



Review

An improved solid-state method for synthesizing $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathode material for lithium ion batteries



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ABSTRACT

High voltage $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathode material was prepared by two steps solid-state method with additive PEG dispersant. XRD, SEM, XPS and electrochemical tests have been carried out, and the results show that the PEG can promote the pyrolysis of MnO_2 and limit the impurities formation. The secondary particle can also be effectively restrained in the pre-calcination of MnO_2 and NiO, and the effect can be last to the final product. The capacity from $\text{Mn}^{3+}/\text{Mn}^{4+}$ couple was reduced and the whole capacity can reach 140.7 mAh g^{-1} with the retention rate of 81.33% after 100 cycles at 0.2C. Meanwhile, the product has better rate performance and surface stability than those prepared by traditional two-step solid-state method.

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1. Introduction

Lithium ion batteries (LIBs) with high-energy density are urgently required in hybrid electric vehicles and electric vehicles

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[1–5]. $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (LNMO) has become a promising cathode material for LIBs due to the high working voltage of 4.7 V (vs. Li/Li^+) and the high energy density of 650 Wh kg^{-1} . At the same time, it also has many advantages such as quick Li^+ migration rate, high capacity utilization, stable cycle performance, rich resources, environment friendly and so on [6]. However, LNMO shows serious energy fading in practical application because of the Mn dissolution and the oxidation of electrolyte when operating at high voltage or high temperature [7–10]. To solve these problems, many researches have been carried out, including doping other elements

(such as Cr [11,12], Al [13] and Mg [14,15]), coating chemical inert substances (such as C [16,17], Al_2O_3 [18,19] and conducting polymer [20]), and optimizing electrolyte [21].

Electrochemical properties of LNMO strongly depend on the elimination of Mn^{3+} , impurity phases and degree of structural disorder in the synthesizing process [22,23]. The synthesizing technology of LNMO can be divided into wet chemistry method and solid-state reaction method [24]. Wet chemistry method has been frequently used in laboratory research, which showed high phase purity and excellent electrochemical performance such as sol-gel method [25], co-precipitation method [26] and hydrothermal method [27]. Solid-state reaction method is rarely reported, which generally produced larger particle size, for example, $\text{Li}_x\text{Ni}_{1-x}\text{O}$ impurity phase and a number of Mn^{3+} ions [28]. But solid-state method has obvious advantages compared with wet chemical method such as simple process, cheap technology and feasibility of large-scale application. Therefore, the development of solid-state synthesizing technology for LNMO material is necessary. Ma and Chen [29,30] prepared LNMO by roasting-milling-roasting method, which displayed uniform size distribution, high specific capacity and stable cycle performance. Wang [31] synthesized the spinel structured Mn-Ni binary oxide by the mixture of NiO and Mn_3O_4 at 900 °C, and then pure spinel phase LNMO was obtained through the solid-state reaction with the binary oxide and Li_2CO_3 at 800 °C. The product could deliver a discharge capacity of 135.3 mAh g^{-1} and the capacity retention could reach 97.3% after 100 charge-discharge cycles, but the capacity from $\text{Mn}^{3+}/\text{Mn}^{4+}$ couple is still high, resulting in a slightly lower energy density.

In this paper, the PEG-400 dispersant was added into the ball-milling procedure of NiO and MnO_2 . The morphology and distribution of particle size of the nickel manganese oxide (NMO) and target product were improved. Meanwhile, the annealing process was used after high-temperature reaction. Electrochemical characterizations revealed that the LNMO-P sample synthesized by our method has improved electrochemical performance.

2. Experimental section

2.1. Materials preparation

The stoichiometric ratio of MnO_2 (AR) and NiO (AR) with proper PEG-400 dispersant were grounded in agate jar with a planetary ball mill for 2 h. The mixture was calcinated at 600 °C for 5 h and the precursor of nickel manganese oxide was prepared. The precursor was mixed with Li_2CO_3 (AR) and subjected to calcination at 800 °C for 24 h in furnace and followed by annealing at 650 °C for 24 h. Excess of 5% Li_2CO_3 was added to compensate the loss during calcination. For comparison, a bare LNMO sample was also prepared by two-steps solid-state reaction and annealed without PEG-400. The heating speeds were all set to 5 °C min^{-1} for both calcination steps, and the samples were naturally cooled down to room temperature inside the furnace. The obtained untreated material was labeled as LNMO and the one treated with PEG-400 was marked as LNMO-P.

2.2. Materials characterization

The phase of the prepared samples were identified by X-ray diffraction (XRD) using a PAN analytical X'Pert³ power diffractometer with a PIXcel detector. X-ray profiles were measured between 10 and 80° (2θ angle) with a monochromatic Cu K α radiation source. The morphologies of the products were examined with a Hitachi SU5000 scanning electron microscope (SEM). X-ray photoelectron spectroscopy (XPS) was performed on a Thermo Scientific ESCALAB 250-Xi model X-ray photoelectron energy spectrum analyzer

(USA). The survey spectra were measured in the binding energy (BE) range of 0–1100 eV; the detailed spectra of Mn 2p region were measured in the range 630–665 eV. The BE values were calibrated with the signal of contaminated carbon C 1s at 284.6 eV. The spectra were fitted using XPSPEAK software (Ver. 4.1) after applying a Shirley background subtraction.

2.3. Electrochemical performances

CR2032 coin cells are utilized for electrochemical tests in this work. Active materials (80 wt%) were mixed and ground with polyvinylidene fluoride (PVDF) powder (10 wt%) as a binder, acetylene black carbon powder (10 wt%) as the conductive assistant material and appropriate amount of NMP as solvent. The mixed slurry was cast upon an Al foil collector. The electrolyte was 1mol LiPF_6 in a mixture of EC-DMC-DEC (volume ratio of 2:2:1) electrolyte. Cyclic voltammetry (CV) test was carried out on a CHI860D electrochemical workstation (Shanghai Chenhua Instrument, China) in the potential range of 3.5–5.0 V at a rate of 0.1 mV s^{-1} . The cells were galvanostatically charged and discharged on a battery test system (LAND CT-2001A, Wuhan, China) between 3.5 and 5.0 V at room temperature. Various currents were used to test the rate capacity, and five cycles were run for each rate. C-Rates have been chosen between 0.2 C and 10 C, reflecting charge and discharge of the full capacity of LNMO being 1 C, i.e., 146.7 mAh g^{-1} . Electrochemistry impedance spectroscopy (EIS) experiments were carried out on the electrochemical workstation in the frequency range mainly from 100 kHz to 0.01 Hz at the amplitude of 5 mV.

3. Results and discussion

The XRD patterns of the mixture of NiO and MnO_2 and the precursors (signed as NMO and NMO-P) were shown in Fig. 1. We can find that the powder of blended raw materials is still composed of MnO_2 and NiO phases after mixed by ball milling (in Fig. 1a). After the mixture was heated at 600 °C for 5 h, the new phases of Mn_2O_3 (JPCDS No. 12-0269) and NiMnO_3 (JPCDS No. 78-0390) can be observed (Fig. 1b), indicating that MnO_2 is decomposed into Mn_2O_3 and O_2 , and NiMnO_3 is formed through the reaction between MnO_2 and NiO. The reaction equations can be described as follows:

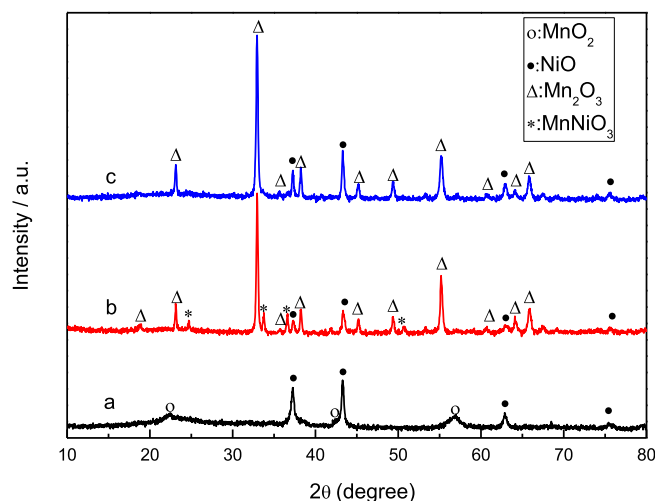


Fig. 1. XRD patterns of the precursors (a), NMO (b) and NMO-P (c).

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