

Short communication

LiNi_{0.5}Mn_{1.5}O_{3.975}F_{0.05} as novel 5 V cathode material

X.X. Xu, J. Yang*, Y.Q. Wang,
Y.N. NuLi, J.L. Wang

Department of Chemical Engineering, Shanghai Jiao Tong
University, Shanghai 200240, PR China

Available online 26 June 2007

Abstract

LiNi_{0.5}Mn_{1.5}O₄ obtained by sol–gel method often shows low capacity and 4 V discharge plateau due to the small amount of Mn³⁺ and impurity phases. In this study, fluorine-doped spinel with nominal composition of LiNi_{0.5}Mn_{1.5}O_{3.975}F_{0.05} was prepared using sol–gel technique and re-annealing in oxygen. XRD measurements reveal that fluorine doping can suppress the formation of NiO impurity. The electrochemical performance of LiNi_{0.5}Mn_{1.5}O_{3.975}F_{0.05} as cathode material for lithium-ion batteries was examined. Comparing with LiNi_{0.5}Mn_{1.5}O₄, fluorine doping enhances the initial capacity from about 130 mAh g⁻¹ to over 140 mAh g⁻¹ between 3.5 and 5.2 V and simultaneously reduces the voltage polarization. About 95% capacity is retained after 40 cycles. By followed re-annealing in oxygen, the 4 V plateau can be obviously restrained.
© 2007 Elsevier B.V. All rights reserved.

Keywords: LiNi_{0.5}Mn_{1.5}O_{3.975}F_{0.05}; Fluorine doping; Re-annealing; 5 V cathode materials; Lithium-ion batteries

1. Introduction

Lithium-ion batteries are regarded as a promising power source for both portable electronic devices and zero emission vehicles (ZEV) due to their long cycle life and high energy density [1]. High-voltage cathodes allow anodes working significantly above 0 V, thus avoiding the problems of lithium electroplating on graphite-based anodes [2]. The use of 5 V cathodes cannot only offer a wider selectivity for anode materials, but also enhance the out-put voltage of batteries.

In recent years, cation-substituted LiM_xMn_{2-x}O₄ (M = Ni, Co, Cu, etc.) spinel compounds have been proposed for 5 V cathode materials, in which LiNi_{0.5}Mn_{1.5}O₄ has been widely investigated due to its high capacity [3–5]. In these spinel compounds, the Mn⁴⁺ ion becomes electrochemically inactive and the replacing metals dominate redox reaction near 5 V [6–10]. Actually, small amount of Mn³⁺ and impurity phases produced by side reactions often exist in LiNi_{0.5}Mn_{1.5}O₄, leading to 4 V plateau, low capacity and poor cycling stability. It is also known that oxygen deficiency is easily formed when samples

are prepared above 600 °C and becomes more serious with the elevation of the temperature [11,12]. The oxygen deficiency is also a source for Mn³⁺ and a reason for the distortion of the spinel. In order to increase and stabilize the 5 V capacity, intensive study has been concentrated on cation doping and the structure optimization [13–18]. In this study, we examined the influence of fluorine anion doping on electrochemical behavior of LiNi_{0.5}Mn_{1.5}O₄. Combining with re-annealing, considerable improvement in the material performance has been achieved.

2. Experimental

2.1. Material preparation

LiNi_{0.5}Mn_{1.5}O₄ and LiNi_{0.5}Mn_{1.5}O_{3.975}F_{0.05} were prepared by sol–gel method in combination with high temperature treatment. Stoichiometric amounts of LiAc·2H₂O, Mn(Ac)₂·4H₂O and Ni(Ac)₂·4H₂O were dissolved in distilled water by stirring. For LiNi_{0.5}Mn_{1.5}O_{3.975}F_{0.05} preparation, LiF was used as fluorine source. The resultant solution was evaporated at 70–80 °C until a transparent sol then gel was obtained. The gel precursors were decomposed at 450 °C in air for 5 h. Then the sample was pressed and calcined at 850 °C in air for 12 h. After grinding, the powder samples were obtained. For the re-annealing process, the

* Corresponding author. Tel.: +86 21 54747667; fax: +86 21 54741297.
E-mail address: yangj723@sjtu.edu.cn (J. Yang).

powder sample was heated again at 600 °C under oxygen flow for 15 h.

Powder XRD patterns were recorded on a Rigaku X-ray diffractometer D/MAX-2200/PC equipped with Cu K α radiation (40 kV, 20 mA) at the rate of 6° min⁻¹ over the range of 10–70° (2 θ).

2.2. Cells assembling and electrochemical test

Electrodes were prepared by uniformly coating a slurry containing 85 wt.% active material, 7 wt.% acetylene black and 8 wt.% polyvinylidene fluoride dissolved in *N*-methyl-2-pyrrolidone on aluminum foil, followed by drying at 80 °C in air and at 120 °C under vacuum. Electrode disks (ϕ 1.25 cm) were punched from the foil and weighed. The active materials in the electrodes were about 3 mg. Electrochemical behavior of the test materials was examined via CR2016 coin cells with lithium metal counter electrode, Entek PE membrane and electrolyte of 1 M LiPF₆ dissolved in a mixture of ethyl carbonate (EC) and dimethyl carbonate (DMC) (1:1 in weight ratio). The cells were assembled in an argon-filled glove box containing less than 1 ppm each of oxygen and moisture.

Charge and discharge of the coin cells were carried out at current densities of 0.08 mA cm⁻² (about 0.25 C) and 0.16 mA cm⁻² (about 0.5 C), respectively with voltage cut-off of 3.5/5.2 V versus Li/Li⁺. Cyclic voltammogram (CV) was obtained on two-electrode coin cell using CHI604B electrochemical workstation.

3. Results and discussion

The XRD patterns of LiNi_{0.5}Mn_{1.5}O₄ and LiNi_{0.5}Mn_{1.5}O_{3.975}F_{0.05} are shown in Fig. 1. Eight well-resolved peaks at 2 θ = 18.8°, 36.4°, 38.1°, 44.3°, 48.5°, 58.7°, 64.5° and 67.8° are indexed as (1 1 1), (3 1 1), (2 2 2), (4 0 0), (3 3 1), (5 1 1), (4 4 0) and (5 3 1) diffractions for the cubic spinel phase (JCPDS file 80–2184). Fig. 1(b) is the magnified part of Fig. 1(a) in the region of 2 θ = 37–44°. It is observed that the LiNi_{0.5}Mn_{1.5}O₄ sample exhibits not only strong responses for spinel phase but also weak responses for NiO phase, revealing the existence of NiO impurity. As reported in previous work, the low-crystalline and pure spinel LiNi_{0.5}Mn_{1.5}O₄ powders synthesized by a sol-gel method would decompose into the mixture of NiO and spinel phase when calcined above 600 °C [19]. In contrast, NiO peaks are hardly detectable for the fluorine-doped sample. The result indicates that fluorine doping does not change the spinel structure but suppresses the formation of NiO phase.

Fig. 2 exhibits the typical charge and discharge profiles of LiNi_{0.5}Mn_{1.5}O₄ and LiNi_{0.5}Mn_{1.5}O_{3.975}F_{0.05}. Both of them have a major 5 V region and a minor 4 V region. But the introduction of fluorine effectively increases the capacity from 131 to 142 mAh g⁻¹ and decreases the voltage polarization. The reason for the capacity enhancement may be, in part, due to the suppression of NiO impurity. The source of fluorine element is LiF and the slight excess of Li may also contribute to the capacity. It is, however, noticed that the capacity near 4 V is also increased,

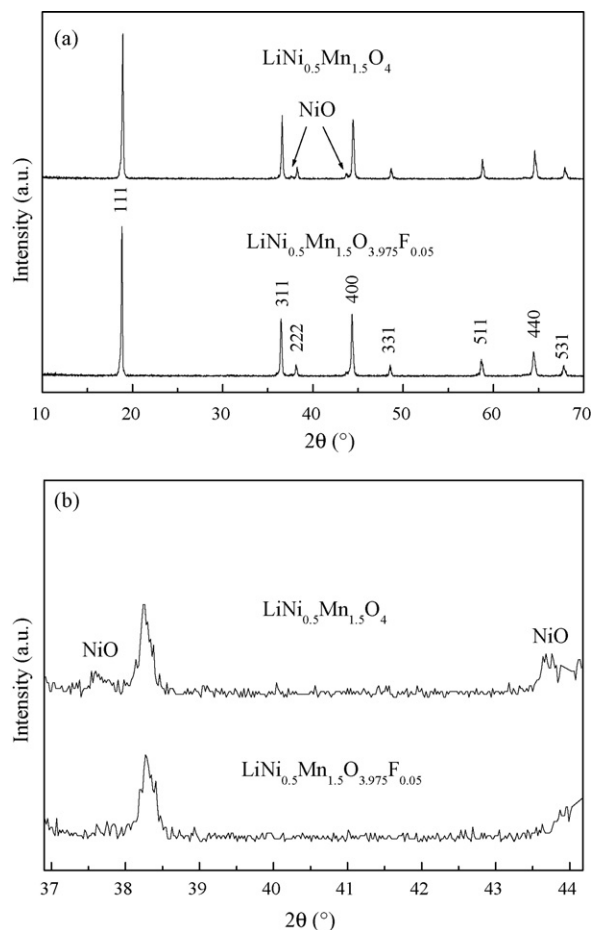


Fig. 1. The XRD patterns of LiNi_{0.5}Mn_{1.5}O₄ and LiNi_{0.5}Mn_{1.5}O_{3.975}F_{0.05} (a) and the partial magnification of (a) (b).

which means that more Mn³⁺ ions exist in the F-containing compound. Therefore, real oxygen content in the prepared samples is dependent on the ratio of Mn⁴⁺ to Mn³⁺.

To further increase the capacity near 5 V region, re-annealing treatment under oxygen flow has been examined. Fig. 3 clearly indicates that 4 V plateau is obviously suppressed and the 5 V capacity is increased comparatively when calcined

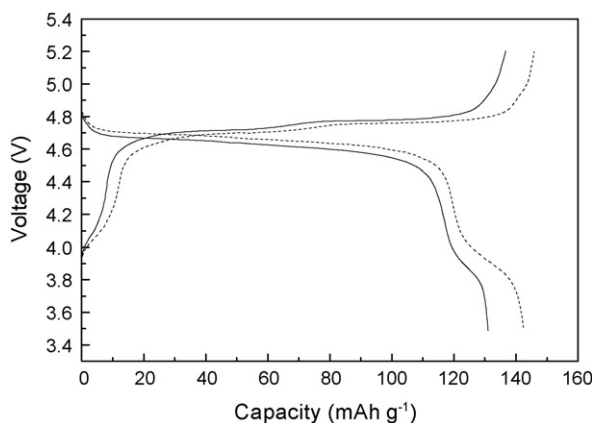


Fig. 2. Typical charge–discharge curves of LiNi_{0.5}Mn_{1.5}O₄ (solid line) and LiNi_{0.5}Mn_{1.5}O_{3.975}F_{0.05} (dash line).

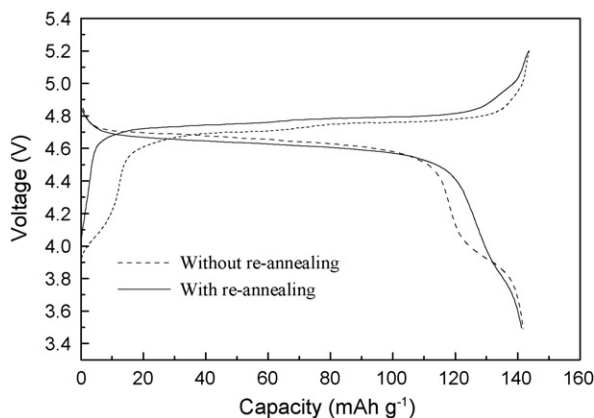


Fig. 3. Typical charge–discharge curves of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_{3.975}\text{F}_{0.05}$ with and without re-annealing.

$\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_{3.975}\text{F}_{0.05}$ sample is further annealed in pure oxygen. It means that more Mn^{3+} can be oxidized into Mn^{4+} at limited high temperature and under oxygen atmosphere.

Fig. 4 shows the cycling behavior of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_{3.975}\text{F}_{0.05}$ and re-annealed $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_{3.975}\text{F}_{0.05}$. Re-annealing treatment can enhance the capacity in the initial several cycles but cannot keep a higher capacity in the subsequent cycles. After electrochemical activation in the first cycle, the reversible capacity of the material without re-annealing can be increased and both the samples gradually provide a comparable capacity in the following cycles. In view of the fact that re-annealed material has smaller voltage polarization, it appears that re-annealing may improve the fine structure and Li-diffusion channels in the material, resulting in higher lithium utilization at the initial cycling stage. But the long-term cycling stability depends on the stability of the material structure and the interface between electrolyte and the electrode. The anti-oxidation ability of the electrolytes is a key factor. The 5 V spinel materials in this study demonstrate good rechargeability. About 95% capacity can be retained after 40 cycles for the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_{3.975}\text{F}_{0.05}$ electrode.

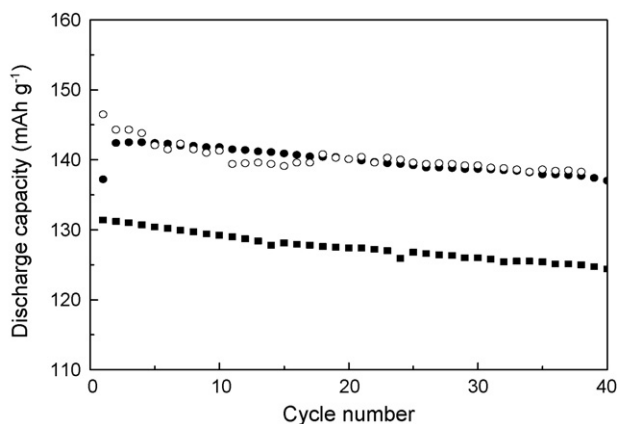


Fig. 4. Cycling performance of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (■), $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_{3.975}\text{F}_{0.05}$ (●) and re-annealed $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_{3.975}\text{F}_{0.05}$ (○).

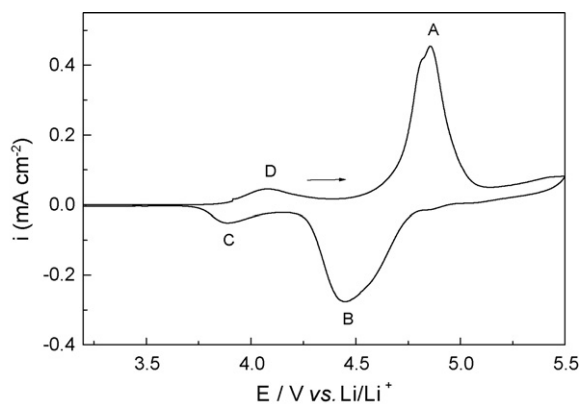


Fig. 5. Cyclic voltammogram of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_{3.975}\text{F}_{0.05}$ at a scan rate of 0.1 mV s^{-1} .

The cyclic voltammogram (CV) of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_{3.975}\text{F}_{0.05}$ at a scan rate of 0.1 mV s^{-1} is shown in Fig. 5. It presents pronounced anodic peak A and cathodic peak B in the 5 V domain, which are attributed to the valence variation of nickel. Although peak A is weaker and wider in comparison with peak B, their areas are almost equal, which indicates the reversible electrochemical behavior of the sample. The $\text{Mn}^{3+/4+}$ redox activity around 4 V is also detectable by peaks C and D.

4. Conclusions

The reversible capacity of 5 V $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathode material synthesized by sol–gel method can be obviously enhanced and the voltage polarization can be reduced by fluorine doping. The performance improvement is mainly related to suppression of NiO impurity phase. However, the fluorine doping will slightly increase 4 V discharge capacity arising from small amount of Mn^{3+} in the spinel structure. By followed re-annealing in pure oxygen, the 4 V plateau can be effectively restrained and 5 V capacity is increased accordingly. The fluorine-doped spinel material demonstrates good rechargeability. About 95% capacity can be retained after 40 cycles. $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_{3.975}\text{F}_{0.05}$ is a promising cathode material for high-voltage lithium batteries.

References

- [1] Y. Sun, Z. Wang, X. Huang, L. Chen, J. Power Sources 132 (2004) 161.
- [2] J.L. Tirado, Mater. Sci. Eng., R 1033 (2003) 40.
- [3] R. Alcántara, M. Jaraba, P. Lavela, J.L. Tirado, Electrochim. Acta 47 (2002) 1829.
- [4] Y.K. Sun, C.S. Yoon, I.H. Ch, Electrochim. Acta 48 (2003) 503.
- [5] J.C. Arrebola, A. Caballero, L. Hernan, J. Morales, Electrochem. Solid-State Lett. 8 (2005) A641.
- [6] H. Kawai, M. Nagata, H. Kageyama, H. Tukamoto, A.R. West, Electrochim. Acta 45 (1999) 315.
- [7] M.M. Thackeray, J. Electrochem. Soc. 144 (1995) L100.
- [8] Q. Zhong, A. Bonakdarpour, M. Zhang, Y. Gao, J.R. Dahn, J. Electrochem. Soc. 144 (1997) 205.
- [9] Y.S. Lee, Y.K. Sun, S. Ota, T. Miyashita, M. Yoshio, J. Electrochem. Commun. 4 (2002) 989.
- [10] Y. Talyosef, B. Markovsky, G. Salitra, D. Aurbach, H.J. Kim, S. Choi, J. Power Sources 146 (2005) 664.

- [11] A. Caballero, L. Hernan, M. Melero, J. Morales, M. Angulo, J. Electrochem. Soc. 152 (1) (2005) A6.
- [12] X. Wang, N. Iltchev, H. Nakamura, H. Noguchi, Electrochem. Solid-State Lett. 6 (2003) A99.
- [13] K. Hong, Y. Sun, J. Power Sources 109 (2002) 427.
- [14] H. Shigemura, H. Sakaebe, H. Kageyama, H. Kobayashi, A.R. West, J. Electrochem. Soc. 148 (2001) A730.
- [15] Y. Ein-Eli, W. Wen, S. Mukerjee, Electrochem. Solid-State Lett. 8 (2005) A141.
- [16] R. Alcántara, M. Jaraba, P. Lavela, J.L. Tirado, J. Electrochem. Soc. 151 (2004) A53.
- [17] J.H. Kim, C.S. Yoon, S.T. Myung, J. Parakash, Y.K. Sun, Electrochem. Solid-State Lett. 7 (2004) A216.
- [18] T.A. Arunkumar, A. Manthiram, Electrochem. Solid-State Lett. 8 (2005) A216.
- [19] B. León, J.M. Lloris, C.P. Vicente, J.L. Tirado, Electrochem. Solid-State Lett. 9 (2006) A96.