Synthesis and electrochemical properties of $LiNi_{0.4}Mn_{1.5}Cr_{0.1}O_4$ and $Li_4Ti_5O_{12}$

G.Q. Liu[1,]*, W. Lei [2], G. Y. Liu[1], H. Z. Luo[3], B. Y. Ma[1], Q. Y. Wu[1], andY.W. Tian[1]

[1]*School of Material and Metallurgy, Northeastern University, Shenyang 110004, China*

[1]*Chinese Acad Sci, Inst Met Res, Shenyang Natl Lab Mat Sci, Shenyang 110016, China*

[3]*The Council for Scientific and Industrial Research (CSIR), South Africa*

Abstract

Spinel compound $LiNi_{0.4}Mn_{1.5}Cr_{0.1}O_4$ (LNMCO) and $Li_4Ti_5O_{12}$ (LTO) were synthesized by different methods. The particle sizes of $LiNi_{0.4}Mn_{1.5}Cr_{0.1}O_4$ and $Li_4Ti_5O_{12}$ were 05-2 um and 0.5-0.8 um, respectively. The $LiNi_{0.4}Mn_{1.5}Cr_{0.1}O_4/Li_4Ti_5O_{12}$ (LNMCO/LTO) cell exhibited good electrochemical properties at high current rate such as 1 C. When specific capacity was determined based on the mass of LNMCO cathode, the LNMCO/LTO cell delivered 125 mAh g^{-1} at 1 C and 77 mAh g^{-1} at 5 C. The capacity retentions after 30 cycles were 94.4 % and 83.1%, respectively.

Keywords: compounds, sol-gel, electrochemistry, x-ray diffraction, cycle voltammetry

Corresponding author: Tel：86-024-83673860; Fax: 86-024-83687731

Email address: liugq@smm.neu.edu.cn

1. Introduction

The 5 V cathode materials for lithium ion batteries consist mainly of $LiCoPO_4$, $LiNiVO_4$ and $LiNi_{0.5}Mn_{1.5}O_4$ [1-3]. The cubic $LiNiVO_4$ compound with inverse spinel structure could conduct charge and discharge at around 5V. However, its crystal structure only delivered moderate discharge capacity of 90 mAh g^{-1} with poor cycle ability. The olivine-type metal phosphate $LiCoPO_4$ could deliver about 60% of the theoretical capacity (166 mAh g^{-1}) due to its limited electronic/ionic transport. Among them, $LiNi_{0.5}Mn_{1.5}O_4$ exhibited the best electrochemical properties. It is acknowledged that the drawback of $LiNi_{0.5}Mn_{1.5}O_4$ is its unfavorable cycle performance at elevated temperature or at higher current rate. Cation doping is considered to be an effective way to modify the intrinsic properties of electrode materials. It will be promising if proper cation doping can be used in spinel $LiNi_{0.5}Mn_{1.5}O_4$ to further improve its electrical conductivity, favoring fast charge and discharge rate.

Spinel $Li_4Ti_5O_{12}$ shows negligible lattice change during intercalation of Li ions. There is no structural change (zero-strain insertion material) in charge–discharge process. It is a promising anode material for lithium ion batteries [4].

New lithium-ion battery systems can be fabricated using $Li_4Ti_5O_{12}$ as anode and $LiNi_{0.5}Mn_{1.5}O_4$ or its derivatives as cathode. In this study, we synthesized $Li_4Ti_5O_{12}$ and Cr-doped compound $LiNi_{0.4}Mn_{1.5}Cr_{0.1}O_4$ in order to increase the rate capability of cathode. A new system $LiNi_{0.4}Mn_{1.5}Cr_{0.1}O_4$/LTO was then fabricated. It exhibited excellent electrochemical properties.

2. Experimental

The stoichiometric amounts of Li_2CO_3 and anatase TiO_2 with a Li: Ti molar ratio of 0.82: 1 were weighed separately. Then they were mixed by planetary ball milling with methanol medium.

The rotating speed was 300 r min^{-1}. The dried and mixed reactant mixture was heated in a muffle furnace at 750 ^{o}C for 24 h in air. The samples were reground, and the final product $Li_4Ti_5O_{12}$ was obtained.

Stoichiometric amounts of $Li(CH_3COO)\ 2H_2O$, $Ni(CH_3COO)_2\ 4H_2O$, $Mn(CH_3COO)_2\ 4H_2O$ and $Cr(NO_3)_3\ 9H_2O$ were used as starting materials and malic acid as chelating agent. In order to compensate for the loss of Li at high reaction temperature, approximate additional 3% of Li salt was made up. At first, the staring materials were dissolved in distilled water and stirred for some time, and then added malic acid into aqueous solution drop by drop. After stirred for 2 hours, the mixed solution was evaporated at 80^0C to form a dried gel. At last, the gel was calcined at 900 ^{0}C for 8 h to turn into product $LiNi_{0.4}Mn_{1.5}Cr_{0.1}O_4$.

The phase identification of the prepared samples was carried out by X-ray diffraction (XRD) using a Multiflex X-ray powder diffractometer (Rigaku Co. Ltd.). The morphologies of the products were examined with a FEI NOVA NANOSEM430 scanning electron microscope (SEM).

The charge-discharge and cycle voltammetry tests were carried out by the same way as other literatures. The mass ratios of active material: conducting carbon black: PVDF binder were 90: 5: 5 and 80: 10: 10 for $LiNi_{0.4}Mn_{1.5}Cr_{0.1}O_4$ electrode and $Li_4Ti_5O_{12}$ electrode, respectively. The electrolyte of 1 M $LiPF_6$ in a 1: 1 (v/v) mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) employed. The electrodes of $LiNi_{0.4}Mn_{1.5}Cr_{0.1}O_4$ and $Li_4Ti_5O_{12}$ were 0.3 and 0.2 mm thick, respectively.

3. Results and discussion

Fig. 1 shows the XRD patterns of the $Li_4Ti_5O_{12}$ and $LiNi_{0.4}Mn_{1.5}Cr_{0.1}O_4$ samples. They were all pure phases, with all the peaks indexable to the F_{d3m} space group. In order to determine the

lattice parameter, a, of the prepared samples, Bragg equation was used.

$$n\lambda = 2d_{hkl}\sin\theta$$

Here n is 1, λ is the wavelength of the incident X-ray beam which is 1.5406 Å, θ is the incident

angle, and d_{hkl} is between the atomic layers of the cubic structure. Because the synthesized

$LiNi_{0.5}Mn_{1.2}Ti_{0.3}O_4$ is face centered cubic, the lattice parameter can be calculated by using the

equation:

$$d_{hkl} = a/D, D = \text{square root of } (h^2 + k^2 + l^2)$$

where a is the lattice parameter and ($h\ k\ l$) are the Miller indices. The lattice parameters are

8.216 and 8.371 Å for $LiNi_{0.5}Mn_{1.2}Ti_{0.3}O_4$ and $Li_4Ti_5O_{12}$, respectively.

Fig. 2 shows the morphologies of the $Li_4Ti_5O_{12}$ and $LiNi_{0.4}Mn_{1.5}Cr_{0.1}O_4$ particles. Most of

the particles of $Li_4Ti_5O_{12}$ were around 0.5 μm, and small amount were larger than 0.5 μm but less

than 0.8 um. The particles of $LiNi_{0.4}Mn_{1.5}Cr_{0.1}O_4$ distributed unevenly, ranging from 0.5 um to 2

um.

The charge-discharge curves of LNMCO, LTO and LNMCO/LTO cell are shown in Fig. 3.

For LNMCO, there were two voltage plateaus at around 4.0 and 4.7 V, respectively. The

electrochemical process taking place at around 4 V involved the oxidation of Mn^{3+} to Mn^{4+},

while the voltage plateau at around 4.7 V were caused by Ni^{2+}/Ni^{3+} and Ni^{3+}/Ni^{4+} transitions. The

oxidation/reduction process of Cr^{3+}/Cr^{4+} should take place at around 4.92 V. Because the amount

of doped Cr was small and the current rate is large, the red-ox process of Cr^{3+}/Cr^{4+} was not

remarkable in these curves. For LTO, the discharge voltage was about 1.49 V. The discharge

voltage of LNMCO/LTO cell was about 3.1 V. Because there are differences in specific

capacities between LNMCO and LTO, the specific capacity of LNMCO/LTO cell can be

determined by either LNMCO or LTO [5]. In this study, we determined the capacity of LNMCO/LTO cell by LNMCO.

Fig. 4 indicates the cycle performances of LNMCO and LTO. The first discharge capacity of LTO were 163 mAh g^{-1} at 1 C and 136 mAh g^{-1} at 5 C, and capacity retentions were 97 % and 95.5% at the 50th cycle, respectively. These performances are better than other solid state methods [6, 7]. For LNMCO, the discharge capacity at 1 C was 134 mAh g^{-1} and the capacity retention was 98% at the 50th cycle. Its discharge capacity at 5 C was 97 mAh g^{-1}, and there was almost no capacity decay after 50 cycles. After 30 cycles, the capacity of LNMCO/LTO cell were 125 and 77 mAh g^{-1} respectively, and capacity retentions were 94.4 and 83.1 % at 1 C and 5 C, respectively.

The cyclic voltammetry (CV) results of LNMCO, LTO and LNMCO/LTO cell are illustrated in Fig. 5. Two main redox processes are clearly seen in CV curves of LNMCO. The redox processes included Mn^{3+}/Mn^{4+} and Ni^{2+}/Ni^{4+}. They took place at around 4.07 V and 4.80 V, respectively. The Ni^{2+}/Ni^{4+} process included Ni^{2+}/Ni^{3+} and Ni^{3+}/Ni^{4+}. For LTO, one cathodic peak that located at 1.46 V corresponds to the voltage flat of the discharge process. This is a process of Li insertion into spinel $Li_4Ti_5O_{12}$. Another anodic peak that located at 1.7 V corresponds to the voltage flat of the charge process. This is a process of Li deintercalation from spinel $Li_4Ti_5O_{12}$. The electrochemical reaction based on Ti^{4+}/Ti^{3+} redox couple is a reversible redox reaction. They are in accordance with the above charge−discharge test results.

The good electrochemical properties of LNMCO/LTO cell are dependent on cathode LNMCO and anode LTO. The synthesized LTO particles are about 0.5 um, and well distributed. The submicron particles should exhibit better electrochemical properties than large particles.

Because the chemical bond of Cr-O is strong, the Cr-doped compound LNMCO can enhance the structure stability. The synthesized LNMCO and LTO improved the electrochemical properties of LNMCO/LTO cell.

4. Conclusion

In this study, spinel compound $LiNi_{0.4}Mn_{1.5}Cr_{0.1}O_4$ and $Li_4Ti_5O_{12}$ were synthesized respectively, and $LiNi_{0.4}Mn_{1.5}Cr_{0.1}O_4/Li_4Ti_5O_{12}$ cells were assembled by using them as cathode and anode. The $LiNi_{0.4}Mn_{1.5}Cr_{0.1}O_4/Li_4Ti_5O_{12}$ cell delivered 125 mAh g^{-1} at 1 C and 77 mAh g^{-1} at 5 C. Its capacity retentions after 30 cycles were 94.4 and 83.1% respectively. The electrochemical properties of $LiNi_{0.4}Mn_{1.5}Cr_{0.1}O_4/Li_4Ti_5O_{12}$ cell are determined by the as-prepared cathode material $LiNi_{0.4}Mn_{1.5}Cr_{0.1}O_4$ and anode material $Li_4Ti_5O_{12}$.

References

[1] G.T.K. Fey, J.R. Dahn, M.J. Zhang, W. Li, *J. Power Sources*, **68**, 549 (1997).

[2] H.H. Li, J. Jin, J.P. Wei, Z. Zhou, J. Yan, *Electrochem. Commun.*, **11**, 95 (2009)

[3] G.Q. Liu, L. Wen, Y.M. Liu, *J. Solid State Electrochem.*, DOI 10.1007/s10008-010-1061-5.

[4] T. Ohzuku, A. Ueda, *J. Electrochem. Soc.*, **142**. 1431 (1995).

[5] H.F. Xiang, X. Zhang, Q.Y. Jin, C.P. Zhang, C.H. Chen, X.W. Ge, *J. Power Source*, **183**, 355 (2008).

[6] X.L. Yao, S. Xie, C.H. Chen, Q.S. Wang, J.H. Sun, Y.L. Li, S.X. Lu, *Electrochim. Acta.*, **50**, 4076 (2005).

[7] G.F. Yan, G.S. Li, L.P. Li, H.S. Fang, *Chin. J. Struct. Chem.*,**28**, 1393 (2009).

Captions:

Fig. 1. XRD patterns of $Li_4Ti_5O_{12}$ and $LiNi_{0.4}Mn_{1.5}Cr_{0.1}O_4$ samples.

Fig. 2. Scanning electron micrograghs of $LiNi_{0.4}Mn_{1.5}Cr_{0.1}O_4$ (a) and $Li_4Ti_5O_{12}$ (b) samples.

Fig. 3. Charge/discharge curves for $Li_4Ti_5O_{12}$, $LiNi_{0.4}Mn_{1.5}Cr_{0.1}O_4$ and $LiNi_{0.4}Mn_{1.5}Cr_{0.1}O_4$ /$Li_4Ti_5O_{12}$ cell at 1 C and 5 C.

Fig. 4. Cycle performances of $Li_4Ti_5O_{12}$, $LiNi_{0.4}Mn_{1.5}Cr_{0.1}O_4$ and $LiNi_{0.4}Mn_{1.5}Cr_{0.1}O_4$ /$Li_4Ti_5O_{12}$ cell at 1 C and 5 C.

Fig. 5. Cyclic voltammogram of $Li_4Ti_5O_{12}$, $LiNi_{0.4}Mn_{1.5}Cr_{0.1}O_4$ and $LiNi_{0.4}Mn_{1.5}Cr_{0.1}O_4$ /$Li_4Ti_5O_{12}$ cell at 1 C and 5 C.
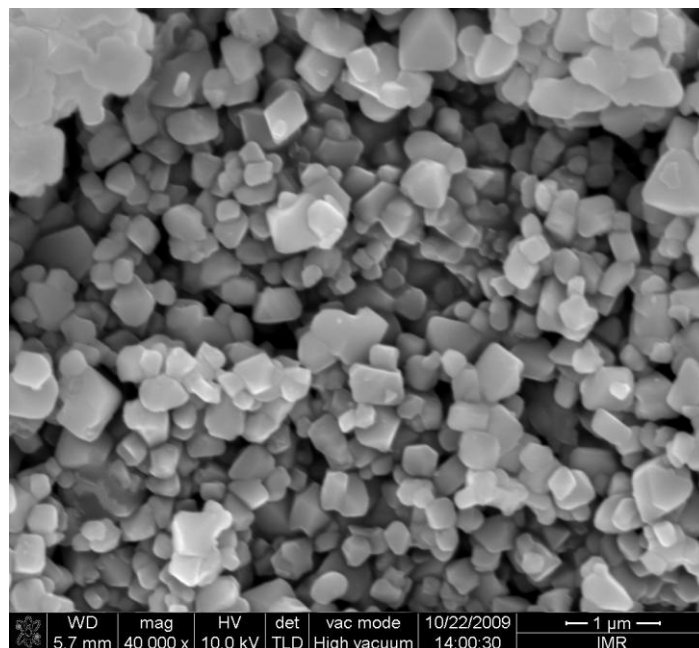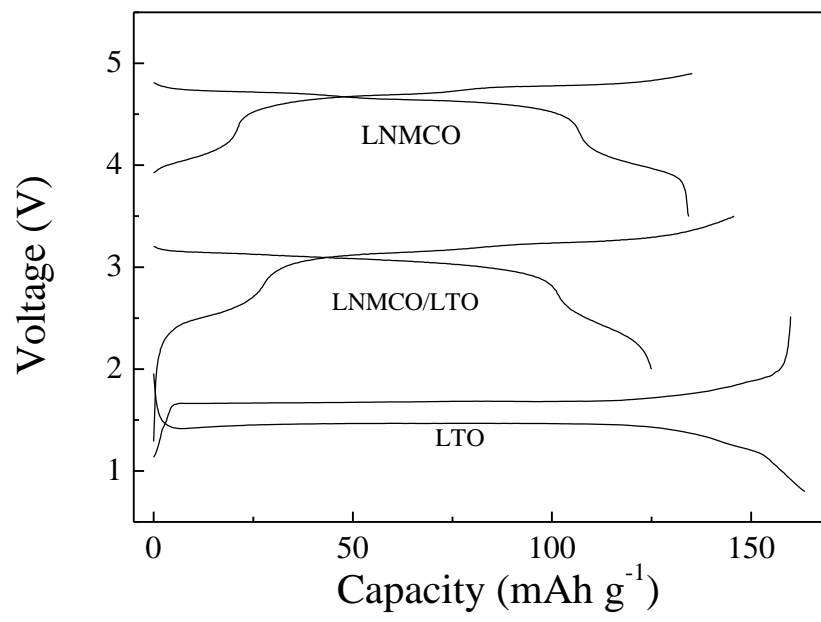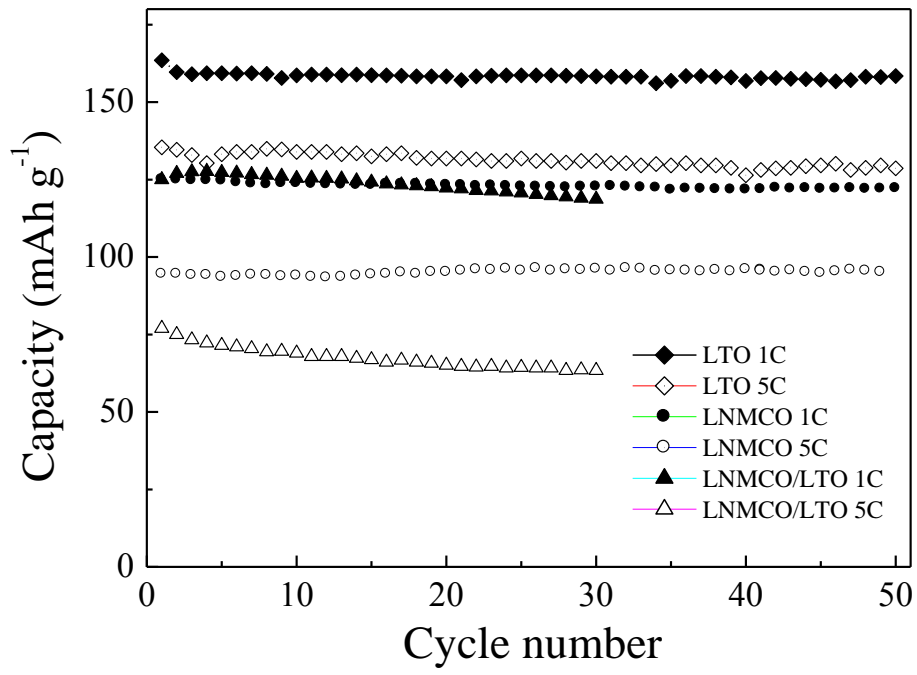
Fig. 1
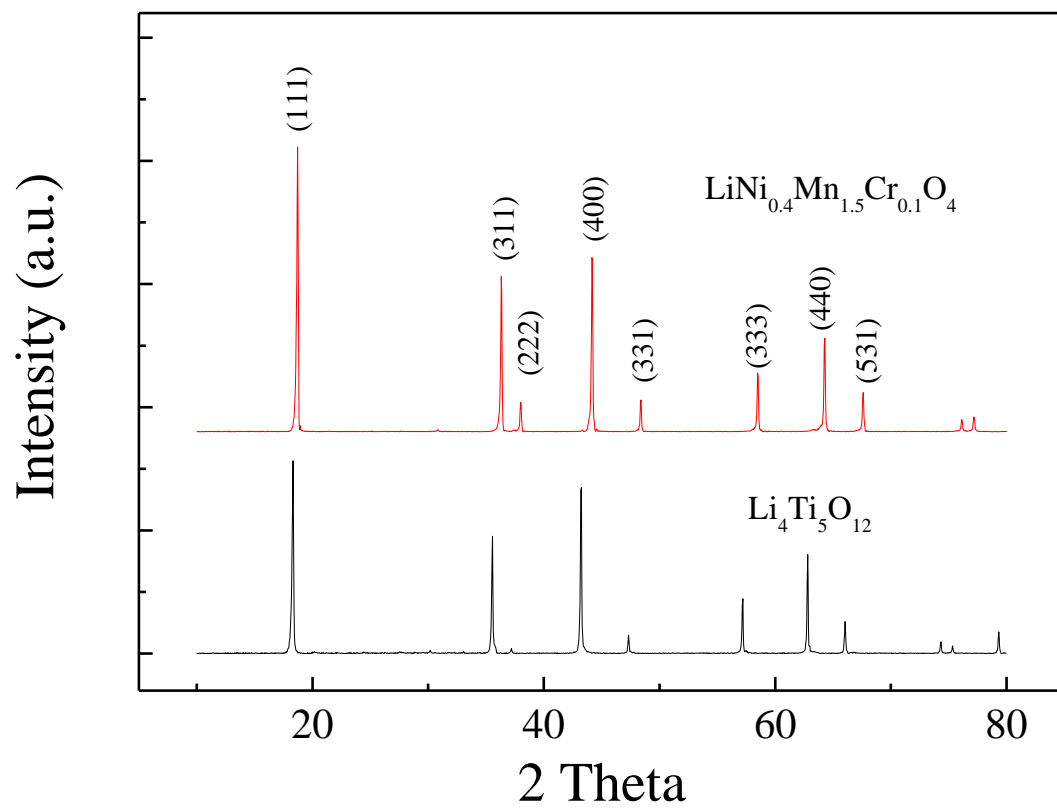
Fig. 2
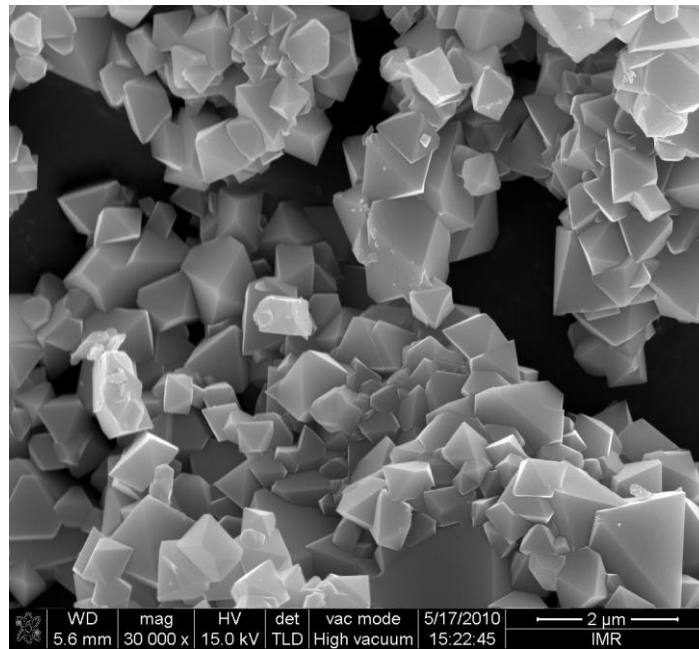
(a)

(b)

Fig. 3

Fig. 4

分开这个图？

做另外一个 anode 的比较

Fig. 5

LTO

LNMCO/LTO

LNMCO