Electrochemical performance of
SrF$_2$-coated LiMn$_2$O$_4$ cathode material for Li-ion batteries

LI Jian-gang(李建刚)[1], HE Xiang-ming(何向明)[2], ZHAO Ru-song(赵如松)[1]

1. School of Chemical Engineering, Beijing Institute of Petrochemical Technology, Beijing 102617, China;
2. Institute of Nuclear and New Energy Technology, Tsinghua University, Beijing100084, China

Abstract: SrF$_2$-coated LiMn$_2$O$_4$ powders with excellent electrochemical performance were synthesized. The electrochemical performance of SrF$_2$-coated LiMn$_2$O$_4$ electrode was studied as function of the level of SrF$_2$ coating. With increasing the amount of the coated-SrF$_2$ to 2.0% (molar fraction), the discharge capacity of LiMn$_2$O$_4$ decreases slightly, but the cyclability of LiMn$_2$O$_4$ at elevated temperature is improved obviously. In view of discharge capacity and cyclability, the 2.0% (molar fraction) coated sample shows optimum cathodic behavior. When being cycled at 55 °C, as-prepared LiMn$_2$O$_4$ remains only 79% of its initial capacity after 88 cycles, whereas the 2.0% (molar fraction) coated sample shows initial discharge capacity of 106 mA·h/g, and 97% initial capacity retention.

Key words: lithium ion batteries; LiMn$_2$O$_4$; surface coating; SrF$_2$

1 Introduction

Spinel LiMn$_2$O$_4$, with economical and environmental advantages, is considered to be one of the most promising cathode materials for rechargeable lithium-ion batteries. Its drawbacks include the significant capacity fading during cycling at elevated temperature due to several probabilities, e.g., manganese dissolution[1−2], Jahn-Teller distortion[3] and electrolyte decomposition[4]. Partial replacement of Mn in LiMn$_2$O$_4$ by some low valence metal ions such as Li$^+$, Ni^{2+}, Co^{3+}, Al^{3+} and Cr^{3+}[5−9] can effectively enhance its cyclability. On the other hand, another appropriate method to reduce capacity fade of LiMn$_2$O$_4$ is surface coating of the spinel to avoid Mn dissolution. Most oxides, such as lithium boron oxide glass (LBO)[10], SiO$_2$[11], ZnO[12], ZrO$_2$[13], Al$_2$O$_3$[14] and P$_2$O$_5$[15], have been reported to be very interesting materials for this purpose. The coated metal oxides are insoluble in water, but cannot readily stable stoichiometry reduce the corrosion of HF. Recently, SUN et al[16] reported the surface modification of LiCoO$_2$ by AlF$_3$. The AlF$_3$ coating layer could reduce the formation of LiF films

that increase cathode/electrolyte interfacial impedance and also suppress Co dissolution by covering LiCoO$_2$ surface from HF attack, therefore improving the capacity retention of LiCoO$_2$ at 4.5 V cut-off cycling.

It is very necessary to study the effects of fluoride-coating on the cyclability of LiMn$_2$O$_4$. To our best knowledge, there are still no literatures on this issue. In this study, SrF$_2$ that is insoluble in HF was investigated to be used as coating material of LiMn$_2$O$_4$. Herein, the effects of coated-SrF$_2$ amount on the structural and electrochemical properties were discussed.

2 Experimental

LiMn$_2$O$_4$ sample was first prepared by annealing the well-ground mixture of stoichiometric EMO and Li$_2$CO$_3$ at 800 °C in air for 20 h. For preparing the SrF$_2$-coated LiMn$_2$O$_4$ cathode material, the prepared LiMn$_2$O$_4$ powders were suspended in the Sr(NO$_3$)$_2$ solution, and then NH$_4$F solution was dropped slowly into the suspended solution. After being stirred for 2 h, the coated LiMn$_2$O$_4$ powders were filtrated and heated under N$_2$ for 5 h. The heat treatment temperature was 300, 400, 500, 600 and 700 °C, respectively. The amount of coated SrF$_2$

corresponds to 0.5%, 1.0%, 2.0% and 4.0% (molar fraction) of the LiMn$_2$O$_4$ powders. Powder X-ray diffraction (XRD7000) was used to characterize the structure of the powders. Particle morphology of the powders was observed using a scanning electron microscope (HITCHI-s3500). The electrochemical characterization was performed using CR2032 coin-type test cells. The cell consisted of a cathode with the composition of 88% coated or uncoated LiMn$_2$O$_4$, 6% carbon black, and 6% PVDF (mass fraction), a lithium metal anode separated by a Celgard 2400 microporous film. The electrolyte was 1.15 mol/L LiPF$_6$/EC+DMC+DEC (3:3:1 in volume ratio). The charge-discharge tests were galvanostatically performed over 3.3–4.3 V at different current densities. AC-impedance measurements were performed using a CHI660B impedance analyzer over the frequency range from 100 kHz to 1 mHz with the amplitude of 10 mV.

3 Results and discussion

3.1 Structural variation after SrF$_2$-coating

XRD patterns of the 4.0% SrF$_2$-coated LiMn$_2$O$_4$ sample heat-treated at 300, 400, 500, 600 and 700 °C respectively for 5 h under N$_2$ are shown in Fig.1. It is obvious that all samples show main peaks attributed to well-defined spinel phase and small amount of SrF$_2$ peaks as impurity. The SrF$_2$ peaks become sharp with increasing the heat-treated temperature from 300 to 700 °C. This indicates that the coated SrF$_2$ exists as a separate phase, and SrF$_2$ crystallization states enhances with increasing heat-treated temperature. The crystal lattice constants of the coated samples, as listed in Table 1, clearly reveal that the values remain almost unchanged at 300–500 °C and decrease obviously over 600 °C. This indicates a possible surface reaction between SrF$_2$ and
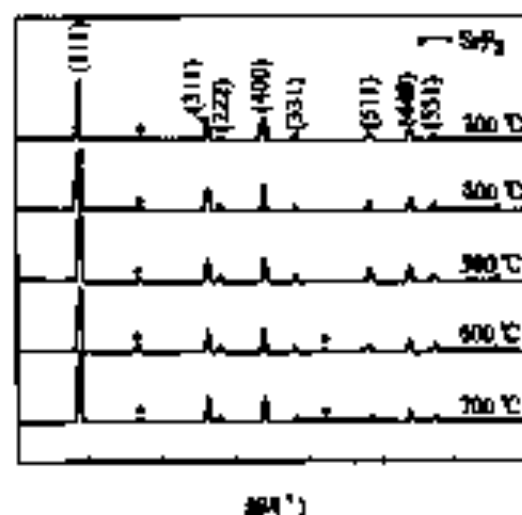
Heat-treated temperature/°C	a/nm
300	0.822 99
400	0.823 03
500	0.823 09
600	0.822 47
700	0.822 31

LiMn$_2$O$_4$ during firing over 600 °C, which may result in the formation of a thin LiMn$_{2-x}$Sr$_x$O$_{4-y}$F$_y$ solid-solution layer. In order to avoid the reaction between SrF$_2$ and LiMn$_2$O$_4$, the heat-treated temperature of the following studied SrF$_2$-coated LiMn$_2$O$_4$ samples are selected to be 400 °C.

XRD patterns of 0, 0.5%, 1.0%, 2.0% and 4.0% SrF$_2$-coated LiMn$_2$O$_4$ samples are shown in Fig.2. The SrF$_2$ peaks can be detected when the coated SrF$_2$ amounts are up to 2.0%, and become stronger with increasing the coated SrF$_2$ amounts to 4.0%. However, the lattice parameters of LiMn$_2$O$_4$ show no detectable changes before and after coating, supporting the postulate that SrF$_2$ exists as a separate phase on the LiMn$_2$O$_4$ particle surface.
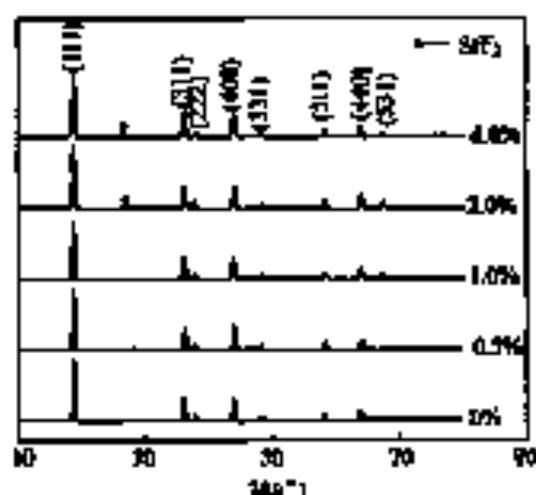

Fig.2 XRD patterns of SrF$_2$-coated LiMn$_2$O$_4$ samples

3.2 Morphology of SrF$_2$-coated LiMn$_2$O$_4$

Fig.3 shows SEM micrograph and EAX(energy dispersed X-ray analysis) image of 2.0% SrF$_2$-coated LiMn$_2$O$_4$. The powders are agglomerated, consisting of many small crystal particles. As can be seen in EP44A image, the distribution of Sr on the powder is fairly uniform.

3.3 Electrochemical characteristics of SrF$_2$-coated LiMn$_2$O$_4$

Fig.4 shows charge-discharge curves for the as-prepared LiMn$_2$O$_4$ and various amounts of SrF$_2$-coated

Fig.1 XRD patterns of 4.0% SrF$_2$-coated LiMn$_2$O$_4$ samples

(a)

SE   31-May-06   WD10.7mm   2μm

(b)
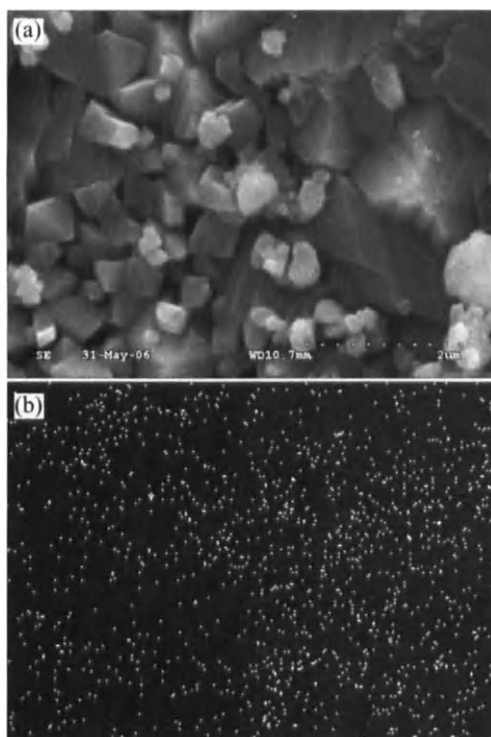
Fig.3 Scanning electron micrograph of 2.0% SrF₂-coated LiMn₂O₄ (a) and Sr-distribution map obtained by energy dispersed X-ray analysis (b)

φ(vs Li/Li⁺)/V

4.4
4.0
3.6
3.2
2.8

1 — 0%
2 — 0.5%
3 — 1.0%
4 — 2.0%
5 — 4.0%

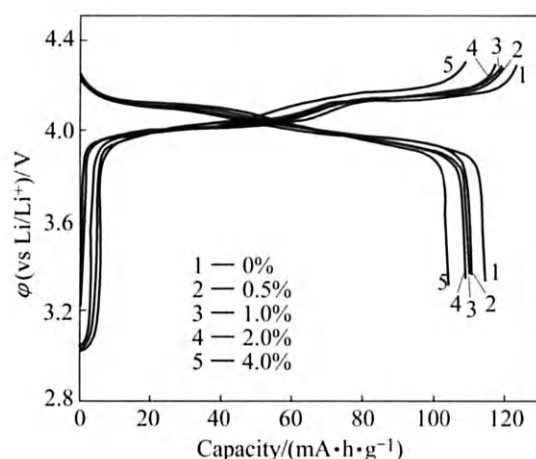0   20   40   60   80   100   120
Capacity/(mA·h·g⁻¹)

Fig.4 Charge-discharge curves of SrF₂-coated LiMn₂O₄ samples

LiMn₂O₄ at room temperature. The as-prepared LiMn₂O₄ shows discharge capacity of 114.4 mA·h/g, which is very close to the data reported in Refs[11–15]. Compared with the base one, the SrF₂-coated LiMn₂O₄ samples show lower capacity. The discharge capacity decreases slightly with increasing amount of SrF₂ coating to 2%, but comes remarkably to 104.4 mA·h/g with increasing amount of the SrF₂ coating to 4%. With increasing amount of the SrF₂ coating, the polarization (voltage difference between the charge and the discharge curves) enhances. Because the SrF₂ coating is inactive, it

can be speculated that the coating may increase the contact resistance between inter-particles and the charge-transfer resistance, leading to the decrease of the capacity. The supposition can be confirmed by the EIS spectra of the as-prepared LiMn₂O₄ and various amounts of SrF₂-coated LiMn₂O₄, as shown in Fig.5.
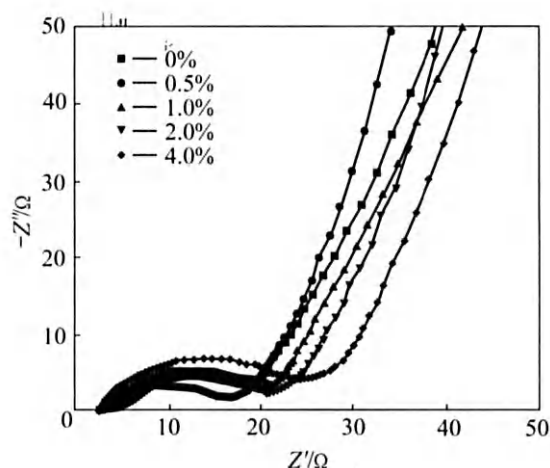
−Z″/Ω

50
40
30
20
10
0

— 0%
— 0.5%
— 1.0%
— 2.0%
— 4.0%

0   10   20   30   40   50
Z′/Ω

Fig.5 EIS spectra of SrF₂-coated LiMn₂O₄ samples

The cyclability of the spinels was tested at 55 °C, using a voltage window of 3.3–4.3 V and a current density of 110 mA/g. The resulting data are plotted in Fig.6. When being charge-discharged for 20 cycles at 55 °C, the as-prepared LiMn₂O₄ sample shows very fast capacity fading, and only 79% of its initial capacity remains. With increase of the amount of the coated SrF₂ from 0% to 2.0%, the discharge capacity of LiMn₂O₄ decreases slightly, but the cyclability of LiMn₂O₄ is improved obviously. As mentioned in other papers, surface coating of LiMn₂O₄ by some noble substances, e.g. SiO₂[11], ZrO₂[13] and Al₂O₃[14], can prevent the direct contact between LiMn₂O₄ particles and electrolyte, and hence lessen the possibility of spinel dissolution and electrolyte decomposition that are the major cause of capacity loss. The AlF₃ coating layer of LiCoO₂ also have been reported to reduce the formation of LiF films that increase the cathode/electrolyte interfacial impedance and also suppress Co dissolution by covering LiCoO₂ surface from HF attack[16]. SrF₂ is very stable even in HF, so it can be speculated that the surface coating of LiMn₂O₄ by SrF₂ can improve the cyclability of LiMn₂O₄ cathode due to the same reason. 2.0% coated sample exhibits the best electrochemical performance. This shows initial discharge capacity of 108 mA·h/g, and 97% initial capacity retention after 20 cycles. Although 4.0% coated sample also shows very good cyclability, its lower capacity is sacrificed due to higher impedance resulted from too much coated SrF₂. The 2.0% coated sample shows optimum cathodic behaviors in view of discharge capacity and cyclability.
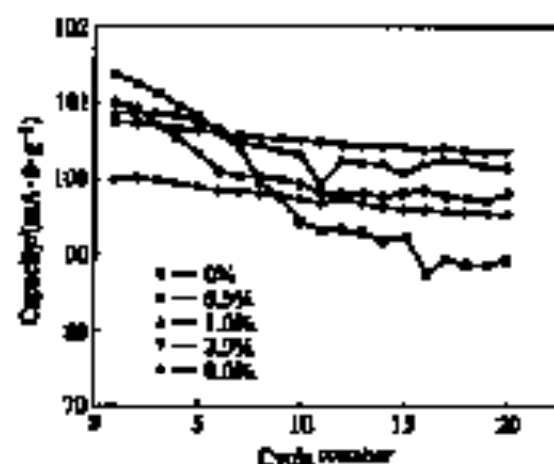
Fig.6 Cyclability of SrF₂-coated LiMn₂O₄ samples at 55 °C

4 Conclusions

1) SrF₂ is coated uniformly on the surface of LiMn₂O₄ particles by using chemical deposition, followed by heat-treatment at 400 °C.

2) Significant improvement of the electrochemical performance of LiMn₂O₄ is achieved by coating SrF₂. With increasing the amount of the coated SrF₂, the discharge capacity of LiMn₂O₄ decreases slightly, but the cyclability of LiMn₂O₄ at elevated temperature is improved obviously.

3) In view of discharge capacity and cyclability the 2.0% coated sample shows optimum cathodic behaviors. It shows initial discharge capacity of 101 mA·h/g, and 97% initial capacity retention after 20 cycles at 55 °C.

4) The SrF₂ coating is favorable to improving the cyclability of LiMn₂O₄ at elevated temperature.

References

[1] XIA Yong-yao, ZHOU Yun-hong, YOSHIO M J. Capacity fading on cycling of 4V Li/LiMn₂O₄ cells [J]. J Electrochem Soc, 1997, 144(8): 2593–2600.

[2] JANG D H, SHIN Y J, OH S M. Dissolution of spinel oxides and capacity losses in 4V Li/LiMn₂O₄ cells [J]. J Electrochem Soc, 1996, 143(7): 2204–2211.

[3] TARASCON J M, MCKINNON W R, COOWAR F, BOWMER T N, AMATUCCI G, GUYOMARD D. Synthesis conditions and oxygen stoichiometry effects on Li insertion into the cubic LiMn₂O₄ [J]. J Electrochem Soc, 1994, 141(5): 1421–1431.

[4] ARORA P, WHITE R. Capacity fade mechanisms and side reactions in Li-ion batteries [J]. J Electrochem Soc, 1998, 145(10): 3647–3667.

[5] TARASCON J M, WANG E, SHOKOOHI F K, MCKINNON W R, COLSON S. The spinel phase of LiMn₂O₄ as a cathode in secondary lithium cells [J]. J Electrochem Soc, 1991, 138(10): 2859–2864.

[6] ROBERTSON A D, LU S H, AVERILL W F, HOWARD J W³⁺ substituted LiMn₂O₄ spinel intercalation cathodes (I): Admetal effects on morphology and electrochemical performance [J]. J Electrochem Soc, 1997, 144(10): 3500–3505.

[7] ARORA P, POPOV B M, WHITE R E. Electrochemical investigations of cobalt-doped LiMn₂O₄ as cathode material for lithium-ion batteries [J]. J Electrochem Soc, 1998, 145(3): 807–814.

[8] LI Guohua, IKUTA H, UCHIDA T, WAKIHARA M. The spinel phases LiM₄Mn₂₋₄O₄ (M=Co, Cr, Ni) as the cathode for rechargeable lithium batteries [J]. J Electrochem Soc, 1996, 143(1): 178–182.

[9] HUANG G, POPOV B M, WHITE R E. Electrochemical investigation of CdO₂-doped LiMn₂O₄ as cathode material for lithium-ion batteries [J]. J Power Sources, 1998, 76(1): 81–90.

[10] CHAN B M, HUR J G, SEFON S L. Microstructure and electrochemical properties of LiBO₂-coated layered Li₁.₀₅Ni₀.₅ cathode material at elevated temperature for Li-ion battery [J]. Electrochimica Acta, 2006, 51(18): 3649–3655.

[11] ZHANG Zi-chen, TANG Zi-long, ZHANG Zong-tah, CHEN Wen-shi, LIU Yu-hua. Surface modification of Li₁.₀₅Mn₁.₉₅O₄ spinel as improved capacity retention [J]. Int J Econ Series, 2002, 16(49/50): 317–321.

[12] SUN Y K, HONG K J, PRAKASH J. The effect of ZnO coating on electrochemical cycling behavior of spinel LiMn₂O₄ cathode materials at elevated temperature [J]. J Electrochem Soc, 2001, 148(7): A576–A579.

[13] THACKERAY M M, JOHNSON C S, KIM J S, LAUZZE K C, VAUGHEY J T, DIETZ N, ABRAHAM D, BAKER S A, KOLTYPIN M, ANDERSON M A. ZrO₂- and Li₂ZrO₃-stabilized spinel and layered electrodes for lithium batteries [J]. Electrochem Commun, 2003, 5: 752–758.

[14] LEE J W, KIM K S, NAHM S S. Electrochemical characteristics of Al₂O₃-coated lithium manganese spinel as a cathode material for a lithium secondary battery [J]. J Power Sources, 2004, 132(1/2): 145–151.

[15] YU Li-hong, QIU Xinping, XI Jingyan, ZHU Wentao, CHEN Liquan. Enhanced high-potential and elevated-temperature cycling stability of LiMn₂O₄ cathode by TiO₂ modification for Li-ion battery [J]. Electrochimica Acta, 2006, 51(18): 6406–6411.

[16] SON J T, PARK J H, MYUNG S T. High-current superior electrode of SrF₂-coated LiCoO₂ cathode [J]. Electrochem Commun, 2004, 6: 681–684.

　　　　　　　　　　　　　　　(Edited by YANG Bing)