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Effect of Cr doping on structure of $LiMnO_2$ ①

GU Yi-jie(谷亦杰), ZHOU Heng-hui(周恒辉), CHEN Ji-tao(陈继涛), CHANG Wen-bao(常文保)
(College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China)

Abstract: The monoclinic and orthorhombic ordered-rocksalt polymorphs of $LiMnO_2$ are of interest as high-capacity cathode materials for rechargeable Li batteries. $LiMnO_2$ and $LiMn_{1-x}Cr_xO_2$ were prepared by a high temperature solid-state route. In comparison with undoping Cr orthorhombic $LiMnO_2$, monoclinic $LiMnO_2$ was preserved with Cr doping. The volume of m-$LiMnO_2$ decreasing with increasing Cr confirms that the length of bond around Cr ion decreases with Mn substituted by Cr ion. A phase transformation mechanism was proposed for understanding the structure relationship between the $LiMnO_2$ and chromium-substituted $LiMnO_2$ oxides.

Key words: $LiMnO_2$; Cr doping; phase transformation mechanism

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1 INTRODUCTION

The layered $LiCoO_2$ compound has been successfully commercialized because of its high energy density and its excellent stability with respect to extended electrochemical cycling. However, from the economic and environmental point of view, cheaper, lesser toxic and safer intercalation materials than $LiCoO_2$ compound are required. $LiMnO_2$ compounds are of interest as intercalation cathodes for rechargeable Li batteries due to their high theoretical capacity (285 mAh/g), low cost and nontoxicity.

Orthorhombic $LiMnO_2$(o-$LiMnO_2$, of space group Pmnm) has an ordered-rocksalt structure in which LiO_6 and MnO_6 octahedra are each arranged in corrugated layers. Monoclinic $LiMnO_2$(m-$LiMnO_2$, space group C2/m) has the cation ordering of α-$NaFeO_2$ structure type, in which the Li ions are located in the octahedral sites between MnO_6 sheets (Fig. 1). In both polymorphs of $LiMnO_2$, the oxygen array is distorted from ideal cubic-close-packing by the cooperative Jahn-Teller distortion due to high-spin Mn^{3+} ($t_{2g}^3 e_g^1$)[1,2]. It has been shown that the monoclinic structure can be stabilized by Al-doping under certain conditions where neither of the end-member is stable in that structure[3]. A recent study on layered $LiMn_{1-x}$-Co_xO_2 oxides reported that the partial substitution of manganese with cobalt induces a structural modification from monoclinic to rhombohedral[4]. Although $LiMnO_2$ doping Cr have been studied[5-7], to our knowledge the structure relationship between the $LiMnO_2$ and chromium-substituted Li-MnO_2 oxides has not been reported. In this work, the $LiMnO_2$ and chromium-substituted $LiMnO_2$ oxides are prepared and their structure property is characterized by using X-ray diffraction. The structure relationship between $LiMnO_2$ and chromium-substituted $LiMnO_2$ oxides was studied and a phase transformation mechanism between m-$LiMnO_2$ and o-$LiMnO_2$ was proposed.

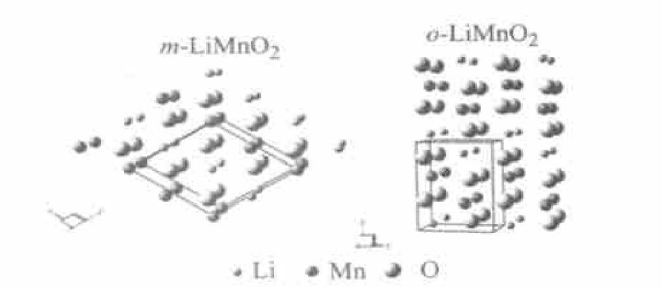

Fig. 1 Structure of m-$LiMnO_2$ and o-$LiMnO_2$

2 EXPERIMENTAL

The synthesis of the $LiMnO_2$ and chromium-substituted $LiMnO_2$ oxides was performed by mixing Mn_2O_3(prepared by thermolysis of MnO_2 in air at 800 ℃), Li_2CO_3(as-received commercial product) and Cr_2O_3. The intimately ground powder was heat treated in tube furnaces in a flow of N_2 gas. They were first calcined at 650 ℃ for 5 h for mixtures and then fired at 1 000 ℃ for further 20 h.

The calcined powders were characterized by X-ray diffraction using a Rigaku diffractometer (D/max2000) with Cu $K_α$ radiation.

3 RESULTS AND DISCUSSION

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Correspondence: ZHOU Heng-hui, PhD; Tel: + 86-10-62757908; E-mail: hhzhou@chem.pkv.edu.cn

The X-ray powder diffraction pattern of the $LiMnO_2$ samples is shown in Fig. 2. All peaks are indexed with an orthorhombic phase. The stoichiometric, orthorhombic $LiMnO_2$ compound present a Pmnm space group, with $Z=2$, Mn and Li being in the 2a special position with an octahedral harmonization of oxygen atoms. The parameters of the unit cell were refined as $a=2.8073$ Ù, $b=4.5775$ Ù and $c=5.7526$ Ù, the volume of the $LiMnO_2$ compound is 73.9312 Ù^3. The parameters of the unit cell are consistent with those obtained by Hoppe et al[1]. Broadened peaks (011), (111) and (012) were observed, which could be caused by stacking faults in crystal structure[8].

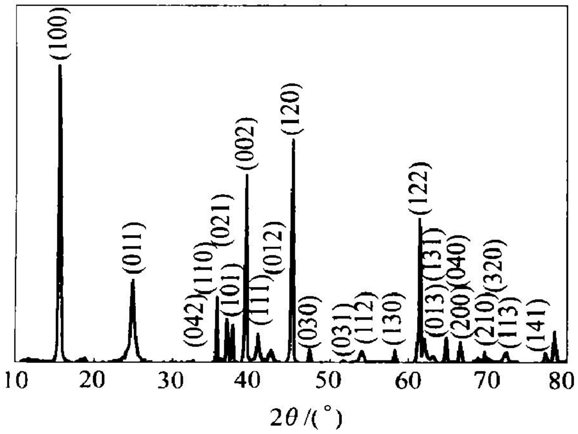

Fig. 2 X-ray diffraction pattern for $LiMnO_2$ with orthorhombic structure

Fig. 3 shows the XRD pattern of $LiMnO_2$ powders with different Cr contents. The peaks for the layered $LiMn_{1-x}Cr_xO_2$ phases correspond to the monoclinic (space group C2/m) crystal structure described by previous authors for layered $LiMnO_2$ obtained by soft chemistry[9, 2]. In general, layered $LiMnO_2$ cannot be synthesized using the conventional solid-state reaction, the doping Cr solid state solution series $LiMnO_2$ prepared at moderately high temperatures has shown that they have the same structure as the monoclinic layered form of $LiMnO_2$ using Rietveld refinement of X-ray and neutron powder diffraction data[7]. It should be noted that the XRD pattern of m-$LiMnO_2$ is very similar to that of tetragonal $Li_2Mn_2O_4$ spinel. The monoclinic $LiMnO_2$ exhibits (202) and (020) peaks, the latter with higher intensity. Tetragonal $Li_2Mn_2O_4$ has (400) and (323) peaks, the former with higher intensity[10]. The main peaks for layered phase are labeled with their (hkl) indices. Positions for peaks characteristic of m-$LiMnO_2$ phase are indicated. With increasing Cr, the peak intensity of o-$LiMnO_2$ phase decreases. Unit cell parameters for the monoclinic layered $LiMn_{1-x}Cr_xO_2$ are listed in Table 1. With increasing Cr, m-$LiMnO_2$ phase shows contracted crystal lattices along a and c axis, which is consisted with the small ion radius of Cr ($r^{3+}_{Mn}=0.64$ Ù and $r^{3+}_{Cr}=0.62$ Ù). With increasing substitution Cr, the broadening of diffraction peaks increase. The broadening of diffraction peaks confirms that present lattice distortion is associated with Cr substitution of Mn ion.

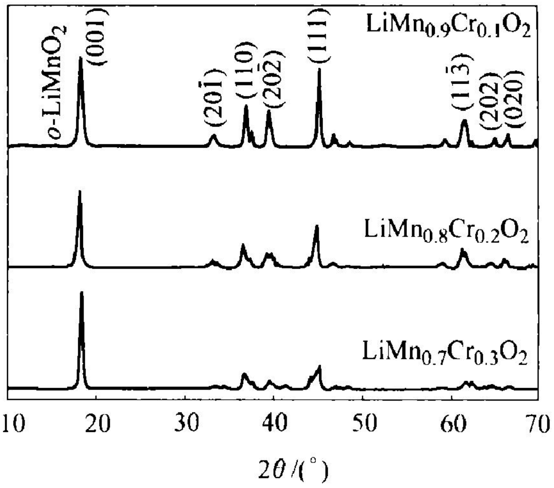

Fig. 3 X-ray diffraction patterns for $LiMnO_2$ with different Cr contents

Table 1 Unite cell parameters for $LiMn_{1-x}Cr_xO_2$ materials

Alloy	a/ Ù	b/ Ù	c/ Ù	β/ (°)	V/ Ù^3
$LiMn_{0.9}Cr_{0.1}O_2$	5.4378	2.8125	5.3825	115.82	74.101
$LiMn_{0.8}Cr_{0.2}O_2$	5.4292	2.8102	5.3579	115.76	73.623
$LiMn_{0.7}Cr_{0.3}O_2$	5.4234	2.8127	5.3494	115.75	73.499

As the structure of undoping Cr is o-$LiMnO_2$, the structure of doping Cr is m-$LiMnO_2$, it is therefore clear that the stabilization of m-$LiMnO_2$ phase is due to the substituted Mn ion by Cr. As high-temperature solid-state reaction always produces o-$LiMnO_2$, m-$LiMnO_2$ is generally considered to be unstable compared with o-$LiMnO_2$[11]. The m-$LiMnO_2$ transforms to o-$LiMnO_2$ upon annealing at 150 ℃[12], indicating metastability of the monoclinic phase.

Fig. 4 represents the projection along b axis of the m-$LiMnO_2$ and a axis of the o-$LiMnO_2$. It is believed that there were two phase transformation probabilities from m-$LiMnO_2$ to o-$LiMnO_2$. The first phase transformation probabilities was defined as unification phase transformation. The first line of m-$LiMnO_2$ shown in Fig. 4 was fixed. The second and third line of m-$LiMnO_2$ as a whole slide $\pm(\boldsymbol{a}+\boldsymbol{c})/2$ on $(10\bar{1})$ in comparison with the first line. The fourth and fifth lines as a whole slide $\pm(\boldsymbol{a}+\boldsymbol{c})$ on $(10\bar{1})$ in comparison with the first line (Fig. 4). The slide direction is the same for the unification phase transformation. The second phase transformation probability was defined as individual phase transformation. The first line of m-Li-MnO_2 was fixed. The second and third lines as a whole slide $\pm(\boldsymbol{a}+\boldsymbol{c})/2$ on $(10\bar{1})$ in comparison with the first line. The fourth and fifth lines as a whole fixed (Fig. 5). Of course, the $LiMnO_2$ needs some atom position adjust in order to obtain lower energy after transformation from m-$LiMnO_2$.

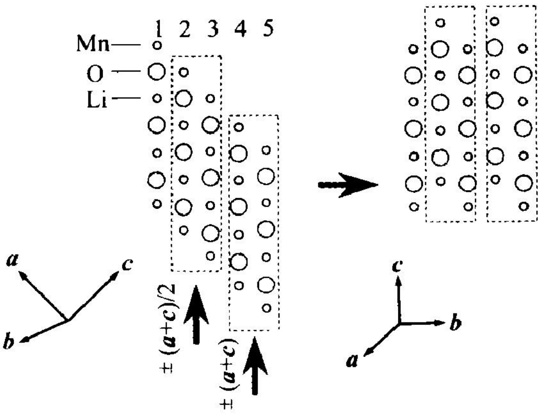

Fig. 4 First phase transformation probability defined as unification phase transformation

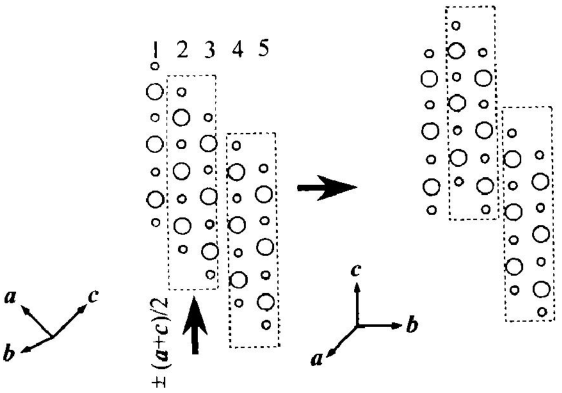

Fig. 5 Second phase transformation probability defined as individual phase transformation

On the basis of the experimental observation, we would like to suggest the following process. When mixtures calcined in a flow of N_2 gas, the mixture first forms m-$LiMnO_2$. In comparison with m-$LiMnO_2$, o-$LiMnO_2$ is more stable, so, m-$LiMnO_2$ would transform o-$LiMnO_2$ through individual phase transformation, unification phase transformation or both of them. There is some m-$LiMnO_2$ that do not transform to o-$LiMnO_2$ in certain condition and exist as stacking fault. The stacking fault image is revealed by TEM using dark field technique[13].

When doping Cr mixtures calcined in a flow of N_2 gas, the mixture first forms m-$LiMnO_2$. The volume of m-$LiMnO_2$ decreasing with increasing Cr confirms that the length of bond around Cr ion decreases with Mn substituted by Cr ion. There are two reasons for the shorter bond length. One is that the ion radius of Cr is smaller than Mn ion. The other one is the higher bond strength of Cr—O than that of Mn—O. From the extended X-ray absorption fine structure analyses at the Mn K-edge show that the substitution of Mn by Cr also gives rise to a shortening of the Mn—O bonds[5]. It is clear that substitution of Mn by Cr increases the sliding resistance on $(10\bar{1})$ of m-$LiMnO_2$ and the resistance prevents slide on $(10\bar{1})$ of m-$LiMnO_2$. So, the Cr doping m-$LiMnO_2$ preserved though o-$LiMnO_2$ was more stable than m-$LiMnO_2$ in thermodynamics. With increasing Cr content, the transformation content from m-$LiMnO_2$ to o-$LiMnO_2$ decreases due to the increase of resistance.

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