Electrochemistry Performance for the Multiple Doping Spinel of Li-Mn-O at Elevated Temperature*

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Abstract: The effect of doping on the electrochemical performance of modified spinel Li-Mn-O, which is used as cathode material in Lithium-ion battery, was studied. The spinel materials $Li_{1.02}M_xMn_{2-x}Q_yO_{4-y}$ (M = Co, Cr, La; $x = a + b + c$; Q = Cl, F;) doped with several ions was prepared by solid-state method after the pretreatment of conversion under low temperature, at elevated temperature. X-ray diffraction showed that all the samples have perfect spinel structure. The results of measurement by SEM indicated that the particles of the samples had uniform size and were distributed evenly. The results of the charge-discharge curves showed that $Li_{1.02}M_xMn_{2-x}F_yO_{4-y}$ and $Li_{1.02}M_xMn_{2-x}Cl_yO_{4-y}$ had better performance than those un-doped or single-element doped materials according to the inhibition of decline of reversible capacity of spinel Li-Mn-O material. Therefore, cycle performance had been improved so obviously that 94.5% of the initial capacity was preserved respectively after 80 cycles, and that 91.5% (102.1 (mA·h)/g) of the initial capacity was preserved respectively after 40 cycles at elevated temperature (at 55 ℃). As cathode material of lithium-ion battery, this multiple doping spinel is one of the most competitive substitutes for $LiCoO_2$.

Key words: lithium-ion battery; multiple doped spinel; cathode material; electrochemical characterization of elevated temperature
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1 Introduction

The lithium-ion battery industry is undergoing expansion rapidly now, representing the largest business of the portable battery industry, for example: mobile telephone, hand computer, and camera power source, etc.[1-3]. However, the present secondary battteries use expensive components ($LiCoO_2$, for example), which are not in sufficient supply to allow the industry to grow at the same rate in the future.

In accordance with the economic and environmental advantages, there is no question that spinel $LiMn_2O_4$ will be used as a cathode material of the lithium-ion batteries instead of $LiCoO_2$, which has been commercialized currently. Now, one of the most important difficulties is to solve the problem of capacity fading on cycling at the elevated temperature. The major factors responsible for the capacity loss at the elevated temperature are ascribed to follows: ① the stable structure defect of spinel $LiMn_2O_4$; ②the slow dissolution of the $LiMn_2O_4$ electrode into electrolyte solution by reason of the disproportion reaction: $2Mn^{3+} \rightarrow Mn^{4+} + Mn^{2+}$; ③ the Jahn-Teller effect; and ④the electrochemical oxidation of the electrolyte at high-voltage.

It is indeed that all above the proposed mechanism are mainly associated with the crystal structure or configurations of $LiMn_2O_4$ materials[4-5]. Therefore, numerous researches have been devoted to these directions[1-5]. Amatucci et al[6] have done many works in order to improve the elevated temperature performance by minimizing the $LiMn_2O_4$/electrolyte interface, which is included directly preparing spinel with small surface, partially substituting Mn with fluorine, and coating spinel with $Li_2O-B_2O_3$. Accordingly, there are two plans to improve the elevated temperature performance, one of these mathods of stabilizing its structure is doping the foreign metal ions[7], these introduce ion includes Li^+, Co^{3+}, Cr^{3+}, Ni^{2+}, La^{3+}, Al^{3+}, F^-, Cl^-, Mg^{2+}, and Ga^{2+}, etc. The other way is coating spinel with Al_2O_3, B_2O_3, SiO_2, etc[6,8,9]. For example, Cr-doping and Li-doping spinel showed the greater improvement in the capacity rention at room temperature, however, showing an increase in capacity fade rate on cycling at 50 ℃, relative to room

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temperature[1,7]. In this paper, the multiple doping spinel $Li_{1.02}M_xMn_{2-x}F_yO_{4-y}$ (M = Co, Cr, La; $x = a+b+c$; $Q = Cl$, F;) had been studied. For example, the elevated temperature performance, and the mechanism responsible for improvement performance compared to the spinel $Li_{1.02}Mn_2O_4$ by means of X-ray diffraction (XRD), scanning electron microscopy (SEM), as well as chemical analysis.

2 Experiment

The spinel $Li_{1.02}Mn_2O_4$ was obtained from the reaction of a mixture of $LiOH \cdot H_2O$ and Mn_3O_4 (Li/Mn = 0.51 in molar ratio). The mixture was preheated at 450 ~ 480 ℃ for 12 ~ 24 hours, and a final heating at 750 ~ 780 ℃ for 48 hour in air, then cooled to room temperature in free. The multiple doping spinel $Li_{1.02}M_xMn_{2-x}F_yO_{4-y}$ was obtained by the same process, and Cr, Co, La, F, Cl and Al source used Cr_2O_3, Co_2O_3, La_2O_3, LiF, LiCl and Al_2O_3.

The chemical composition of each samples was determined by chemical analysis. The structure of the each compound was determined by X-ray diffraction, with Cu Kα radiation on a Rigaku 2500 X-ray diffractometer (Rigaku Ltd., Japan), under the condition of 40 kV, 100 mA, 8°/min and 5 ℃ ~ 80 ℃. The scanning electron microscopy (SEM) picture was taken in a JSM-6360 LV Scanning Electron Microscope (JEOL, Japan Electron Ltd).

The room temperature (25 ℃) cycling performance and elevated temperature (55 ℃) cycling performance of each samples were tested by Lithium-ion Battery Automatic Testing System (PCBT-138-32D-A, WUHAN LIXING POWER SOURCES CO., LTD.) in a CR2032 — type button cell, which consists in some $Li_{1.02}Mn_2O_4$ or $Li_{1.02}M_xMn_{2-x}O_4$ powders (active materials, 85% in weight) and conducting binder (acetylene black-polytetrafluoroethylene composite, 2: 1), then followed by immersing in 1 M $LiPF_6$-ethylene carbonate (EC) /diethyl carbonate (DEC) /dimethyl carbonate (DMC) (1: 1: 1 in volume, Korea) electrolyte solution. The anode used metal Li. Celgard 2400 (USA) microporous polypropylene files used as separators. The Li/$Li_{1.02}Mn_2O_4$ (or $Li_{1.02}M_xMn_{2-x}F_yO_{4-y}$) cells were cycled between the voltages limits of 3.0 and 4.3 V, the typical charge/discharge current sate was C/5 (30 mA/g), except where otherwise specified.

3 Results and discussion

The X-ray diffraction patterns of $Li_{1.02}Mn_2O_4$, $Li_{1.02}M_xMn_{2-x}F_yO_{4-y}$ are shown in Fig. 1. XRD patterns reveals that no additional peaks resulted from Li_2MnO_3 and defect spinel was observed, and showed that all the samples have perfect spinel structure. $Li_{1.02}Mn_2O_4$ and $Li_{1.02}M_xMn_{2-x}F_yO_{4-y}$ still kept its sharp peak. Nevertheless, the intensity were decreased with the increase of number of the doped element. The constants of crystal lattice are also be decreased (from 0.8242nm/$Li_{1.02}Mn_2O_4$ to 0.8231nm/$Li_{1.02}M_xMn_{2-x}F_yO_{4-y}$). The volume of the crystal lattice had been constricted (from 0.5599nm^3/$Li_{1.02}Mn_2O_4$ to 0.5576nm^3/$Li_{1.02}M_xMn_{2-x}F_yO_{4-y}$). It has been well recognized that the stability of spinel can be improved by the addition of various metal or nonmetal ions (multiple doped). These modifiers (metal ions) substitute for Mn^{3+} occupying the 16 d octahedral sites in the spinel framework, thus stabilize the structure, thereby allowing a homogenous lithium insertion and extraction over the entire 4 V intercalated region.

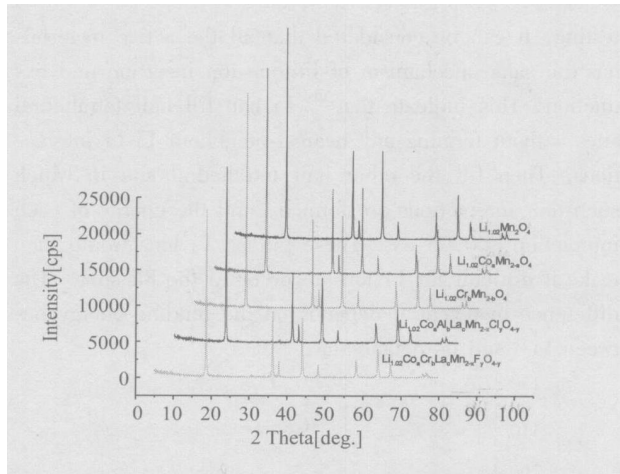

Fig 1　XRD Patterns of $Li_{1.02}M_xMn_{2-x}F_yO_{4-y}$

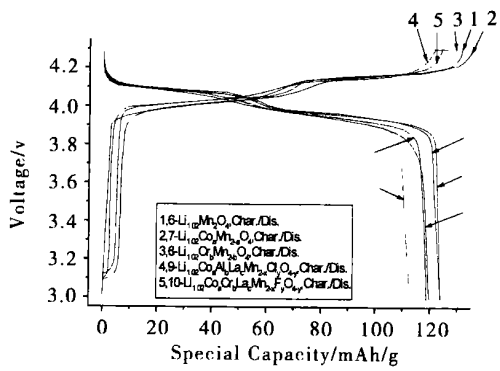

Fig 2　Charge/Discharge curves of the first cycle

The initial charge/discharge curves for these active materials are shown in Fig. 2. The Li-doped spinel $Li_{1.02}Mn_2O_4$ and Li, Co-doped spinel $Li_{1.02}CoaMn_{2-a}O4$ are higher initial discharge capacity (~ 123.5mAh/g), and multiple doped spinel $Li_{1.02}M_xMn_{2-x}F_yO_{4-y}$ have lower initial discharge capacity (~ 112.2mA·h/g and ~ 118.1mA·h/g), at room temperature (25 ℃). All the initial charge/discharge curves are similar in the process of

testing. It can be considered that all the active materials has the same mechanism of lithium-ion insertion and extraction. This indicate that[10] Li can fill half tetrahedral sites without forming any nearest-neighbour Li-Li interactions. Then fill the other half tetrahedral site in which such four interactions are formed, and the energy of each interaction is 0.05 eV. These pinned Li ions would then make it difficult for Li ions to order in the 8a sites. The difference in potential depends on the binding energy between Li^+ and its neighbours.

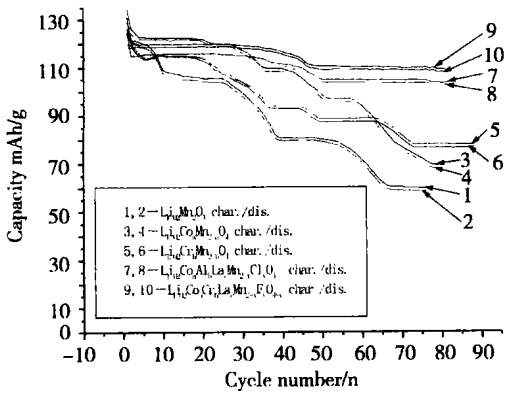

Fig 3 The cycle performance of spinel $Li_{1.02}M_xMn_{2-x}F_yO_{4-y}$ at room temperature

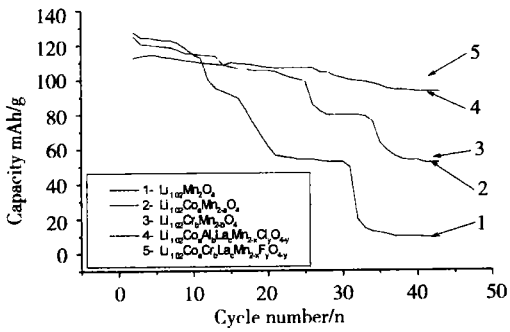

Fig 4 The cycle performance of spinel $Li_{1.02}M_xMn_{2-x}F_yO_{4-y}$ at elevated temperature

The electrochemical cycling behaviors (room temperature, 25 ℃) of avtive materials, lithium—rich spinel $Li_{1.02}Mn_2O_4$ and multiple doped spinel $Li_{1.02}M_xMn_{2-x}F_yO_{4-y}$ are shown in Fig. 3. The results of these curves showed that synthetic materials $Li_{1.02}M_xMn_{2-x}F_yO_{4-y}$ and $Li_{1.02}M_xMn_{2-x}Cl_yO_{4-y}$ had better performance than those only rich-lithium doped and single-element (Co or Cr) doped materialsaccording to the inhibition of decline of reversible capacity of spinel Li-Mn-O material. Therefore, cycle performance had been improved so obviously that 94.5% of the initial capacity was preserved respectively after 80 cycles. The elevated temperature performance of the multiple doping spinel has been obviously improved (Fig. 4), especially the sample of $Li_{1.02}Co_aCr_bLacMn_{2-a-b-c}F_yO_{4-y}$ (curves 5), at 55 ℃. That 91.5% (102.1mA·h/g) of the initial capacity (111.6mA·h/g) was preserved respectively after 40 cycles at elevated temperature (55 ℃). Commonly, the initial capacity can be estimated for the compound $LiM_xMn_{2-x}O_4$ by the following formula[10]: $C=148(1-(4-Z)X)$, where Z is the valance of the doped-ion, and X is the molar fraction of the dopant. For the same doped-level, of course, M^{3+} shows much higher initial capacity. The improvement of cycle number could be ascribed to that either lithium and metal ions presented in the 16*d* octahedral sites to stabilize the structure, thereby allowing a homogenous lithium insertion and extraction over the entire 4 V intercalated region, and to reduce the dissolution of Mn^{2+} into the electrolyte.

According to the XRD, all samples are single-phase spinel as determined, and are indexed to a cubic spinel, and space group $Fd3m$. The doped metal ions (M^{3+}) substitute for Mn^{3+} occupying the 16*d* octahedral sites in the spinel framework, and stabilize the spinel structure. The doped nonmetal ions (F^- or Cl^-) substitute for O^{2-} combining with Mn^{3+} and M^{3+} to form stronger chemical bond than un-doped spinel. SEM indicated that the particles of the samples had uniform size (Fig. 5) and were

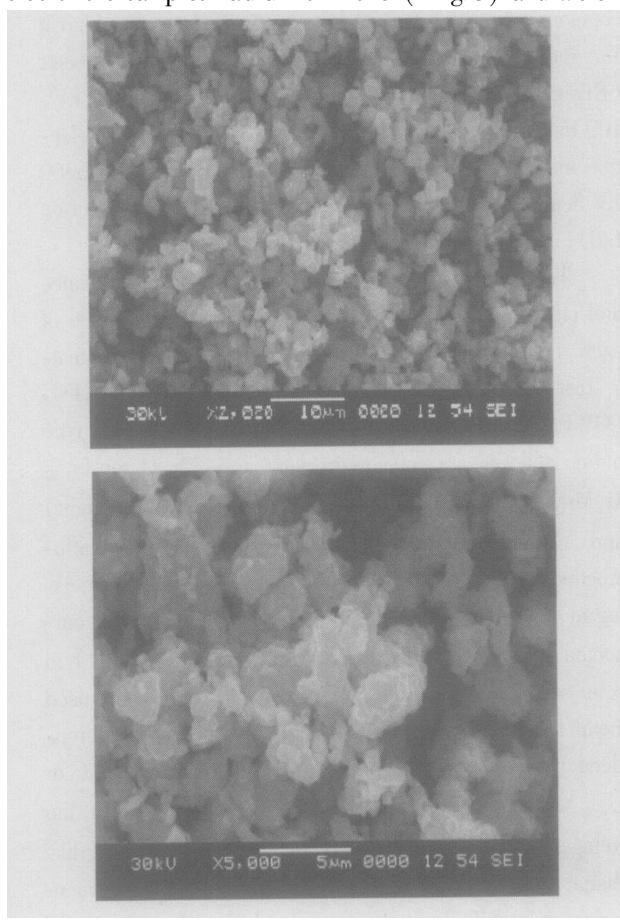

Fig 5 SEM pictures of sample $Li_{1.02}Co_aCr_bLacMn_{2-a-b-c}F_yO_{4-y}$

distributed evenly. We speculate that the better cycling performance at elevated temperature rest with the stable

one-phase structure, and the stabilization of spinel structure rest with the bond force between O and Mn. It is very beneficial for spinel structure that multiple ions were doped in samples. Yoshio, et al[10] demonstrated that the major factors responsible for the capacity loss at the elevated temperature are ascribed to follows: ① the transformation of unstable two-phase on the high-voltage region to a more stable one-phase structure, accompanying by the loss of MnO; ② direct dissolution of Mn_2O_3 in the electrolyte solution; and ③ the decomposition of electrolyte solution on the electrode. Those works suggested that the single—phase reaction is still a major factor, but not only factor to affect the elevated performance. In other world, the spinel having an excellent elevated temperature performance must show a one—phase insertion/extraction.

4 Conclusion

The spinel material $Li_{1.02}M_xMn_{2-x}F_yO_{4-y}$ doped with several ions was prepared by solid-state method. XRD and SEM showed that the samples have perfect spinel structure and uniform size and were distributed evenly. The charge/discharge test and X-ray diffraction measurement indicate that the multiple ions doping of Co^{3+}, Cr^{3+}, La^{3+}, Al^{3+}, F^- or Cl^- significantly improved the structure stability and cycling performance of sample at the elevated temperature. As cathode material of lithium-ion battery, this multiple doping spinel is one of the most competitive substitutes for $LiCoO_2$.

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尖晶石型 Li-Mn-O 多元素掺杂的高温电化学特性

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摘　要：采用高温固相浸渍法合成了多元复合掺杂尖晶石型锰酸锂 $Li_{1.02}M_xMn_{2-x}Q_yO_{4-y}$ 正极材料。XRD 表征合成的产物均为良好的尖晶石型结构材料；SEM 表明所合成的产物颗粒均匀且有良好的粒径分布。以该物质作为锂离子电池的正极材料组装成扣式电池，经充放电循环测试可知：多元素掺杂的尖晶石型锰酸锂正极材料 $Li_{1.02}Co_aCr_bLa_cMn_{2-a-b-c}F_yO_{4-y}$ 较富锂尖晶石和单元素 Co、Cr 掺杂的正极材料能够更好地抑制电池的可逆容量在充放电过程中的衰减，循环性能有了很大改善，表现出很好的电化学可逆特性，80 次循环后放电容量仍能保持 94.5%以上；特别是高温 (55 ℃) 性能更加突出，40 次循环后放电容量仍能保持 102.1mA h/g (91.5%) 以上。作为锂离子电池的正极材料，该复合掺杂材料是众多取代钴酸锂材料中最具竞争力的材料之一，也有望成为锂离子动力电池的正极材料。

关键词：锂离子电池；多元掺杂；正极材料；高温电化学性能

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