

Available online at www.sciencedirect.com



Trans. Nonferrous Met. Soc. China 19(2009) 1499-1503

Transactions of Nonferrous Metals Society of China

www.tnmsc.cn

# Synthesis and electrochemical performances of LiNi<sub>0.6</sub>Co<sub>0.2</sub>Mn<sub>0.2</sub>O<sub>2</sub> cathode materials

ZHONG Sheng-kui(钟胜奎)<sup>1,2</sup>, LI Wei(李 伟)<sup>1</sup>, LI Yan-hong(李艳红)<sup>3</sup>, ZUO Zheng-guang(邹正光)<sup>1,2</sup>, TANG Xin(唐 鑫)<sup>1,2</sup>

 Department of Material and Chemistry, Guilin University of Technology, Guilin 541004, China;
 Key Laboratory of New Processing Technology for Nonferrous Metals and Materials, Ministry of Education, Guilin University of Technology, Guilin 541004, China

Received 10 August 2009; accepted 15 September 2009

**Abstract:**  $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$  was prepared from  $\text{LiOH}\cdot\text{H}_2\text{O}$  and  $\text{MCO}_3$  (M=Ni, Co, Mn) by co-precipitation and subsequent heating. XRD, SEM and electrochemical measurements were used to examine the structure, morphology and electrochemical characteristics, respectively.  $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$  samples show excellent electrochemical performances. The optimum sintering temperature and sintering time are 850 °C and 20 h, respectively. The  $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$  shows the discharge capacity of 148 mA·h/g in the range of 3.0–4.3 V at the first cycle, and the discharge capacity remains 136 mA·h/g after 30 cycles. The carbonate co-precipitation method is suitable for the preparation of  $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$  cathode materials with good electrochemical performance for lithium ion batteries.

Key words: lithium ion batteries; LiNi<sub>0.6</sub>Co<sub>0.2</sub>Mn<sub>0.2</sub>O<sub>2</sub>; cyclic voltammogram (CV)

## **1** Introduction

Research on cathode materials of lithium-ion battery was mainly concentrated in the transition metal oxides of layered structure such as LiCoO<sub>2</sub>, LiNiO<sub>2</sub>, LiMnO<sub>2</sub> and their derivatives. LiCoO<sub>2</sub> is one of the first commercial lithium-ion battery cathode materials, but its application is limited because of the scarce cobalt resources, high prices and a certain degree of toxicity [1-3]. It is hard to prepare LiNiO<sub>2</sub> and the crystal structure will change during the charge-discharge process, resulting in much attenuation of its capacity[4-5]. LiMnO<sub>2</sub> with layered structure has high theoretical specific capacity of 285 mA·h/g. However, during the process of charging and discharging, the structure easily changes to the spinel structure, resulting in fast attenuation of capacity[6]. Recently, intensive effort has been directed towards the development of  $\text{LiNi}_{x}\text{Co}_{v}\text{Mn}_{1-x-v}\text{O}_{2}$  (e.g.  $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_{2}$ ) as possible replacement for LiCoO<sub>2</sub>[7-11]. It was reported that the

capacity obtained for LiNi<sub>x</sub>Co<sub>y</sub>Mn<sub>1-x-y</sub>O<sub>2</sub> was dependent upon composition, synthesis technology and charge/ discharge voltage. The first discharge specific capacity reported is often more than 180 mA·h/g with good cycling stability in the first 30 or 50 cycles when being charged to 4.6 V (vs Li/Li<sup>+</sup>). However, the cycling stability of this kind of material in more cycles has been less discussed because of the appearance of Li-branch on the surface of Li anode after some cycles.

In this work, a two-stage technique consisting of co-precipitation and high temperature sintering was employed to prepare the layered  $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$  cathode material. Effects of the heating temperature and time on structure and electrochemical properties are tested.

### **2** Experimental

#### 2.1 Preparation of cathode materials

The precursor  $(Ni_{0.6}Co_{0.2}Mn_{0.2})CO_3$  was prepared by the co-precipitation method. Cobalt acetate (Co(CH<sub>3</sub>-

Foundation item: Projects(0991025, 0842003-5 and 0832259) supported by Natural Science Foundation of Guangxi Province, China; Project supported by the Joint Graduate Innovation Talent Cultivation Base of Guangxi Province, China; Project(GuiJiaoRen [2007]71) supported by the Research Funds of the Guangxi Key Laboratory of Environmental Engineering, Protection and Assessment Program to Sponsor Teams for Innovation in the Construction of Talent Highlands in Guangxi Institutions of Higher Learning, China
Corresponding author: ZHONG Sheng-kui; Tel: +86-773-5896446; E-mail: zhongshk@glite.edu.cn

DOI: 10.1016/S1003-6326(09)60059-5

 $COO_{2}$ ), nickel acetate (Ni(CH<sub>3</sub>COO)<sub>2</sub>), and manganese acetate (Mn(CH<sub>3</sub>COO)<sub>2</sub>) were dissolved in deionized water with n(Co):n(Ni):n(Mn) of 2:6:2 to obtain a mixture. Then, sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>) solution was added into the mixture with 1:1(volume ratio) of NH<sub>3</sub>-to-H<sub>2</sub>O to obtain a solution with the pH value of about 11. It was subsequently heated at 60 °C for 3 h to react, then was rested for about 2.5 h. It was calcined at 100 °C for 4 h to obtain the precursor (Ni<sub>0.6</sub>Co<sub>0.2</sub>- $Mn_{0,2}$ )CO<sub>3</sub>. Then, the dried (Ni<sub>0.6</sub>Co<sub>0.2</sub>Mn<sub>0.2</sub>)- CO<sub>3</sub> were ground together with LiOH·H2O in the molar ratio  $n(\text{CO}_3^{2^-}):n(\text{Li}^+)$  of 1:2. The powders were subsequently annealed at a temperature from 750 °C to 950 °C in air for 20 h followed by a natural cooling to obtain  $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_{2}$  powers. To investigate the effect of annealing time, the powders were further annealed at 850 °C for different time of 10, 20 and 30 h, respectively.

#### 2.2 Sample characterization

The powder X-ray diffraction (XRD, X Pert-Pro) measurement using Cu  $K_{\alpha}$  radiation was employed at room temperature to identify the crystalline phase of the synthesized materials. The particle size and morphology of the LiNi<sub>0.6</sub>Co<sub>0.2</sub>Mn<sub>0.2</sub>O<sub>2</sub> powders were observed by scanning electron microscope (JEOL, GSM-6380LV) with an accelerating voltage of 15 kV.

#### 2.3 Electrochemical performances evaluation

The electrochemical characterizations were performed using CR2025 coin-type cell. For positive electrode fabrication, the prepared powders were mixed with 10%(mass fraction) carbon black and 10%(mass fraction) polyvinylidene fluoride in N-methyl pyrrolidinone until slurry was obtained. And then, the blended slurries were pasted onto an aluminum current collector, and the electrode was dried at 120 °C for 10 h in vacuum. The test cell consisted of the positive electrode and lithium foil negative electrode separated by a porous polypropylene film, with 1 mol/L LiPF<sub>6</sub> in EC:EMC:DMC (1:1:1 in volume ratio) as the electrolyte. The assembly of the cells was carried out in a dry Ar-filled glove box. The cells were charged and discharged over a voltage range from 3.0 V to 4.3 V versus Li/Li<sup>+</sup> at room temperature. Cyclic voltammograms were tested in the three-electrode system using metallic foils as both counter and reference electrodes at a scanning rate of 0.1 mV/s in the voltage range of 3.0-4.5 V.

#### **3** Results and discussion

# 3.1 XRD patterns of synthesized LiNi<sub>0.6</sub>Co<sub>0.2</sub>Mn<sub>0.2</sub>O<sub>2</sub> samples

Fig.1 shows the XRD patterns of prepared LiNi<sub>0.6</sub>-



Fig.1 XRD patterns for  $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$  powders heated at 750 °C, 850 °C and 950 °C

Co<sub>0.2</sub>Mn<sub>0.2</sub>O<sub>2</sub> powders heated at 750, 850 and 950 °C. All peaks are indexed on the basis of the  $\alpha$ -NaFeO<sub>2</sub> structure(*R*3*m*). It is clear that all samples have a typical hexagonal layered structure because both the (006)/(102) and the (018)/(110) are well resolved, especially when the heating temperature is above 850 °C.

The X-ray diffraction patterns of  $\text{LiNi}_{0.6}\text{Co}_{0.2}$ -Mn<sub>0.2</sub>O<sub>2</sub> powders annealed for different time from 10 to 30 h at 850 °C are shown in Fig.2. The XRD patterns of all samples are consistent with single phase of  $\alpha$ -NaFeO<sub>2</sub> structure. It is also clear that all samples have a typical hexagonal layered structure.



Fig.2 XRD patterns for  $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$  powders annealed at 850 °C for different time

# 3.2 SEM images of synthesized LiNi<sub>0.6</sub>Co<sub>0.2</sub>Mn<sub>0.2</sub>O<sub>2</sub> samples

Fig.3 shows the scanning electron microscopy (SEM) images of the LiNi<sub>0.6</sub>Co<sub>0.2</sub>Mn<sub>0.2</sub>O<sub>2</sub> powders annealed at 750, 850 and 950 °C for 20 h. With increasing calcination temperature, the primary particle size gradually increases. It could be noticed that LiNi<sub>0.6</sub>Co<sub>0.2</sub>Mn<sub>0.2</sub>O<sub>2</sub> powders calcined at 850 °C exhibit



Fig.3 SEM images of LiNi $_{0.6}$ Co $_{0.2}$ Mn $_{0.2}$ O $_{2}$  powders annealed at 750 °C(a), 850 °C(b) and 950 °C(c) for 20 h

relatively uniform particle size, as shown in Fig.3(b), while  $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$  powders annealed at 750 and 950 °C consist of some primary particles and larger secondary ones. This indicates that raising the calcined temperature not only increases particle size, but also affects the uniformity of the materials.

Fig.4 shows the SEM images of the  $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_{2}$  powders annealed at 850 °C for 10, 20 and 30 h. With increasing calcination time, the primary particle size gradually increases. It could be noticed that LiNi<sub>0.6</sub>Co<sub>0.2</sub> Mn<sub>0.2</sub>O<sub>2</sub> powders calcined for 20 h exhibit relatively uniform particle size, as shown in Fig.4(b), while LiNi<sub>0.6</sub>Co<sub>0.2</sub> Mn<sub>0.2</sub>O<sub>2</sub> powders annealed for 10 and 30 h consist of some primary particles and larger secondary ones. This indicates that raising the calcined time not only increases particle size, but also affects the uniformity of the materials.

#### **3.3 Electrochemical characteristics**

Fig.5 shows the first charge-discharge curves of  $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$  cells calcined at various temperatures at the rate of 0.5*C* in the voltage range of 3.0–4.3 V at room temperature. As seen in Fig.5, the initial charge capacities for  $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$  calcined at of 750, 850



Fig.4 SEM images of  $LiNi_{0.6}Co_{0.2} Mn_{0.2}O_2$  powders annealed at 850 °C for 10 h (a) , 20 h (b) and 30 h (c)



Fig.5 Initial charge-discharge curves of  $LiNi_{0.6}Co_{0.2}$   $Mn_{0.2}O_2$  samples calcined at different temperatures

and 950  $^{\circ}$ C are about 156, 163 and 160 mA·h/g, and the discharge capacities are about 137, 148 and 142 mA·h/g, respectively. The corresponding coulombic efficiency is 87.8%, 90.7% and 88.7%, respectively. It is clearly seen that the electrode reaction reversibility is enhanced considerably when the heating temperature is selected as

850 °C. This is because the homogenous particle of  $\text{LiNi}_{0.6}\text{Co}_{0.2} \text{Mn}_{0.2}\text{O}_2$  leads to a uniform depth of charge (DOC) of each particle, which increases the utilization of the material. Accordingly, the coulombic efficiency is increased.

Fig.6 shows the specific discharge capacity with the cycle number for the LiNi<sub>0.6</sub>Co<sub>0.2</sub>Mn<sub>0.2</sub>O<sub>2</sub> cell in the voltage range between 3.0 and 4.3 V. It can be seen that the 850 °C-annealed LiNi<sub>0.6</sub>Co<sub>0.2</sub>Mn<sub>0.2</sub>O<sub>2</sub> cell delivers a discharge capacity of 148 mA·h/g at 0.2C in the first cycle. For comparison, the initial specific discharge capacities are 137 and 142 mA·h/g for the samples annealed at 750 and 950 °C, respectively. It is noticed that the initial specific discharge capacity increases with increasing the annealing temperature from 750 to 850  $^{\circ}$ C, and decreases with further increasing the annealing temperature from 850 to 950 °C. The following factors might cause this trend. First, the crystallinity of powders is one important factor affecting the electrochemical discharge capacity. The higher annealing temperature leads to higher crystallinity that helps to increase the electrode capacity. Second, the particle size of electrode material is also related to its electrochemical performance. During the first cycle, part of overall capacity is consumed to form a surface layer on the electrode particles. The larger particle size means a smaller specific surface area, resulting in lower capacity loss. Third, too high annealing temperature may be accompanied by the appearance of cation mixing and impurity phases. On the other hand, the irreversible capacity losses after 30 cycles are 12.5%, 8.2%, and 14.8%, respectively, as the annealing temperature increases from 750 to 950 °C. The irreversibility comes mainly from the fact that a part of Ni<sup>3+</sup> cannot be reduced to Ni<sup>2+</sup> after the first cycle. Another main contributor is the formation of surface layer on the electrode material, especially for some material with small particle sizes.



Fig.6 Cycling performance of  $LiNi_{0.6}Co_{0.2}$   $Mn_{0.2}O_2$  samples calcined at different temperatures

Fig.7 shows the first charge-discharge curves of  $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$  cells calcined at 850 °C for different time at the rate of 0.2*C* in the voltage range of 3.0–4.3 V at room temperature. As seen in Fig.7, it is clear that the initial charge capacities for  $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$  calcined for 10, 20, 30 h are about 158, 163, 164 mA·h/g, and the discharge capacities are about 139, 148, 145 mA·h/g, respectively. The corresponding coulombic efficiencies are 87.9%, 90.7% and 88.4%, respectively. It is clearly seen that the electrode reaction reversibility is enhanced considerably when the heating time is 20 h.



Fig.7 Initial charge-discharge curves of  $LiNi_{0.6}Co_{0.2}$   $Mn_{0.2}O_2$  samples calcined at 850 °C for different time

The electrochemical cycling performance of  $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$  samples is shown in Fig.8. It can be seen that the initial discharge capacities of  $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$  calcined for 10, 20 and 30 h are 139, 148, 145 mA·h/g, with the capacity losses of 10.8%, 8.2%, and 9.0% after 30 cycles, respectively. It is noticed that the initial specific discharge capacity increases with increasing the annealing time from 10 to 20 h and the



Fig.8 Cycling performance of  $LiNi_{0.6}Co_{0.2}$   $Mn_{0.2}O_2$  samples calcined at 850 °C for different time

capacity loss decreases with further increasing the annealing time from 10 to 20 h, then increases with increasing the annealing time from 20 to 30 h.

The initial cyclic voltammogram (CV) curves for  $LiNi_{0.6}Co_{0.2} Mn_{0.2}O_2$  electrode at a scanning rate of 0.1 mV/s is shown in Fig.9. It can be seen that the oxidation peak of  $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$  is observed at around 4.05 V, coupled with the reduction peak at 3.67 V. The appearance of only one couple of peak in the  $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2/Li$  cell between 3.0 and 4.6 V means that no structural transitions exist from hexagonal to monoclinic.



Fig.9 CV curves of  $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$  electrode in first cycle

### **4** Conclusions

1)  $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$  cathode materials are prepared by co-precipitation and subsequent heating. XRD and SEM analyses show that the structures and morphology of the  $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$  samples heated at different temperatures and time are different, which results in different electrochemical performances.

2) The LiNi<sub>0.6</sub>Co<sub>0.2</sub>Mn<sub>0.2</sub>O<sub>2</sub> sample annealed at 850  $^{\circ}$ C for 20 h shows the best electrochemical properties with the first specific discharge capacity of 148 mA·h/g in the range of 3.0–4.3 V with the capacity losses of 8.2% after 30 cycles.

3)  $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$  is tested to be a promising cathode material for lithium ion batteries.

#### References

- KOKSBANG R, BARKER J, SHI H. Cathode materials for lithium rocking chair batteries [J]. Solid State Ionics, 1996, 84: 1–21.
- [2] RANDOLPH A L, MARCUS J P, ESTHER S T, KENNETH J T. A study of the overcharge reaction of lithium-ion batteries [J]. J Power Sources, 2001, 97/98: 681–684.
- [3] WON S Y, KWANG B K. Synthesis of LiCoO<sub>2</sub> using acrylic acid and its electrochemical properties for Li secondary batteries [J]. J Power Sources, 1999, 81/82: 517–523.
- [4] ARAI H, OKADA S, SAKURAI Y, YAMAKI J I. Reversibility of LiNiO<sub>2</sub> cathode [J]. Solid State Ionics, 1997, 95(3/4): 275–282.
- [5] ZHONG S W, ZHAO Y J, LIAN F. Characteristics and electrochemical performance of cathode material Co-coated LiNiO<sub>2</sub> for Li-ion batteries [J]. Trans Nonferrous Met Soc China, 2006, 16(1): 137–141.
- [6] CEDER G, MISHRA S K. The stability of orthorhombic and monoclinic-layered LiMnO<sub>2</sub> [J]. Electrochem. Solid-State Lett, 1999, 2(11): 550–552.
- YU L Y, QIU W H, LIAN F, LIU W, KANG X L, HUANG J Y. Comparative study of layered 0.65 Li[Li<sub>1/3</sub>Mn<sub>2/3</sub>]O<sub>2</sub>·0.35LiMO<sub>2</sub> (M=Co, Ni<sub>1/2</sub>Mn<sub>1/2</sub> and Ni<sub>1/3</sub>Co<sub>1/3</sub>Mn<sub>1/3</sub>) cathode materials [J]. Materials Letters, 2008, 62 (17/1): 3010–3013.
- [8] LI Z G, WANG T D, KANG X Y. Synthesis and characterization of LiCo<sub>1/3</sub>Ni<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub> prepared by Pechini process [J]. Rare Metals, 2006, 27 (6): 7–11.
- [9] SMART M C, WHITACRE J F, RATNAKUMAR B V, AMINE K. Electrochemical performance and kinetics of Li<sub>1+x</sub>(Co<sub>1/3</sub>Ni<sub>1/3</sub>Mn<sub>1/3</sub>)<sub>1-x</sub>O<sub>2</sub> cathodes and graphite anodes in low-temperature electrolytes [J]. J Power Sources, 2007, 168(2): 501–508.
- [10] SURENDRA K M, HADAR S, ZVI S F, DANIELA K. A comparative study of electrodes comprising nanometric and submicron particles of LiNi<sub>0.50</sub>Mn<sub>0.50</sub>O<sub>2</sub>, LiNi<sub>0.33</sub>Mn<sub>0.33</sub>Co<sub>0.33</sub>O<sub>2</sub>, and LiNi<sub>0.40</sub>Mn<sub>0.40</sub>Co<sub>0.20</sub>O<sub>2</sub> layered compounds [J]. J Power Sources, 2009, 189(1): 248–255.
- [11] HUI C, YAO Z, JIAN Z, BAO J X. Synthesis and electrochemical characteristics of layered LiNi<sub>0.6</sub>Co<sub>0.2</sub>Mn<sub>0.2</sub>O<sub>2</sub> cathode material for lithium ion batteries [J]. Solid State Ionics, 2005, 176(13/14): 1207–1211.
- [12] NI J F, ZHOU H H, CHEN J T, ZHANG X X. Improved electrochemical performance of layered LiNi<sub>0.4</sub>Co<sub>0.2</sub>Mn<sub>0.4</sub>O<sub>2</sub> via Li<sub>2</sub>ZrO<sub>3</sub> coating [J]. Electrochimica Acta, 2008, 53(7): 3075–3083.
- [13] KOSOVA N V, DEVYATKINA E T, KAICHEV V V. Optimization of Ni<sup>2+</sup>/Ni<sup>3+</sup> ratio in layered Li(Ni,Mn,Co)O<sub>2</sub> cathodes for better electrochemistry [J]. J Power Sources, 2007, 174: 965–969.
- [15] LI J G, LI W, QIAN Z, HE X M. Synthesis and characterization of LiNi<sub>0.6</sub>Mn<sub>0.4-x</sub>Co<sub>x</sub>O<sub>2</sub> as cathode materials for Li-ion batteries [J]. J Power Sources, 2009, 189(1): 28–33.

(Edited by YANG Bing)