Chinese Chemical Letters Vol. 14, No. 12, pp 1303 – 1305, 2003
http://www.imm.ac.cn/journal/ccl.html

Synthesis and Electrochemical Property of Calcium Doped $LiNi_{0.8}Co_{0.2}O_2$ Solid Solution

Jin Long WANG, Zi Cheng LI, Bin XIONG, Lei XIE, Liang Jie YUAN, Ju Tang SUN*

College of Chemistry and Molecular Sciences, Wuhan University, Wuhan 430072

Abstract: A divalent ion doped $LiNi_{0.8}Co_{0.2}O_2$ solid solution, $LiNi_{0.79}Co_{0.20}Ca_{0.01}O_2$, was synthesized in air at 720℃. The structure and electrochemical property as cathode material of lithium ion batteries were measured by XRD and charge-discharge system. The solid solution showed high capacity and good cycle-ability. The second discharged capacity reached 190 $mAh \cdot g^{-1}$ at the current density of 100 $mA \cdot g^{-1}$.

Keywords: Lithium ion battery, calcium, cobalt, lithium nickel oxide, solid solution.

Today, batteries with high capacity, good cyclability, long life and environmental goodness are much required to meet some pressing demands of our modern society. In principle, lithium ion cells can satisfy these requirements[1]. But the properties of the cathode materials have limited the further development of the lithium ion cells.

The studied cathode materials before were mainly $LiCoO_2$, $LiMn_2O_4$, $LiNiO_2$. The $LiCoO_2$ has disadvantages including cost and environmental risk although it is easily prepared and has a good electrochemical performance. The price of $LiMn_2O_4$ and $LiNiO_2$ was lower, but the specific capacity of $LiMn_2O_4$ is low and $LiNiO_2$ is difficult to prepare[2, 3].

Recent studies revealed that $LiNi_{1-x}Co_xO_2$ possesses the advantages of $LiCoO_2$ and $LiNiO_2$, which include high capacity, good cyclability, easy preparation and low cost[4]. In this paper, a Ca-doped lithium nickel cobalt oxide powder was obtained by sintering the pretreated precursor in air. The precursor was prepared by the rheological phase reaction method[5]. The advantages of this method are small reaction volume, homogeneous mixing of reactant, and retention of the original metal element ratio in the prepared process. The crystal structure was characterized by the powder X-ray diffraction. The charge- discharge experimental was carried out at a constant current density of 100 $mA \cdot g^{-1}$.

The analytical reagent grade $LiOH \cdot H_2O$, NiO, Co_2O_3, and $Ca(OH)_2$ were fully mixed in the molar ratio of 1∶0.79∶0.20∶0.01. Then the reactants were confected with a proper amount of water to the rheological body and dried at 60°C. Then it was sintered at 720°C for 12 h in air. The product was cooled slowly to the ambient

---

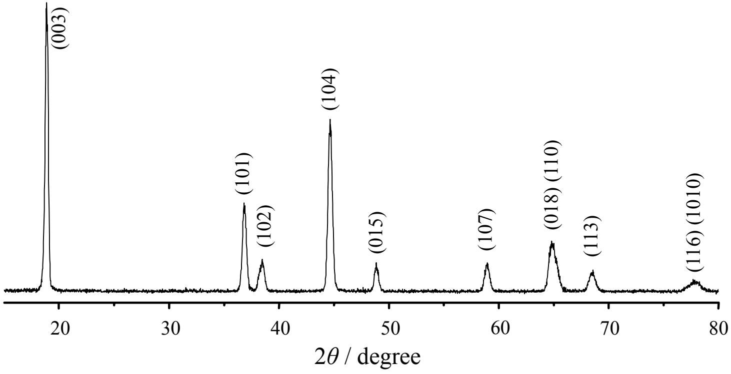
[*] E-mail: jtsun@whu.edu.cn

temperature and ground to suitable particle size for use.

The contents of Ni, Co and Ca of sample were determined by the EDTA complexometric titration and atomic absorption spectrum. The experimental data (Ni 47.61, Co 11.96, Ca 0.40 %) agree with the calculated values (Ni 47.56, Co 12.09, Ca 0.41 %).

The X-ray powder diffraction pattern was obtained on Shimadzu XRD-6000 model X-ray diffractometer with a Ni-filter, a graphite monochromator, and Cu $K\alpha_1$ radiation (λ = 1.54056 Å) from 15 to 80° at the scan speed of 2°·min^{-1}. The XRD pattern of $LiNi_{0.79}Co_{0.20}Ca_{0.01}O_2$ cathode material was shown in **Figure 1**. It indicated that all diffraction lines can be indexed as a hexagonal lattice with α-$NaFeO_2$ structure type. The intensity ratio of I_{003}/I_{104} is 1.66. It showed that the prepared material in air possessed a layer structure[4, 6]. The lattice parameters are a = 2.8607, c = 14.1442 Å, which are smaller to those of pure $LiNiO_2$ (a = 2.878, c = 14.19 Å).

Figure 1 XRD pattern of $LiNi_{0.79}Co_{0.20}Ca_{0.01}O_2$



The electrochemical cell consisted of a working electrode and a lithium foil counter-electrode. It was assembled in an Ar-filled glove box. The working electrode slurry was prepared with the mixing 85% active materials, 5% acetylene black and 10% polytetrafluoroethylene (PTFE) binder in isopropanol. Then the slurry was spread with a roll mill and then dried at 120°C for 24 h. The working electrode was pressed onto a stainless steel wire current collector. The electrolyte used was a 1 mol·L^{-1} solution of $LiClO_4$ dissolved in a 1:1 mixture (V/V) of ethylene carbonate (EC) and propylene carbonate (PC). The cell was charged and discharged between 4.35 and 2.50 V *vs.* Li^+/Li at a constant current density of 100 mA·g^{-1}.

The charge-discharge curves have been recorded on Neware Battery Testing System V4.0 (made in Xinwei Corporation, Shenzhen) at room temperature. The cycle behavior within 50 cycles was shown in **Figuer 2**. We note that the charge and discharge capacity of the first cycle is very low, possibly because the cathode had not been activated. But after it activated, the charge and discharge capacity quickly rose to 211 and 190 mAh·g^{-1}, respectively. After 50 cycles, the discharge capacity reduced to 156 mAh·g^{-1}, the capacity maintained at 82%. In comparison with the charge-discharge results of $LiNi_{0.8}Co_{0.2}O_2$ reported in literature[7], the adding of Ca^{2+} raised the cycle-ability of material. The fluctuations of the charge-discharge capacities in the range 4-50 cycles were 5 ~ 6 %. The fluctuations were possibly due to the variation of the environmental temperature in day and at night. The second and third cycle discharge-charge curves were shown in **Figure 3**. The discharge capacity was mainly concentrated on between 3.4 ~ 4.06 V.

Figure 2 The variation in the discharge and charge capacity with the cycle number of $LiNi_{0.79}Co_{0.20}Ca_{0.01}O_2$/Li test cell

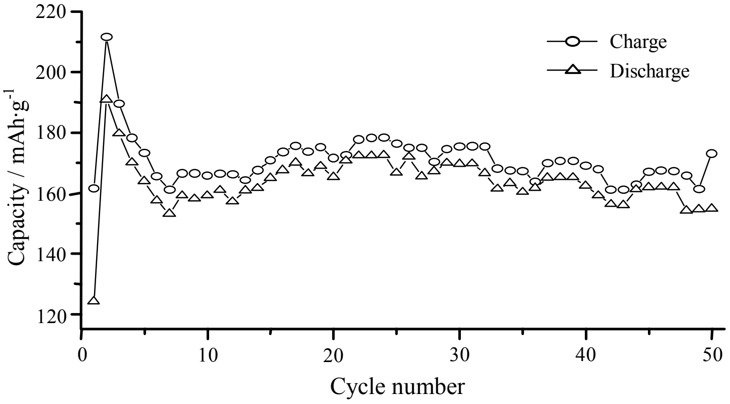
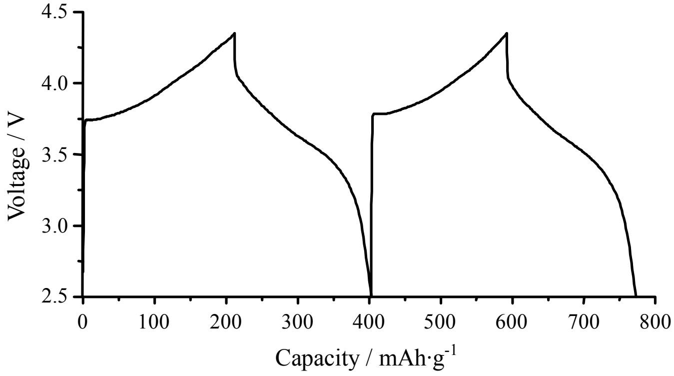


Figure 3 The second and third cycle discharge-charge curves of $LiNi_{0.79}Co_{0.20}Ca_{0.01}O_2$/Li test cell



Acknowledgment

This work was supported by the National Natural Science Foundation of China (No. 29971024).

References

1. B. Scrosati, *Electrochimica Acta*, **2000**, *45*, 2461.
2. Y. Tian, X. Zhai, H. Gao, Y. Zhai, *J. Inorg. Mater.*, **1999**, *14*, 483.
3. K. K. Lee, W. S. Yoon, K. B. Kim, K. Y. Lee, S. T. Hong, *J. Power Sources*, **2001**, *97-98*, 308.
4. J. Ying, C. Wan, C. Jiang, *J. Inorg. Mater.*, **2001**, *16*, 821.
5. J. Sun, W. Xie, L. Yuan, K. Zhang, Q. Wang, *Mater. Sci. Eng. B*, **1999**, 64. 157.
6. Y. M. Choi, S. I. Pyun, S. I. Moon, *Solid State Ionics*, **1996**, *89*, 43.
7. J. Cho, G. Kim, H. S. Lim, *J. Eletrochem. Soc.*, **1999**, *146*, 3571.

Received 16 December, 2002