Materials Research Bulletin 73 (2016) 192–196

Contents lists available at ScienceDirect

Materials Research Bulletin

journal homepage: www.elsevier.com/locate/matresbu

High rate performance of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ cathode material synthesized by a carbon gel–combustion process for lithium ion batteries

Jian Chen[a,*], Na Zhao[a], Guo-Dong Li[b,*], Fei-Fan Guo[b], Junwei Zhao[a], Yinggang Zhao[a], Tiekun Jia[a], Fang Fu[a], Jili Li[a]

[a] Department of Materials Science and Engineering, Luoyang Institute of Science and Technology, Luoyang 471023, PR China
[b] State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, College of Chemistry, Jilin University, Changchun 130012, PR China

ARTICLE INFO

Article history:
Received 3 May 2015
Received in revised form 2 September 2015
Accepted 3 September 2015
Available online 7 September 2015

Keywords:
A. Electronic materials
A. Nanostructure
A. Oxides
B. Microstructure
D. Electrochemical properties

ABSTRACT

The $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ electrode material was prepared via a carbon gel–combustion process using resorcinol–formaldehyde gel as fuel and nitrate as an oxidizer. The carbon gel process ensures the molecular-level homogeneity of the chemical product. The gas derived from carbon gel separates the raw material particles and restrains the growth of the grains to some extent, and well-crystallized nanosized powders are obtained with calcination at 700 °C for 6 h. As the cathode material for lithium-ion batteries, the discharge capacity of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ was as high as 175.6 mA h g^{-1} in the first cycle at 0.5 C, and it could remain 163.0 mA h g^{-1} within the voltage range of 2.5–4.4 V after 50 cycles. The electrode also showed outstanding rate capacities at high discharge rates such as 30 C and 50 C, suggesting the applications of the material in high power lithium-ion batteries.

1. Introduction

During the past decade, lithium transition oxides such as $LiCoO_2$, $LiMnO_2$ and $LiNiO_2$ with layered structures have been studied extensively as promising cathode materials for lithium-ion batteries [1]. Among those, $LiCoO_2$ has been used as a major cathode material since Sony Corporation firstly introduced lithium ion batteries in 1990 [2]. However, its relatively high cost and toxicity limit the widespread applications of the material. Isostructural $LiNiO_2$ with $LiCoO_2$ is a more promising electrode material because of its higher capacity and excellent economic characteristic [1]. But stoichiometric $LiNiO_2$ is not easily synthesized compared to the $LiCoO_2$ and $LiMn_2O_4$ due to the reduction of Ni^{3+}, and the structure of $LiNiO_2$ is instable owing to a sequential change in crystal structure during the charge process [3]. $LiMnO_2$ is comparatively inexpensive and environmental friendliness compared to $LiCoO_2$ and $LiNiO_2$. Generally, there are two types of $LiMnO_2$ with different crystal structures, the orthorhombic with an ordered rock salt structure of the space group *Pmnm* and the monoclinic phases with space group *C2/m* [4]. The preparation of $LiMnO_2$ with monoclinic structure is difficult for the strict synthesis conditions such as sintering temperature and the pressure of oxygen, and most studies on $LiMnO_2$ electrode materials are orthorhombic phase [5]. Furthermore, $LiMnO_2$ suffers from Mn dissolution and the phase transition from o–$LiMnO_2$ to spinel phase during the cycling, which limits their applications in high power lithium ion batteries [6]. Recently, to overcome the obstacles of single transition metal oxides, tremendous approaches have been investigated to develop multiple transition metal oxides by cationic substitution, including $LiNi_{1/2}Mn_{1/2}O_2$ [7–9], $Li(Ni_xCo_{1-2x}Mn_x)O_2$ [10,11], and so on. In particular, the $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ with rhombohedral structure as one of the most promising cathode materials has been widely investigated for lower cost, better thermal stability and higher capacity of closer to 200 mA h g^{-1} [2,12–14]. The valence states of metal ions in $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ are +2, +3 and +4 for Ni, Co and Mn, respectively. The extraction and insertion of lithium ions take place during charge/discharge process by the oxidation and reduction of Ni^{2+}/Ni^{4+} and Co^{3+}/Co^{4+} ions with Mn^{4+} remaining inactive [1]. The presence of tetravalent manganese could effectively improve the structural stability of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ during lithium ion insertion/deinsertion.

Up to now, some methods have been developed for the synthesis of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ electrode materials, including the solvothermal technique [15], sol–gel method [13], solid-state process [16,17], microemulsion route [18,19], rheological phase method [20], Pechini method [21], co-precipitation process

* Corresponding authors.
E-mail addresses: chemcj@126.com (J. Chen), lgd@jlu.edu.cn (G.-D. Li).

http://dx.doi.org/10.1016/j.materresbull.2015.09.004
0025-5408/

[2,22–27]. However, many reported methods require expensive raw material, long annealing times or several grinding steps, and it is inevitable to increase the cost and complexity of the preparation process. For instance, the mixed hydroxide method has been used as a common preparation technique to get the precursor of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$, in which a $M(OH)_2$ (M = Ni, Co, Mn) precursor is precipitated from a metal salt solution under alkaline conditions [10,16,24–27]. But the precipitated $Mn(OH)_2$ is easily oxidized to MnOOH or MnO_2 in aqueous solution, and the pH value of the solution must be accurately controlled during synthesis process [17]. Furthermore, the traditional hydroxide co-precipitation method for the synthesis of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ must be heated at 1000 °C for more than 10 h [16,24,25]. The particle size is inevitably increased due to the long annealing time and high sintering temperature, which is not favorable to improve the electrochemical properties of electrode materials. Thus, it is still a great challenge that using a simple and cost effective method for synthesis of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ electrode materials with superior electrochemical performance. Compared to above methods, the combustion method presents some advantages such as low-cost reagents, simple equipment, easy introduction of the dopants into the final product and effective limitation of powders agglomeration [28]. The process based on the reaction between inorganic reagents (generally nitrates) and fuels (e.g., urea, glycine, citric acid), and it is an effective technique to synthesize electrode materials with nanoscale particle size [29,30].

In this work, the $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ sample was synthesized via a carbon gel–combustion process using resorcinol–formaldehyde (RF) gel as fuel and nitrate as an oxidizer. The carbon gel process between resorcinol and formaldehyde ensures the molecular-level homogeneity of the chemical product. The vigorous gas generated from pyrolysis of carbon gel and nitrate during sintering treatment effectively limits the contact between the particles with nanoscale particle obtained. Furthermore, the released heat is favorable to reduce the required sintering temperature and time of the reaction. The high rate performance of the $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ as the cathode material was measured systematically.

2. Experimental

2.1. Powder preparation and treatment

In a typical synthetic condition, stoichiometric amounts of 0.02 mol of lithium nitrate ($LiNO_3$), nickel nitrate hexahydrate ($Ni(NO_3)_2{\cdot}6H_2O$), cobalt nitrate hexahydrate ($Co(NO_3)_2{\cdot}6H_2O$) and manganous nitrate ($Mn(NO_3)_2$) (50 wt.% in water) were dissolved in 30 mL ethanol. A green solution was obtained. After stirring for 30 min, 2.2 g resorcinol and 3.0 mL formaldehyde (36.5 wt.% in water) were added to the solution with continued stirring. Then the resulting solution was placed into a 50 mL Teflon-lined stainless steel autoclave and maintained at 85 °C for 48 h. After the autoclave was cooled to room temperature, the resulting precursor was dried at 80 °C for 12 h. Finally, the generated precursor was ground and heated at 700 °C for 6 h to obtain the $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ sample.

2.2. Measurements

The crystal structure of the as-synthesized product was examined by X-ray diffraction using Cu Kα radiation (λ = 1.5406 Å) with 2θ ranging from 10° to 70°. The morphology and particle size were observed through a field emission scanning electron microscope (JEOL JSM-6700F) and a transmission electron microscope (Hitachi H-8100). The elemental compositions were characterized using the energy dispersive spectroscopy (EDS) (Oxford INCA, Britain), and the metal ion molar ratios of Li:Ni:Co:Mn in $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ samples were calculated from inductive coupled plasma atomic emission spectrometry (ICP-AES, ICAP-6300). The cathodes were fabricated from a mixture of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ (80 wt.%), polyvinylidene fluoride (PVDF) (10 wt.%) and carbon black (10 wt.%) in *N*-methyl-2-pyrrolidone. The slurry was then spread onto an aluminum foil and dried at 120 °C for 24 h in a vacuum oven. The batteries were assembled in an argon-filled gloved-box, in which oxygen and moisture level less than 1 ppm, and the electrolyte was 1 M $LiPF_6$ in a mixture of EC (ethylene carbonate), DMC (dimethyl carbonate) and EMC (ethylmethyl carbonate) (1:1:1 by weight). The coin cell was fabricated using the lithium metal as a counter electrode. The active material loaded on the electrode disks was about 2.5 mg cm^{-2}. Cyclic voltammetry (CV) measurements were performed on a CHI 660E electrochemical workstation. CVs were conducted in the cut-off voltage range of 2.5–4.4 V versus Li/Li^+ at a scan rate of 0.1 mV s^{-1}. Electrochemical measurements were conducted on a LAND CT2001A cell testing apparatus in the voltage range of 2.5–4.4 V at room temperature.

3. Results and discussion

XRD pattern of the $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ is shown in Fig. 1. All of the diffraction peaks can be indexed to standard patterns of hexagonal α–$NaFeO_2$ crystal structure with $R\bar{3}m$ space group. The XRD spectrum of the sample exhibits broad peaks showing extremely fine crystallite size. Furthermore, there are not other detectable diffraction peaks for impurity phases. The lattice parameters *a* and *c* of the $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ obtained by the least-square method are 2.866 and 14.239 Å, which are in good agreement with the reported works [18,21,23,31]. From previous studies, the higher *c*/*a* value of the sample (*c*/*a* = 4.968) indicates the well-defined hexagonal layered structure as reported by Hashem et al. [2]. In addition, the intensity ratio of the (0 0 3) to (1 0 4) peaks in the XRD patterns could be used to identify the cation mixing extent of layered structure [2]. Generally, the undesirable cation mixing would take place when the integrated intensity ratio is less than 1.2 [17]. In the present study, the $I_{(003)}/I_{(104)}$ ratio of the sample is 1.3. The high intensity ratio of the (0 0 3) to (1 0 4) peaks and the obvious splitting of the peaks assigned to the (0 0 6, 1 0 2) and (1 0 8, 1 1 0) doublets also indicate the sample possesses a well-layered structure [31]. The metal ion molar ratio of Li:Ni:Co:Mn in the sample measured by ICP-AES analysis is Li:Ni:Co:Mn = 0.997:0.332:0.335:0.334 within the experimental error limits.

The electrochemical performance of active material is greatly affected by the morphology and particle size [27]. Fig. 2a shows that most of the ground precursor particles are bulk and the

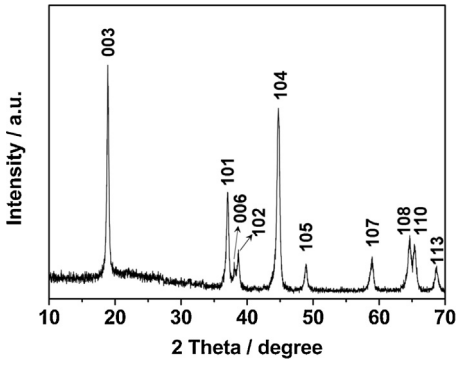

Fig. 1. Powder XRD pattern of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ sample.