring extra cost. Another way to improve their electrochemical performances is lithium non-stoichiometric content [15,16]. But the control of the non-stoichiometric Li is vital to the performances [16,17] and also very difficult to mass production.

According to literature [2,4,18], the valence of Ni, Co and Mn in $Ni_xCo_{1-x-y}Mn_y(OH)_2$ or $Ni_xCo_{1-x-y}Mn_yCO_3$ precursors is 2+. It is different from that of the resultant products $LiNi_xCo_{1-x-y}Mn_yO_2$ in which the valence of Co is 3+, Mn are 4+, Ni are 2+ or 3+ [4,18]. Oxidizing atmosphere is theoretically required to synthesize $LiNi_xCo_{1-x-y}Mn_yO_2$ cathode material. For $LiNi_xCo_{1-2x}Mn_xO_2$ cathode [19], such as $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ [20] and $Li(Ni_{0.4}Co_{0.2}Mn_{0.4})O_2$ [21], in which Ni ions are preferably in 2+ states due to the same stoichiometric ratio of Ni and Mn, air atmosphere is adequate to synthesis this kind of materials with excellent electrochemical performances. However, the achievement of excellent electrochemical properties for $LiNi_xCo_{1-x-y}Mn_yO_2$ materials with high content of Ni $(x \geqslant 0.6)$ needs to be preparing in pure O_2 flow atmosphere because Ni is difficult to be oxidized [22–24]. Therefore, it can be proposed that oxygen-rich preparing atmosphere may be a facile and easy controllable way to improve the electrochemical performances of $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ cathode materials. Nevertheless, $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ compound, as a promising cathode material, has not received enough attention. The working mechanism relevant to the influence of preparing atmosphere on

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the performances of $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ cathode materials has not been systematically investigated yet.

In this work, oxygen content dependences of the properties of the cathode material are systemically investigated in detail. The effects of oxygen content on subtle structural change are also discussed for better synthesizing the cathode material with excellent electrochemical performances.

2. Experimental

$Ni_{0.5}Co_{0.2}Mn_{0.3}(OH)_2$ precursor was prepared by co-precipitation firstly and from Jinchuan Group Co., Ltd. China. The as-prepared $Ni_{0.5}Co_{0.2}Mn_{0.3}(OH)_2$ and Li_2CO_3 (99.9%) were mixed thoroughly by ball mill in molar ratio of Li: $(Ni_{0.5}Co_{0.2}Mn_{0.3})$ = 1.08:1 using deionized water as grinding aid. The milled mixture was dried at 120 °C for 12 h, and calcined at 900 °C for 15 h in atmosphere with oxygen concentration of 10 vol.%, 20 vol.%, 30 vol.% and 40 vol.%, then $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ samples were obtained and marked in N-L532, A-L532, O-L532, O2-L532, respectively. The schematic of gas controlling and material preparation apparatus are shown in Fig. 1.

CR2032 type coin cell was assembled to test the electrochemical performances of the prepared $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ powders. The positive electrode was prepared by mixing of 94 wt.% active materials, 3 wt.% acetylene black (Alfa), and 3 wt.% polyvinylidene difluoride (PVDF, Solvay) binder using appropriate amount of N-methyl-2-pyrrolidine (NMP, Alfa) as solvent. The mixed cathode slurry was evenly coated on aluminum foil, then dried at 120 °C for 12 h in a vacuum oven and pressed with 20 MPa pressures. The formed cathode foil was assembled into a CR2032 battery in an argon-filled glove box, with Li foil as anode, 1 M $LiPF_6$ in ethylene carbonate (EC): dimethyl carbonate (DMC) (1:1 vol.%) as electrolyte and a Celgard-2400 as separator. The cells were firstly charged to 4.25 V, and kept charging at 4.25 V until the current density was 5 mA g^{-1}, then they were discharged to 3 V. The electrochemical performance measurements were operated on a high precision battery performance testing system (Neware, Shenzhen, China) at different current densities at 25 °C.

The X-ray diffraction (XRD) patterns were obtained on a Bruker DX1000 diffractometer, using Cu Kα radiation, operating at 40 kV and 25 mA in the angular range of 2θ = 10–70° with an acquisition step of 0.02° and a scan rate of 0.2 per minute. The collected XRD data were analyzed by the rietveld refinement program Maud 2.14. A scanning electron microscope (Hitachi S-4800) was used to examine the particle size and morphologies of the prepared samples.

3. Results and discussion

Fig. 2 shows the initial charge/discharge profiles of the samples in the first cycle at current density of 0.2 C (30 mA g^{-1}) in voltage range of 3.0–4.25 V. From Fig. 2, it can be seen that the sample N-L532 has initial reversible charge/discharge capacities of 179.9 mAh g^{-1}/150.3 mAh g^{-1} at 0.2 C. When the oxygen content increase to 20 vol.%, the charge/discharge specific capacity become well. However, no significant differences in charge/discharge

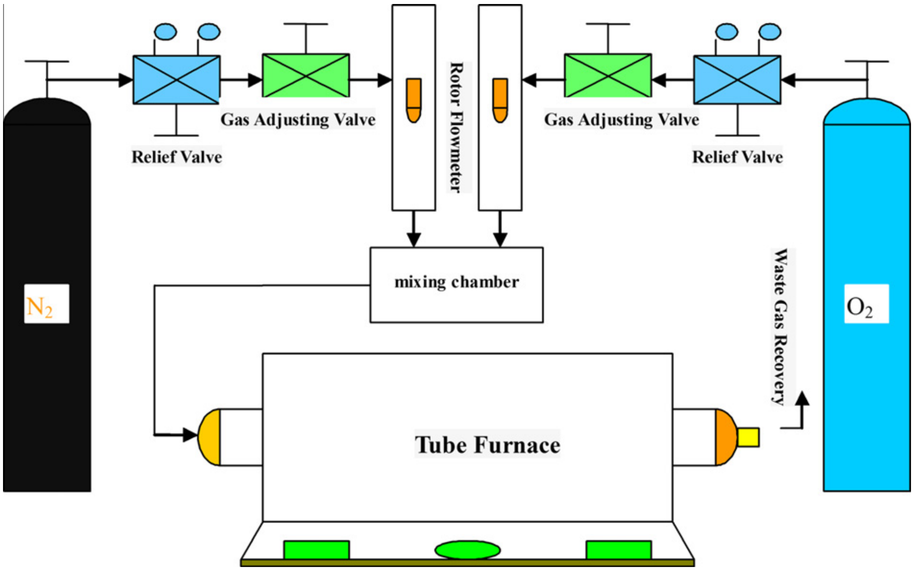

Fig. 1. The schematic of gas controlling and material preparation device for synthesizing $LiNi_{0.5}Mn_{0.3}Co_{0.2}O_2$ cathode material.

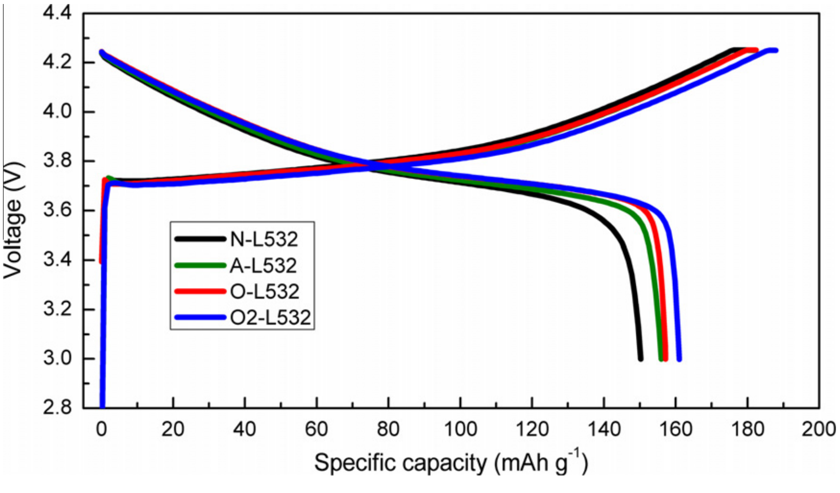

Fig. 2. Initial charge/discharge curves of the prepared samples at 0.2 C over 3.0–4.25 V.