Vol. 10 №. 3 **Trans. Nonferrous Met. Soc. China** Jun. 2000

Article ID: 1003 - 6326(2000)03 - 0386 - 03

Lithium ion battery cathode material $LiNi_yCo_zMn_{1-y-z}O_2$ ①

LI Nai-jun(李乃军)[1], ZHAI Xiu-jing(翟秀静)[2], TIAN Yan-wen(田彦文)[2]

1. *Teachers College, Shenyang University, Shenyang 110015, P. R. China;*
2. *College of Material and Metallurgy, Northeastern University, Shenyang 110006, P. R. China*

Abstract: A new lithium ion battery cathode material, composite oxide $LiNi_yCo_zMn_{1-y-z}O_2$, was synthesized. The structure and physical properties of the material, including composition, distribution of size, density and specific surface area, were discussed. The characteristic of charge and discharge, reversible specific capacity and cycle property were also studied. The relationship between the structure and properties of the composite oxides was explored. The results show that the composite oxide with a reasonable composition is beneficial to the improvement and enhancement of the properties.

Key words: lithium ion; batteries; cathodic material; $LiNi_yMn_{1-y-z}O_2$; $LiNiO_2$ **Document code: A**

1 INTRODUCTION

Lithium ion battery is a new generation of recharge battery following Cd-Ni and Ni-H_2 batteries[1]. For the improvement of output voltage, specific energy and cycle properties of lithium ion battery, one of the hot spots in research is to develop the cathode-embedding material with high voltage, capacity and good reversibility. The cathode materials that were studied mostly include three kinds of rich lithium transition metal oxides $LiCoO_2$, $LiNiO_2$, and $LiMn_2O_4$[2]. Among them, the preparation process of $LiCoO_2$ is comparatively simple, its property is stable and $LiCoO_2$ has been commercially produced. But $LiCoO_2$ has disadvantages of high price and pollution[3]. $LiNiO_2$ has a stratiform structure, the sequence of cubic close-packing is made up by oxygen atom[4]. The locations of 3 (a) and 3 (b) in the octahedron of cubic close-packing are occupied by nickel and lithium. Any dislocations in the structure[5] influence the electrochemical properties of $LiNiO_2$, which makes the preparation very onerous, and the commercial application of $LiNiO_2$ was also affected. Among the three kinds of oxides, $LiMnO_x$ is the cheapest and has the lowest pollution, but it has the disadvantages of lower specific capacity and polyphase products[6].

In order to lower the production cost, reduce the pollution and improve the cycle properties of lithium ion battery cathode material, this kind of composite oxide has been synthesized[7~10], such as $Li_xCo_{1-y}Ni_yO_2$, $LiCo_xNi_yFe_{1-x-y}O_2$ and so forth. Based on this consideration, the material $LiNi_yCo_zMn_{1-y-z}O_2$ was synthesized, its structure and properties are studied and the comparisons with $LiNiO_2$ are carried out in this paper.

2 EXPERIMENTAL

The analytically pure LiOH, $Ni(OH)_2$, MnO_2, Co_3O_4 were mixed and pressed with mass fractions of Li, Ni, Mn and Co of 1.1∶0.8∶0.1∶0.1, 1.1∶0.7∶0.2∶0.1, 1.1∶0.6∶0.2∶0.2 and 1.1∶0.6∶0.3∶0.1 respectively. And then the composite oxide, $LiNi_yCo_zMn_{1-y-z}O_2$, was synthesized with synthesis temperature of 650 ~ 750 ℃, synthesis time of 12 ~ 17 h and under atmosphere of oxygen.

The compound composition was determined by atomic absorption spectrum. The characteristic of charge and discharge of $LiNi_yCo_zMn_{1-y-z}O_2$ was measured by DC-5 battery electrochemistry measurement. The determination of cycle voltammogram curve was completed by BG&GPARC273A potentialstat. The structure of $LiNi_yCo_zMn_{1-y-z}O_2$ was determined by Japan Rigaku D/MAX-3B X-ray diffractometer. The distribution of the particle size was measured by IAS-4 image particle-size analyzer.

3 RESULTS AND DISCUSSION

The physical properties of $LiNi_yCo_zMn_{1-y-z}O_2$, including compound composition, distribution of particle size, density and specific surface area, were studied. The compound electrochemical properties, charge and discharge curves, specific capacity, cycle voltammogram curves and so on, were also compared and discussed. The structure of the compound was studied by X-ray diffractometery.

3.1 Composition of compounds

The compositions of synthetic composited oxide $LiNi_yCo_zMn_{1-y-z}O_2$ ($0 < y < 1$, $0 < z < 1$), deter-

① **Received date:** Nov.3, 1999; **accepted date:** Mar.11, 2000

mined by atomic absorption spectrum, were $Li_{1.01}Ni_{0.80}Co_{0.09}Mn_{0.10}O_2$, $Li_{0.99}Ni_{0.69}Co_{0.20}Mn_{0.09}O_2$, $Li_{0.98}Ni_{0.60}Co_{0.2}Mn_{0.19}O_2$ and $Li_{0.99}Ni_{0.59}Co_{0.29}Mn_{0.10}O_2$, respectively.

3.2 Distribution of size

The particle size distribution of composite compounds $Li_{1.01}Ni_{0.80}Co_{0.09}Mn_{0.10}O_2$ and $Li_{0.99}Ni_{0.69}Co_{0.20}Mn_{0.09}O_2$ was determined. The average particle size of the two was 0.5 ~ 0.6 μm, which meets the requirement of the battery material.

3.3 Density and specific surface area

The bulk and tap density and the specific surface area of compounds were examined. The results are shown in Table 1.

Table 1 Density and specific surface area of compounds

Compound	Bulk density / ($g \cdot cm^{-3}$)	Tap density / ($g \cdot cm^{-3}$)	Specific surface area / ($m^2 \cdot g^{-1}$)
$Li_{1.01}Ni_{0.80}Co_{0.09}Mn_{0.10}O_2$	1.48	2.51	0.60
$Li_{0.99}Ni_{0.69}Co_{0.20}Mn_{0.09}O_2$	1.49	2.53	0.58
$LiNiO_2$	1.47	2.52	0.62

The results show that there is no obvious difference in bulk density, tap density, specific surface area between the composite oxides and $LiNiO_2$. The above indexes all meet the requirement of the battery material.

3.4 Electrochemical properties of compounds

The electrochemical properties of the compounds were represented mainly in the curves of charge and discharge, reversible specific capacity and the cycle voltammogram curves.

3.4.1 Curves of charge and discharge

The charge and discharge curves of the four compounds and $LiNiO_2$ are shown in Fig.1. From Fig.1 it can be seen that the charge capacity of the compounds is near that of $LiNiO_2$; the discharge platform of $Li_{1.01}Ni_{0.80}Co_{0.09}Mn_{0.10}O_2$ and $Li_{0.99}Ni_{0.69}Co_{0.20}Mn_{0.09}O_2$ is increased; the discharge is smooth and discharge capacity is enhanced. The discharge voltage of $Li_{0.98}Ni_{0.60}Co_{0.20}Mn_{0.19}O_2$ and $Li_{0.99}Ni_{0.59}Co_{0.29}Mn_{0.10}O_2$ is lower and discharge velocity is rapid, but the electrochemical properties are not perfect. The results above prove that the electrochemical properties of the compound are affected by chemical components, and the properties of composite compound are also affected by the content of each substances.

3.4.2 Reversible specific capacity

The reversible specific capacity of $Li_{1.01}Ni_{0.80}Co_{0.09}Mn_{0.10}O_2$, $Li_{0.99}Ni_{0.69}Co_{0.20}Mn_{0.09}O_2$ and

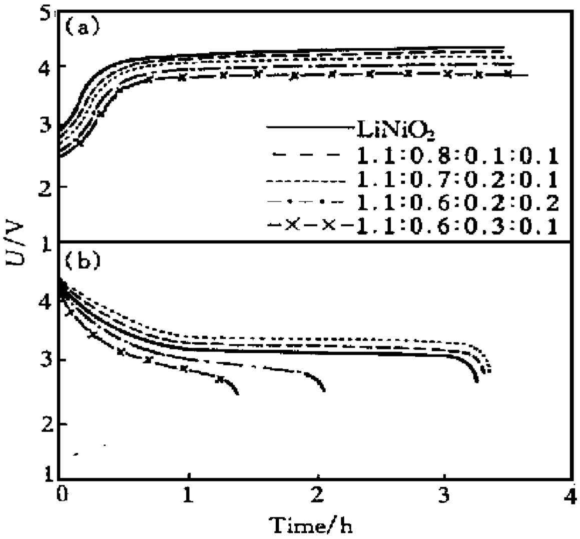

Fig.1 Charge and discharge curves of $LiNi_yCo_zMn_{1-y-z}O_2$ and $LiNiO_2$
(a) —Charge; (b) —Discharge

$LiNiO_2$ was determined and the results are 164, 165, 156 $mA \cdot h \cdot g^{-1}$, respectively. The reversible specific capacity of the two composite compounds are enhanced from 156 $mA \cdot h \cdot g^{-1}$ to 164 ~ 165 $mA \cdot h \cdot g^{-1}$ as compared with $LiNiO_2$; the electrochemical properties are also improved.

3.4.3 Cycle voltammogram curves

The cycle voltammogram curves of compounds $Li_{1.01}Ni_{0.80}Co_{0.09}Mn_{0.10}O_2$, $Li_{0.99}Ni_{0.69}Co_{0.2}Mn_{0.09}O_2$ and $LiNiO_2$ was determined. It is found that the cycle voltammogram curves of the two compounds and $LiNiO_2$ were similar to each other, which indicates that the mechanism of charge and discharge is identical, lithium ion is embedded in and out in the locations of octahedron and tetrahedron respectively.

3.5 Structure of $LiNi_yCo_zMn_{1-y-z}O_2$

The XRD curves of $Li_{1.01}Ni_{0.80}Co_{0.09}Mn_{0.10}O_2$ and $Li_{0.99}Ni_{0.69}Co_{0.20}Mn_{0.09}O_2$ are shown in Fig.2, compared with that of $LiNiO_2$ in Fig.3. Peak (003) of the two composite compounds are decreased in intensity, the feature peak (120) appears near peak (104), but its intensity is weaker. The results indicate that the crystal lattice parameters of $Li_{0.99}Ni_{0.69}Co_{0.20}Mn_{0.09}O_2$ are: $a = 2.880$ Å and $c = 14.168$ Å. The two composite compounds are solid solutions of $LiNiO_2$, $LiCoO_2$ and $LiMnO_2$.

To keep balance of valence, cobalt and manganese are all in high valence, the average valence of $Li_{1.01}Ni_{0.80}Co_{0.09}Mn_{0.1}O_2$ is 3.38, and that of $Li_{0.99}Ni_{0.69}Co_{0.20}Mn_{0.09}O_2$ is 3.35 by valence analysis. The high valence of cobalt and manganese would be beneficial to the embedding in and out of lithium ion, so that the discharge platforms of the two composite compounds have been enhanced and the reversible

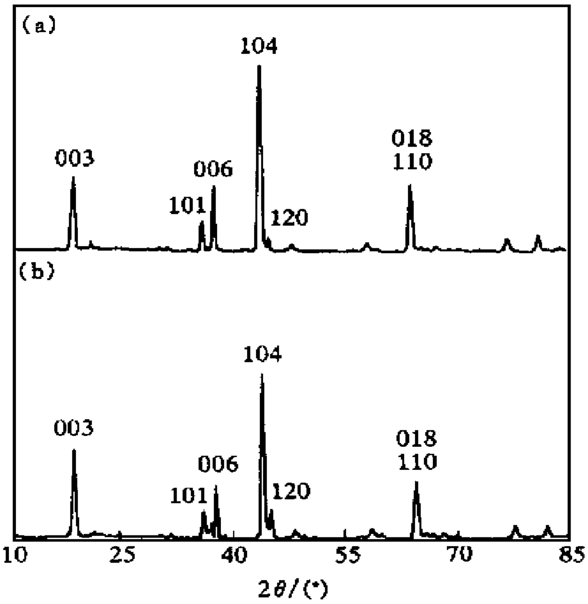

Fig.2 XRD curves of compounds
(a) —$Li_{1.01}Ni_{0.80}Co_{0.09}Mn_{0.10}O_2$; (b) —$Li_{0.99}Ni_{0.69}Co_{0.20}Mn_{0.09}O_2$

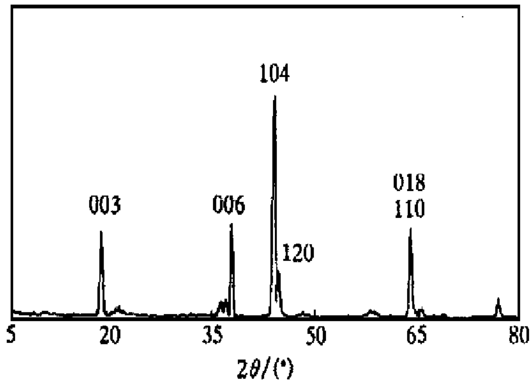

Fig.3 XRD curves of $LiNiO_2$

discharge capacity has been improved.

4 CONCLUSIONS

1) The physical properties of $Li_{1.01}Ni_{0.80}Co_{0.09}$-$Mn_{0.10}O_2$, $Li_{0.99}Ni_{0.69}Co_{0.20}Mn_{0.09}O_2$ and $LiNiO_2$ (such as distribution of particle size, density and specific surface area) are similar to each other.

2) In the composite compounds, the discharge platforms of $Li_{1.01}Ni_{0.80}Co_{0.09}$-$Mn_{0.1}O_2$ and $Li_{0.99}$-$Ni_{0.69}Co_{0.20}Mn_{0.09}O_2$ are enhanced. Reversible specific capacity is improved. The cycle voltammogram curves of the two compounds are similar to that of $LiNiO_2$, which shows that the mechanism of charge and discharge is the same.

3) The structure analysis indicates that composite oxides belong to hexagonal system. Cobalt and manganese in the compounds exist in high valence, which conforms to the results of electrochemical determination.

REFERENCES

[1] HU Xing-ren. Today world battery market [J]. Battery, (in Chinese), 1994, 24(4): 179.

[2] CHEN Dai-jun. The development of battery and lithium-ion battery [J]. Battery, (in Chinese), 1996, 26(3): 139.

[3] ZHAN Hui and ZHOU Yun-hong. The development of lithium-ion battery cathode material [J]. Voltage-Supply Technology, (in Chinese), 1999, 23: 102.

[4] Rougier A, Sadoune I and Gravereau P. Effect of cobalt substitution on cationic distribution in $LiNi_{1-y}Co_yO_2$ electrode materials [J]. Solid State Ionics, 1996, 90: 83.

[5] WANG Chao-qun, REN Xiao-hua, JIANG Wen-que. High close-packing $Li(OH)_2$ cathode material [J]. Trans Nonferrous Metal Soc China, 1999, 9(3): 504.

[6] Koetschau I, Richard M N and Dahn J R. Orthorhombic $LiMnO_2$ as a high capacity cathode for lithium-ion cells [J]. J Electrochem Soc, 1995, 142(9): 2906.

[7] Jones C D W, Rossen E and Dahn G R. Structure and electrochemistry of $LiCr_yCo_{1-y}O_2$ [J]. Solid State Ionics, 1994, 68: 65.

[8] Gummow R J and Thackeray M M. Characterization of $Li/Li_xCo_{1-y}Ni_yO_2$ electrodes for rechargeable lithium cells [J]. J Electrochem Soc, 1993, 140: 3365.

[9] GAO Hong, ZHAI Yu-chun, ZHAI Xiu-jing, et al. Lithium-ion battery's cathode material $LiNi_yCo_{1-y}O_2$ [J]. Battery, 1998(3): 15～17.

[10] LI Yu-zheng. The research development of new Lithium-ion battery [J]. Battery, (in Chinese), 1997, 27(2): 83.

(Edited by LONG Huai-zhong)