Available online at www.sciencedirect.com

ScienceDirect

Journal of Power Sources 175 (2008) 564–569

JOURNAL OF POWER SOURCES

www.elsevier.com/locate/jpowsour

Short communication

Morphology and electrochemical performance of $Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O_2$ cathode material by a slurry spray drying method

Bin Lin [a,b], Zhaoyin Wen [a,b,*], Zhonghua Gu [a], Shahua Huang [a,b]

[a] *Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, PR China*
[b] *Graduate School, Chinese Academy of sciences, 1295 DingXi Road, Shanghai 200050, PR China*

Received 20 June 2007; received in revised form 14 September 2007; accepted 19 September 2007
Available online 22 September 2007

Abstract

The spherical $Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O_2$ powders with appropriate porosity, small particle size and good particle size distribution were successfully prepared by a slurry spray drying method. The $Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O_2$ powders were characterized by XRD, SEM, ICP, BET, EIS and galvanostatic charge/discharge testing. The material calcined at 950 °C had the best electrochemical performance. Its initial discharge capacity was 188.9 mAh g^{-1} at the discharge rate of 0.2 C (32 mA g^{-1}), and retained 91.4% of the capacity on going from 0.2 to 4 C rate. From the EIS result, it was found that the favorable electrochemical performance of the $Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O_2$ cathode material was primarily attributed to the particular morphology formed by the spray drying process which was favorable for the charge transfer during the deintercalation and intercalation cycling.

Keywords: Lithium ion battery; $Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O_2$; Slurry spray drying; Spherical; Cathode material

1. Introduction

Extensive research has been carried out over past years to find alternative cathode materials to replace the presently popular $LiCoO_2$ for use in Li-ion battery. Recently, a layered transition metal oxide with hexagonal structure, $Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O_2$, was introduced by Ohzuku and Makimura as a candidate of cathode material to replace $LiCoO_2$ [1]. This material has attracted significant interests because of its many advantages such as higher reversible capacity with milder thermal stability at charged state [2], lower cost and less toxicity than $LiCoO_2$. Thus, $Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O_2$ might be one of the most promising candidates of cathode material for high-energy, high-power lithium-ion batteries [3]. As known, the performance of the powders used as cathode materials in lithium-ion batteries is strongly affected by their preparation processes [4]. Therefore, it is important to select a suitable method to prepare high performance $Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O_2$ [5].

$Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O_2$ was first prepared by conventional solid-state reaction method [1,6]. However, such method requires prolonged heat treatment at relatively high temperature with repeated intermediate grinding because of the heterogeneity of the precursors. In order to overcome these disadvantages, various new techniques, such as glycine-nitrate combustion [7], hydroxide co-precipitation [8–10], carbonate co-precipitation [11–13], ultrasonic spray pyrolysis [14], solution spray drying [4], sol–gel [15] process, etc., have been developed and applied to prepare high quality $Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O_2$. They lead to homogeneous materials with small particle size but these complex synthetic routes based on solution precursors require expensive initial or intermediate reagents, long time to dry the precursor. Moreover, the abundant use of organic acid or hydroxides, which are caustic to the production equipment, makes these methods not fit for the industrial-scale production for the materials.

Nakahara et al. [16] and Wen et al. [17] ever reported excellent electrochemical performance of particulate $Li_4Ti_5O_{12}$ prepared by slurry spray drying process with LiOH or Li_2CO_3 and TiO_2 as precursors. Different from the solution spray drying mentioned above, the slurry spray drying process uses the insoluble carbonates or oxides as precursor without any caustic reagents. The rapid heat and mass transfer occurring during the drying

---

* Corresponding author at: Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, PR China. Tel.: +86 21 52411704; fax: +86 21 52413903.
E-mail address: zywen@mail.sic.ac.cn (Z. Wen).

0378-7753/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.jpowsour.2007.09.055

process result in dried granules having a large variety of shapes, i.e., from uniform solid spheres to elongated, pancake, donut-shaped, needlelike or hollow granules [18]. And the morphology has important effect on cell's performance.

In this paper, porous and spherical $Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O_2$ powders were prepared by a slurry spray drying process with Li_2CO_3, NiO, Co_3O_4 and $MnCO_3$ as precursors and polyvinyl butyral (PVB) as forming agent of pores, which could overcome the disadvantages of the solid-state reaction and various solution-based techniques. Moreover, the cost of the slurry spray drying method was much lower than the chemical processes. The morphology of the precursor and $Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O_2$ powders were investigated. The electrochemical properties of $Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O_2$ powders as cathode materials were studied by means of charge–discharge tests and electrochemical impedance spectroscopy in half cells.

2. Experimental

The proper amounts of precursors Li_2CO_3, NiO, Co_3O_4 and $MnCO_3$ (10% excess Li was used to compensate possible Li loss during the calcination and sintering process) were mixed in alcohol solvent by rotary ball milling at a speed of 300 rpm for 2 h to form a slurry, then 6 wt.% PVB was added and dissolved in the slurry and mixed for another 1 h. Then, the slurry was spray-dried with a spray-drier (Niro 2108, Denmark, air inlet temperature was 150 °C). The dried spherical powders were heated at 900–1000 °C for 10 h in an alumina crucible.

For comparison, $Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O_2$ was also prepared using a conventional solid-state reaction method with the same reagents used above. The precursor was obtained simply by grinding stoichiometric amounts of Li_2CO_3, NiO, Co_3O_4 and $MnCO_3$ in the same way as they did for the slurry spray drying method. The calcining process was the same as above.

Powder X-ray diffraction (XRD, Rigaku RINT-2000) measurement using Cu Kα radiation was employed to identify the crystalline phase of the synthesized materials. The scan range was 10–80° with a scan step of 0.02° and a scan speed of $10^\circ\ min^{-1}$. The chemical composition of the synthesized materials was determined by an inductively coupled plasma spectrometer (ICP, IRIS Advantage 1000). Scanning electron microscope (SEM, JEOL JSM-6700F) was applied to observe the morphology and particle size of the synthesized materials. The specific surface area was analyzed by the BET method using a Micromeritics Tristar 3000 in which the N_2 gas adsorption was employed. Each sample was heated to 150 °C for 4 h to remove any adsorbed water before the measurement.

The electrochemical performance of $Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O_2$ powders was evaluated with coin-type cells (CR 2025) using a lithium foil counter electrode and an electrolyte consisting of a 1 M $LiPF_6$ solution in EC:DMC (1:1, v/v) at room temperature. Microporous polypropylene membrane (Celgard) was used as the separator. The working electrode was prepared from a paste of 80 wt.% $Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O_2$ with 10 wt.% conductive acetylene black and 10 wt.% PVDF binder in NMP solvent. The paste was then coated on an aluminum foil, and finally dried under vacuum at 100 °C for 10 h before electrochemical evaluation. The battery was assembled in a glove box (VAC AM-2) filled with pure argon. All the cells were allowed to age for 10 h before testing. The galvanostatic charge–discharge tests were conducted on a LANDCT2001A battery test system with the cut-off voltages of 2.5 and 4.5 V (versus Li/Li^+) under a specific current density (a nominal specific capacity of $160\ mAh\ g^{-1}$ was assumed to convert the current density into *C* rate). The electrochemical impedance spectroscopy (EIS) analysis was performed using a CHI760C Electrochemical Workstation over the frequency range from 0.1 MHz to 1 mHz with the amplitude of 5 mV.

3. Results and discussion

3.1. Phase analysis

Fig. 1 showed the XRD patterns of $Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O_2$ compounds prepared by both slurry spray drying and solid-state reaction method at 900–1000 °C, which were referred as SD900, SD950, SD1000 and SSR900, SSR950, SSR1000, respectively, where SD and SSR indicating spray drying and solid-state reaction, and the number indicating the treating temperature. As shown, the pure phase $Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O_2$ was obtained by solid-state reaction only at the calcining temperature above 950 °C. However, with regard to the slurry spray drying method, the pure phase could be obtained at the temperature as low as 900 °C. As can be seen in Fig. 1, regardless of calcination temperature, the intensity ratio of the (0 0 3)/(1 0 4) diffraction lines was higher than 1.2, indicating a low degree of cation mixing in the structure. The significant peak splitting of (0 0 6)/(1 0 2) and (1 0 8)/(1 1 0) could be observed in the XRD patterns for slurry spray drying samples which was known to be an indicator of the layered structure like $LiCoO_2$ and $LiNiO_2$ [5,19]. The lattice parameters of SD1000 powder were *a* = 2.859 and *c* = 14.228 Å calculated by least square

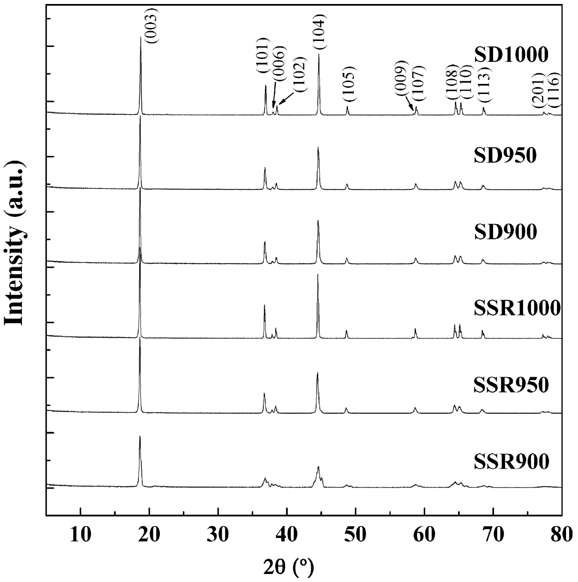

Fig. 1. XRD patterns of $Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O_2$ powders prepared by different methods.