

Structure and electrochemical characteristics of $\text{LiMn}_{0.7}\text{M}_{0.3}\text{O}_2$ ($\text{M}=\text{Ti}, \text{V}, \text{Zn}, \text{Mo}, \text{Co}, \text{Mg}, \text{Cr}$)

Z.P. Guo*, S. Zhong, G.X. Wang, H.K. Liu, S.X. Dou

Institute for Superconducting and Electronic Materials, University of Wollongong, Northfields Avenue, Wollongong, NSW 2522, Australia

Received 21 February 2002; received in revised form 2 May 2002; accepted 2 May 2002

Abstract

A series of compounds $\text{LiMn}_{0.7}\text{M}_{0.3}\text{O}_2$ ($\text{M}=\text{Ti}, \text{V}, \text{Zn}, \text{Mg}, \text{Mo}, \text{Co}, \text{Cr}$) with different doping elements were synthesized. It was found that the ionic size of the doping elements is not a discriminating factor in the structure of $\text{LiMn}_{0.7}\text{M}_{0.3}\text{O}_2$ compounds. The $\text{LiMn}_{0.7}\text{M}_{0.3}\text{O}_2$ ($\text{M}=\text{Cr}, \text{Zn}, \text{Mg}, \text{V}$) forms in the hexagonal structure, while the $\text{LiMn}_{0.7}\text{M}_{0.3}\text{O}_2$ ($\text{M}=\text{Co}, \text{Ti}, \text{Mo}$) shows an orthorhombic structure. The $\text{LiMn}_{0.7}\text{M}_{0.3}\text{O}_2$ compounds have less crystal distortion compared with o(orthorhombic)- LiMnO_2 . All substituted materials cycled between 4.4 and 2 V in Li cells show higher stability of capacity compared with the standard o- LiMnO_2 . AC impedance analysis results show that the charge transfer process and lithium ion diffusion process for doped LiMnO_2 compounds are better than that for un-substituted compounds.

© 2002 Elsevier Science B.V. All rights reserved.

Keywords: Energy storage materials; Electrode materials; Chemical synthesis; Electrochemical reactions; X-ray diffraction

1. Introduction

LiMnO_2 compounds have come to be of interest as intercalation electrodes for rechargeable lithium batteries because of their high theoretical capacity (285 mAh g^{-1}), about twice that of LiMn_2O_4 , and low cost relative to LiCoO_2 [1]. One significant drawback of the manganese compounds is that they are difficult to synthesize in the layered $\alpha\text{-NaFeO}_2$ structure, which is common to LiCoO_2 and LiNiO_2 . When synthesized under equilibrium conditions, LiMnO_2 forms an orthorhombic structure with space group $Pmmn$ [2]. Metastable layered LiMnO_2 with space group $C2/m$ has been made through ion-exchange processes starting from the layered $\alpha\text{-NaMnO}_2$ precursor [3–5]. In addition, partial substitution of Mn by Cr and Al have been shown to stabilize the layered structure. Reasons for this could include: (1) Cr^{3+} and Al^{3+} cations prevent Mn ion migration during cycling, which would prevent cations redistribute, thus reducing the tendency of the layered structure converting to the more stable spinel. (2)

Cr^{3+} and Al^{3+} dilute the Jahn–Teller distortion by partial substitutions for the Mn ions [6].

Although Cr and Al doped layered LiMnO_2 have been studied, to our knowledge the stabilization of o(orthorhombic)-, m(monoclinic)- or h(hexagonal)- LiMnO_2 by doping with other elements has not been reported. We chose to study $\text{LiM}_x\text{Mn}_{1-x}\text{O}_2$ ($\text{M}=\text{Ti}, \text{V}, \text{Zn}, \text{Mo}, \text{Co}, \text{Mg}$) because these LiMO_2 compounds with M close to Mn in the periodic table form the layered $\alpha\text{-NaFeO}_2$ structure [6]. Besides its scientific interest, understanding the doping effect of these elements on LiMnO_2 may be of practical interest in designing layered lithium–manganese oxides which form in different structures.

Ammundsen et al. [7] have recently developed a high-temperature solid-state synthesis for $\text{LiAl}_x\text{Mn}_{1-x}\text{O}_2$ and $\text{LiCr}_x\text{Mn}_{1-x}\text{O}_2$ which allows well-ordered layered phases to be obtained. Based on previous research, we successfully synthesized a series of $\text{LiM}_{0.3}\text{Mn}_{0.7}\text{O}_2$ materials using Li_2CO_3 , MnCO_3 and M oxides (to emphasize the doping effect, we chose large doping level composite $\text{LiM}_{0.3}\text{Mn}_{0.7}\text{O}_2$). In this paper, the structure and electrochemical performance of $\text{LiM}_{0.3}\text{Mn}_{0.7}\text{O}_2$ compounds have been studied. The electrochemical performance of doped LiMnO_2 , especially the capacity fade rate, has been improved.

*Corresponding author. Tel.: +61-2-4221-3017; fax: +61-2-4221-5731.

E-mail address: zg04@uow.edu.au (Z.P. Guo).

2. Experimental

$\text{LiMn}_{0.7}\text{M}_{0.3}\text{O}_2$ ($\text{M}=\text{Ti, V, Co, Mg, Zn, Mo}$ and Cr) ($\text{LiMn}_{0.7}\text{Cr}_{0.3}\text{O}_2$ was synthesized here for comparison) were prepared by a solid state reaction from a mixture of Li_2CO_3 , MnCO_3 and relevant metal oxides with a pre-determined $\text{Li}/\text{Mn}/\text{M}$ ratio of 1.1:0.7:0.3 (the excess of Li was included to compensate for loss during firing). The mixture was preheated at 650°C for 5 h under argon flow, then heated to and maintained at 1000°C under argon atmosphere for 8 h. The samples were reground between firings.

X-ray diffraction (XRD) data were recorded on a Philips 1730 diffractometer using $\text{Cu K}\alpha$ radiation. The lattice was refined against an internal silicon standard.

The electrochemical performance of $\text{LiMn}_{0.7}\text{M}_{0.3}\text{O}_2$ compounds as cathodes was measured using a Teflon test cell with an internal spring to maintain an adequate pressure on the electrode stack. The cathode consists of 85% active material, 10% carbon black and 5% binder (PVDF). The electrolyte used in the cell was 1 M LiPF_6 —ethylene carbonate (EC)/dimethyl carbonate (DMC) (1:1 v/v). The anodes were lithium foil disks. Two sheets of Celgard 2700 formed the separator. Cells were cycled between 2.0 and 4.4 V; the typical charge and discharge rate was $C/5$ (0.4 mA cm^{-2}). AC impedance measurements were carried out utilizing an EG&G Model 6310 electrochemical impedance analyzer. Electrochemical impedance software (EG&G Model 398) was used to control a computer for conductivity and stability measurements. AC impedance was measured potentiostatically over a frequency range of 100–0.01 Hz at six points per decade of frequency with a 5-mV AC input signal applied between working and reference electrodes (lithium was used as reference electrode, and the working electrode was the $\text{LiMn}_{0.7}\text{M}_{0.3}\text{O}_2$ compound).

3. Results and discussion

3.1. Crystal structure and morphology

XRD patterns for samples with different metal element substitutions are shown in Fig. 1. The spectra for Ti, Co and Mo substitution show typical patterns for the orthorhombic structure with space group $Pmmn$. The patterns for the Cr, Zn, Mg and V substitution samples show that the major phase is hexagonal, while the remaining peaks in the diffraction patterns correspond to Li_2MnO_3 impurities. $\text{LiMn}_{0.7}\text{Cr}_{0.3}\text{O}_2$ shows the weakest peak intensities for Li_2MnO_3 . The amount of Li_2MnO_3 is slightly greater than for other $\text{LiMn}_{0.7}\text{M}_{0.3}\text{O}_2$ ($\text{M}=\text{Zn, V, Mg}$) compounds, but it remains a minor phase throughout. The identification of these phases is discussed in greater detail below. As observed for layered $\text{Li}_{2-x}\text{Cr}_y\text{Mn}_{2-y}\text{O}_4$ phases with different substitution level y [8], a change of symmetry occurs from monoclinic to hexagonal occurs between the compositions $\text{Li}_2\text{Cr}_{1.3}\text{Mn}_{0.7}\text{O}_4$ and $\text{Li}_2\text{Cr}_{1.4}\text{Mn}_{0.6}\text{O}_4$. However, $\text{LiMn}_{1-x}\text{M}_x\text{O}_2$ in this study shows a hexagonal structure at much lower substitution level ($x=0.3$). Possible reason for this is the excess of Li used ($\text{Li}/(\text{Mn}+\text{M})=1.1$).

The hexagonal and monoclinic unit cells differ mainly in the relative positioning of the layers perpendicular to the c -axis. The layered form of LiMnO_2 prepared by low-temperature ion-exchange of NaMnO_2 is monoclinic rather than hexagonal because of a cooperative Jahn–Teller distortion caused by the Mn^{3+} ion. Within the compositions of $\text{LiMn}_{0.7}\text{M}_{0.3}\text{O}_2$ with hexagonal structure, the lower valence cations, such as Mg^{2+} and Zn^{2+} , could introduce holes in the Mn valence bands, effectively creating Mn^{4+} ions, and thereby decreasing the Jahn–Teller distortion; the higher valence cations, such as Cr^{3+} ,

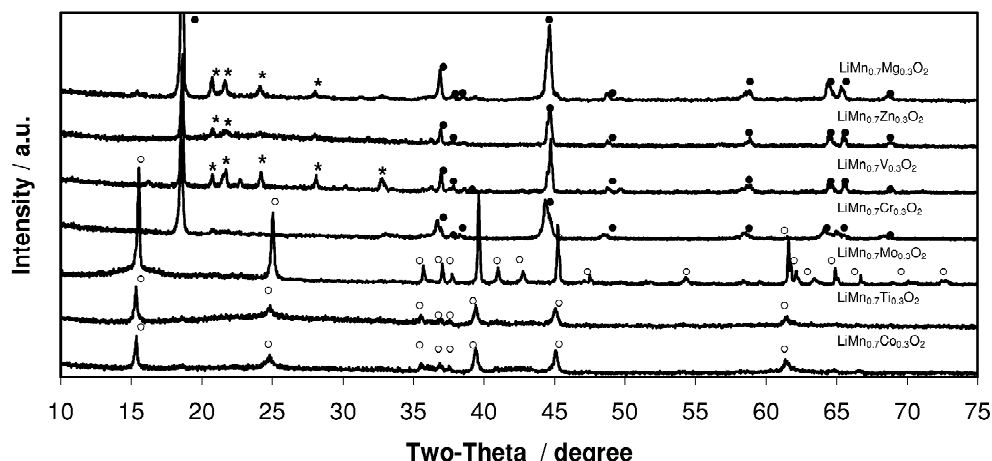


Fig. 1. Powder XRD patterns of $\text{LiMn}_{0.7}\text{M}_{0.3}\text{O}_2$ materials: (•) h-LiMnO_2 ; (○) o-LiMnO_2 ; (*) Li_2MnO_3 .

could dilute the J–T effect by partial substitutions for the Mn ions [6].

It should be noted that the XRD pattern of h-LiMnO₂ is very similar to that of LiMn₂O₄ spinel, as there are Li₂MnO₃ impurities involved in the XRD patterns. There are two peaks at about 65° in the XRD patterns, which demonstrate that the main phases for Cr, Mg, V, Zn-substituted samples are hexagonal. Ammundsen et al. [7] have also argued that these two phases can be distinguished from each other by the hexagonal *c/a* ratio. The *c/a* ratio for a spinel-type compound has a value of 4.9, but it usually greater than 5 for the hexagonal structure compound. To make sure of the structure of samples, unit cell parameters for LiMn_{0.7}M_{0.3}O₂ are calculated and reported in Table 1. It was found that the *c/a* ratios for the LiMn_{0.7}M_{0.3}O₂ (M=Cr, Mg, V, Zn) are larger than 5, which demonstrated that the main phase of these samples is hexagonal. Compared with other reports [9,10], the lattice constants for the o-LiMn_{0.7}M_{0.3}O₂ (M=Ti, Co, Mo) show a smaller *a*-value and a larger *b*-value which may be caused by the M substitution. Considering the ion radius, for a doping element M which has octahedral coordination, it was found that the ionic size of doping elements is not a discriminating factor in the structure of Mn-based compounds. A layered structure is usually obtained independent of the size of the ionic radius of the doping element M.

The results of SEM observation of individual compounds are shown in Fig. 2. It was found that the doping elements have great influence on the crystal morphology of LiMn_{1-x}M_xO₂ compounds. The crystalline size and morphology are different for doped compounds with different elements. The SEM images are shown only for LiMn_{0.7}Zn_{0.3}O₂, LiMn_{0.7}Mo_{0.3}O₂ and LiMn_{0.7}Co_{0.3}O₂, which represent the h(hexagonal)-LiMn_{1-x}M_xO₂ and o-LiMn_{1-x}M_xO₂ compounds, respectively. As shown in Fig. 2b, LiMn_{0.7}Mo_{0.3}O₂ typically grows as a needle-shaped crystal. During the high temperature heating process, the LiMn_{0.7}Mo_{0.3}O₂ crystals sufficiently grew extensively along a particular direction. This means that there was liquid phase at the crystal boundary at the firing temperature, which is possibly caused by the addition of Mo. For

LiMn_{0.7}Zn_{0.3}O₂, there are also some needle-shaped crystals. Whereas, the LiMn_{0.7}Co_{0.3}O₂ compound only has flake-shaped crystals. The crystal sizes of LiMn_{0.7}Mo_{0.3}O₂ and LiMn_{0.7}Co_{0.3}O₂ are larger than that of LiMn_{0.7}Zn_{0.3}O₂. The as grown o-LiMn_{0.7}M_{0.3}O₂ samples obtained are naturally harder than h-LiMn_{0.7}M_{0.3}O₂ and difficult grind into fine powder. The larger particle o-LiMn_{1-x}M_xO₂ materials are difficult to be activated when they are used to prepare cathodes for lithium ion batteries, because the particles can crack during the charge/discharge cycling. This result is consistent with the electrochemical test results below.

3.2. Electrochemical characterization

Fig. 3 shows the plot of specific discharge capacity vs. number of cycles for LiMn_{0.7}M_{0.3}O₂ cells (in order to clearly show the curves, here we just show the results for LiMn_{0.7}M_{0.3}O₂ (M=Cr, Zn, Mo and V)). The data were collected at a current density of 0.4 mA cm⁻² between 4.4 and 2 V. The o-LiMn_{0.7}M_{0.3}O₂ electrodes showed a very small initial discharge capacity of about 35 mAh g⁻¹, and the capacity continued to increase on cycling. Compared with the result for o-LiMnO₂ prepared by the same solid-state route, the discharge capacity of o-LiMn_{0.7}M_{0.3}O₂ electrodes is smaller, but the cyclability of electrodes has been improved. Undoped o-LiMnO₂ loses capacity at a rate of about 0.3% per cycle after 20 cycles, while o-LiMn_{0.7}Mo_{0.3}O₂, h-LiMn_{0.7}Cr_{0.3}O₂ and h-LiMn_{0.7}Zn_{0.3}O₂ and h-LiMn_{0.7}V_{0.3}O₂ show a lower capacity loss rate (0.17, 0.11, 0.23 and 0.19% per cycle, respectively). For h-LiMn_{0.7}M_{0.3}O₂ (M=Mg, V, Zn, Cr), although their initial capacities are different, all samples show good cyclability at room temperature. Compared with o-LiMnO₂, every doping element can improve the electrochemical performance of the LiMn_{0.7}M_{0.3}O₂ cathode. The reason could be that the doping element M may play a double role: In most cases, M changes the inter-atomic forces in the lattice, but in the case of Zn and Mg, in addition to that, the doping element may alter the valence of Mn from 3+ to 4+. Both these actions have the result of diminishing the crystal lattice distortion, i.e. decreasing

Table 1
Crystallographic dimensions of the LiMn_{0.7}M_{0.3}O₂ compounds

Composition	Doping ion radius of M (Å)	Main phase	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	<i>c/a</i>
LiMn _{0.7} V _{0.3} O ₂	0.680	Hexagonal	2.8325	–	14.3016	5.0491
LiMn _{0.7} Cr _{0.3} O ₂	0.755	Hexagonal	2.8401	–	14.3268	5.0445
LiMn _{0.7} Mg _{0.3} O ₂	0.860	Hexagonal	2.8412	–	14.2890	5.0292
LiMn _{0.7} Zn _{0.3} O ₂	0.880	Hexagonal	2.8344	–	14.3177	5.0514
LiMn _{0.7} Co _{0.3} O ₂	0.685	Orthorhombic	2.7265	5.9177	4.5579	–
LiMn _{0.7} Ti _{0.3} O ₂	0.745	Orthorhombic	2.7054	5.9569	4.5571	–
LiMn _{0.7} Mo _{0.3} O ₂	0.830	Orthorhombic	2.7288	5.9145	4.5560	–
o-LiMnO ₂ (calculated values)		Orthorhombic	2.806 ±0.001	5.756 ±0.001	4.572 ±0.001	

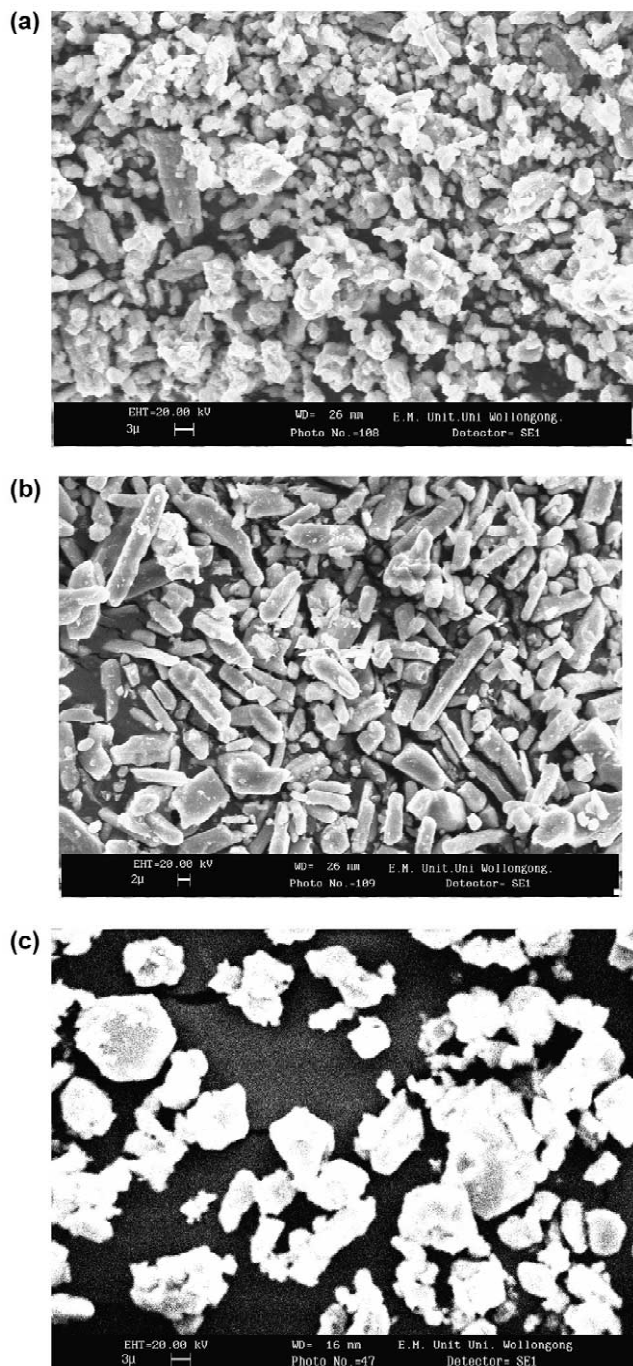


Fig. 2. (a) SEM image of $\text{LiMn}_{0.7}\text{Zn}_{0.3}\text{O}_2$; (b) SEM image of $\text{LiMn}_{0.7}\text{Mo}_{0.3}\text{O}_2$; (c) SEM image of $\text{LiMn}_{0.7}\text{Co}_{0.3}\text{O}_2$.

the J–T distortion, thereby enhancing the stability of the crystal structure.

To obtain more details on the electrode process, AC impedance measurements (EIS) were performed. EIS experiments were performed on working electrodes made from $\text{LiMn}_{0.7}\text{M}_{0.3}\text{O}_2$ compounds at the OCV state. The electrodes were equilibrated for 8 h after assembling in a glove-box filled with argon, and then AC excitation was applied. For all electrodes, one semicircle and an inclined

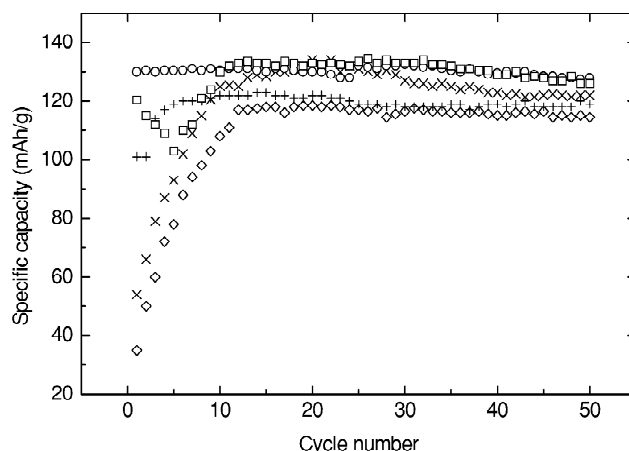


Fig. 3. Cycling data for Li ion cells containing $\text{LiMn}_{0.7}\text{M}_{0.3}\text{O}_2$ cathodes: (○) $\text{LiMn}_{0.7}\text{Cr}_{0.3}\text{O}_2$; (+) $\text{LiMn}_{0.7}\text{V}_{0.3}\text{O}_2$; (□) $\text{LiMn}_{0.7}\text{Zn}_{0.3}\text{O}_2$; (×) o- LiMnO_2 ; (◇) $\text{LiMn}_{0.7}\text{Mo}_{0.3}\text{O}_2$.

line were observed. The semicircle appearing in the high frequency region can be attributed to the impedance of the charge transfer reaction. The inclined line in the middle and low frequency region can be attributed to the diffusional impedance. The situation at the $\text{LiMn}_{0.9}\text{M}_{0.1}\text{O}_2$ electrode can be approximately represented by the equivalent circuit in Fig. 4. R_s is the ohmic internal resistance of the cell, but this factor encompasses several factors including the solution resistance as well as the electrical resistance of the anode and cathode materials. C_{dl} represents the double layer capacitance; R_{ct} is the cathode charge-transfer resistance, which is related to the exchange current density (i_0) of electrodes by the formula: $i_0 = RT/(nFR_{ct})$; W_o is the diffusion impedance, the $W_o - T$ value represents the Warburg coefficient, which is related to the diffusion coefficient of the lithium ions into the cathode by the formula: $W_o - T = L^2/D$ (L is the effective diffusion thickness, and D is the effective diffusion coefficient of the lithium ions). Table 2 lists the results calculated from AC impedance spectra based on the equivalent circuit shown in Fig. 4 using ZView2.3C software. Comparing the $\text{LiMn}_{0.7}\text{M}_{0.3}\text{O}_2$ compounds with the standard o- LiMnO_2 , it was found that all the doped compounds have a lower R_{ct} , a larger i_0 and a smaller $W_o - T$. This means that the $\text{LiMn}_{0.7}\text{M}_{0.3}\text{O}_2$ is more electrochemically reactive than the o- LiMnO_2 , which is in qualitative agreement with cyclability of samples. This indicates that the doping elements have more or less improved the electrochemical performance of $\text{LiMn}_{1-x}\text{M}_x\text{O}_2$ compounds.

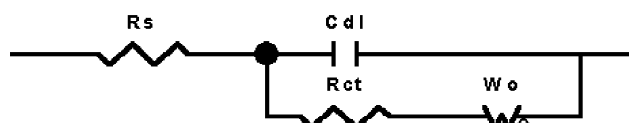


Fig. 4. Equivalent circuit for the $\text{LiMn}_{0.7}\text{M}_{0.3}\text{O}_2$ electrodes.

Table 2

Results of AC impedance analysis of the $\text{LiMn}_{0.7}\text{M}_{0.3}\text{O}_2$ compounds

Compounds	R_s (Ω)	C_{dl} ($\text{F} \times 10^{-6}$)	R_{ct} (Ω)	$W_o - T$	i_0 ($\times 10^{-4}$)
$\text{LiMn}_{0.7}\text{V}_{0.3}\text{O}_2$	15.21	9.4932	22.16	24.9	11.58
$\text{LiMn}_{0.7}\text{Cr}_{0.3}\text{O}_2$	13.19	9.6025	13.49	17.1	19.31
$\text{LiMn}_{0.7}\text{Mg}_{0.3}\text{O}_2$	13.24	9.7654	16.56	19.4	15.50
$\text{LiMn}_{0.7}\text{Zn}_{0.3}\text{O}_2$	13.15	9.7413	12.43	16.4	20.65
$\text{LiMn}_{0.7}\text{Co}_{0.3}\text{O}_2$	13.46	2.1962	41.25	51.61	6.23
$\text{LiMn}_{0.7}\text{Ti}_{0.3}\text{O}_2$	13.52	2.2367	42.60	62.38	6.03
$\text{LiMn}_{0.7}\text{Mo}_{0.3}\text{O}_2$	14.49	2.7825	39.81	50.09	6.45
o- LiMnO_2	15.36	2.7568	110.52	97.78	2.32

4. Conclusions

The doping effect of elements M (M=Cr, Ti, V, Zn, Mg, Mo, Co) on the structure and electrochemical performance of LiMnO_2 compounds has been investigated. Contrary to expectations from previous reports, the $\text{LiMn}_{0.7}\text{M}_{0.3}\text{O}_2$ (M=Cr, Zn, V, Mg) compounds have a hexagonal phase, not a monoclinic phase. However, $\text{LiMn}_{0.7}\text{M}_{0.3}\text{O}_2$ (M=Ti, Mo, Co) form an orthorhombic structure. The doping elements have great influence on the crystal morphology of $\text{LiMn}_{1-x}\text{M}_x\text{O}_2$ compounds. Normally, the as grown o- $\text{LiMn}_{1-x}\text{M}_x\text{O}_2$ samples are harder than h- $\text{LiMn}_{1-x}\text{M}_x\text{O}_2$ samples, which makes it more difficult to grind. Compared with the standard o- LiMnO_2 , all doped compounds have a lower R_{ct} , a larger i_0 and a smaller $W_o - T$, implying that they should have better electrochemical performance. Charge/discharge tests show that the capacity fade rate for all of the doped LiMnO_2 compounds are better than for non-substituted compound.

References

- [1] M.M. Thackeray, Prog. Solid State Chem. 25 (1997) 1.
- [2] T.A. Hewston, B.L. Chamberland, J. Phys. Chem. Solids 48 (1987) 97.
- [3] F. Capitaine, P. Gravereau, C. Delmas, Solid State Ionics 89 (1996) 197.
- [4] A.R. Armstrong, P.G. Bruce, Nature 381 (1996) 499.
- [5] M. Tabuchi, K. Ado, H. Kobayashi, H. Kageyama, C. Masquelier, A. Kondo, R. Kanno, J. Electrochem. Soc. 145 (1998) L49.
- [6] G. Ceder, S.K. Mishra, Electrochem. Solid-State Lett. 2 (1999) 550.
- [7] B. Ammundsen, J. Desilvestro, T. Groutso, D. Hassell, J.B. Metson, E. Regan, R. Steiner, P.J. Pickering, J. Electrochem. Soc. 147 (2000) 4078.
- [8] I.I. Davidson, R.S. McMillan, H. Sleg, B. Luan, I. Kargina, J.J. Murray, I.P. Swainson, J. Power Sources 81–82 (1999) 406.
- [9] R. Hoppe, G. Brachtel, M. Jansen, Z. Anorg. Allg. Chem. 417 (1975) 1.
- [10] T. Ohzuku, A. Ueda, T. Hirai, Chem. Express 7 (1992) 193.