

# LiMn<sub>2-x</sub>Cr<sub>x</sub>O<sub>4</sub> spinel prepared by a modified citrate route with combustion

Ke Du<sup>\*</sup>, Jingying Xie, Jiulin Wang, Hong Zhang

Shanghai Institute of Microsystem and Information Technology, Chinese Academy of Sciences (CAS),  
865 Changning Road, Shanghai 200050, China

## Abstract

A series of LiMn<sub>2-x</sub>Cr<sub>x</sub>O<sub>4</sub> ( $x = 0, 0.01, 0.05, 0.1, 0.2$ ) has been synthesized by a modified citrate route with combustion. The influence of the substitution of Cr for Mn on the electrochemical performances was investigated and compared. The results show that Cr substitution in spinel LiMn<sub>2</sub>O<sub>4</sub> can effectively depress the capacity fading over 4 V and improve the cycleability.

© 2003 Elsevier Science B.V. All rights reserved.

**Keywords:** LiMn<sub>2-x</sub>Cr<sub>x</sub>O<sub>4</sub>; Special capacity; Cycleability; Discharge voltage plateau

## 1. Introduction

Much work has been done to improve the performance of LiMn<sub>2</sub>O<sub>4</sub> as cathode material for lithium ion battery [1–5]. Unfortunately, it has not been completely successful to substitute LiCoO<sub>2</sub> with spinel LiMn<sub>2</sub>O<sub>4</sub> due to the gradual degradation of its capacity on cycling. Elemental substitution and doping are effective ways to improve the cycleability. Many elements have been studied. Among them, it was reported that Co- and Cr-substituted (-doped) LiMn<sub>2</sub>O<sub>4</sub> spinels synthesized by solid-state reaction showed an obvious improvement in the cycle life without dramatically sacrificing the initial capacity [5,6].

Recently, soft-chemical synthesis techniques and different combustion processes have been developed to synthesize spinel LiMn<sub>2</sub>O<sub>4</sub> [7–9], for example, using citric acid as chelating and combustion-assistant agent has successfully synthesized spinel LiMn<sub>2</sub>O<sub>4</sub> with high capacity [9]. Compared with the normal sol-gel or Pechini route [10,11], the drying process under vacuum is replaced by a simple spontaneously combusting in air in this process, so it is time- and cost-saving. Also compared to the solid-state reaction [12,13], the combustion process can make the distribution of the element more homogeneous at the atomic level, so it provides possibilities to obtain LiMn<sub>2</sub>O<sub>4</sub> spinel

with homogeneous composition, in particular, for doped and substituted systems. In this paper, the LiMn<sub>2-x</sub>Cr<sub>x</sub>O<sub>4</sub> ( $x = 0, 0.01, 0.05, 0.1, 0.2$ ) has been successfully synthesized by a modified citrate route with combustion and the Cr-substituted LiMn<sub>2-x</sub>Cr<sub>x</sub>O<sub>4</sub> show better cycleability than un-substituted one, although there is a fade of the initial capacity.

## 2. Experiment

Lithium nitrate (LiNO<sub>3</sub>), 50% aqueous solution of manganese nitrate (Mn(NO<sub>3</sub>)<sub>2</sub>) and chromic nitrate ninohydrate (Cr(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O) were homogeneously mixed by the appropriate Li/Mn/Cr atom ratio (Li:(Mn + Cr) = 1.05:2), and then were added to a mixed solution of citric acid and ethylene glycol. Heating the resulting solution to about 90 °C, a reaction occurred violently. The pH value of solution was adjusted by adding ammonia solution gradually. With ammonia addition, a white precipitate formed, but when pH value increased more, the precipitate dissolved and a red-brown solution resulted. Heating the solution on an electric cooker at about 250 °C, after removing water and organic compound and gas escaping, a spontaneous combustion without flame happened quickly. As a result, a dark-grey plummy precursor was quickly formed. This combustion process took only several minutes. Calcining the precursor in air at 800 °C for a few hours, the black powder of LiMn<sub>2-x</sub>Cr<sub>x</sub>O<sub>4</sub> with spinel structure was synthesized.

<sup>\*</sup> Corresponding author. Tel.: +86-21-625110708936;

fax: +86-21-32200534.

E-mail address: [duke@mail.sim.ac.cn](mailto:duke@mail.sim.ac.cn) (K. Du).

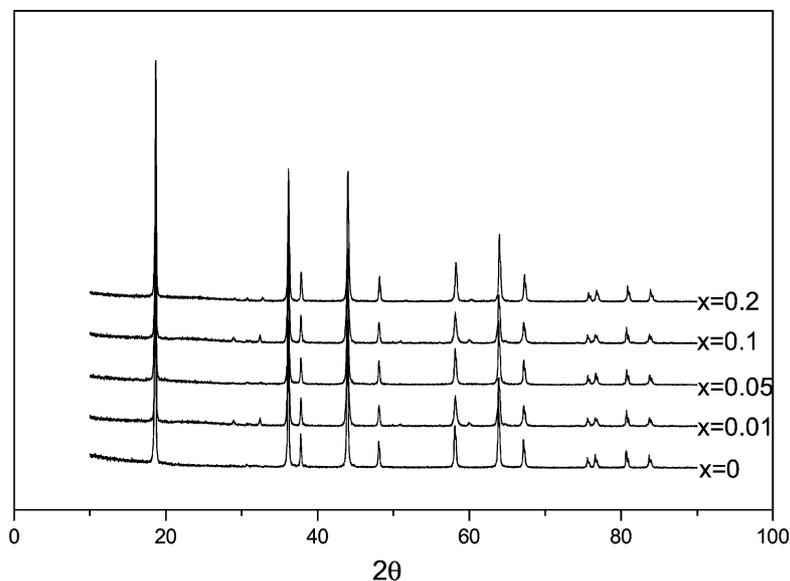


Fig. 1. XRD patterns of  $\text{LiMn}_{2-x}\text{Cr}_x\text{O}_4$  ( $x = 0, 0.01, 0.05, 0.1, 0.2$ ).

The structure of  $\text{LiMn}_{2-x}\text{Cr}_x\text{O}_4$  obtained was examined by X-ray diffraction (XRD) with  $\text{Cu K}\alpha$  radiation. The real composition ratio of Li/Mn/Cr was detected by IRIS Advantage ICP-AES.

Electrochemical measurements were carried out by using coin-type cells (2025) with  $\text{LiMn}_{2-x}\text{Cr}_x\text{O}_4$ /acetylene black/PTFE (85/10/5 wt.%) as cathode, Li foil as the anode, 1M  $\text{LiClO}_4/\text{EC} + \text{DME}$  (50:50 vol.%) as electrolyte, and a polyethylene membrane as the separator. The cell was assembled in a glove box filled with  $\text{Ar} + \text{H}_2$  mixing gas, and charge-discharged on a Land instrument at room temperature.

A three-electrode electrochemical cell was employed for cyclic voltammetry from 2.5 to 4.5 V at a scanning rate of 0.1 mV/s on a Solartron SI 1287 electrochemical interface.

### 3. Results and discussion

Fig. 1 presents the XRD pattern of  $\text{LiMn}_{2-x}\text{Cr}_x\text{O}_4$  ( $x = 0, 0.01, 0.05, 0.1, 0.2$ ). All the peaks in each pattern can be well indexed as those of spinel structure. Obviously substitution of Cr ( $x \leq 0.2$ ) for Mn does not change the crystal structure of  $\text{LiMn}_2\text{O}_4$ . However, with the increase of Cr amount, the lattice constant becomes smaller as shown in Table 1. For example, the lattice constant of  $\text{LiMn}_{1.8}\text{Cr}_{0.2}\text{O}_4$  is 0.2% less than that of  $\text{LiMn}_2\text{O}_4$ . That indicates the Cr is really incorporated into  $\text{LiMn}_2\text{O}_4$  lattice. It is commonly accepted that the substitution of  $\text{Cr}^{3+}$  with smaller ion radius (0.615 Å) for  $\text{Mn}^{3+}$  (0.645 Å) leads to a lattice cell contraction.

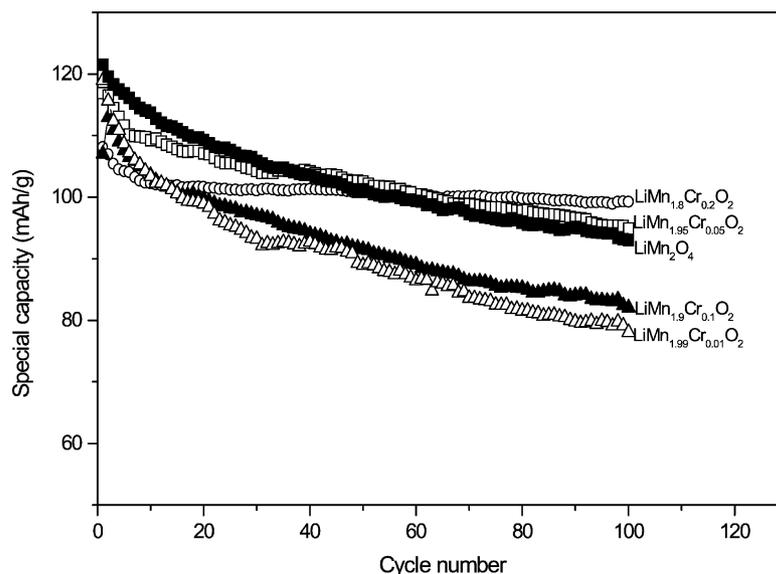


Fig. 2. Capacity fade versus cycle number for  $\text{LiMn}_{2-x}\text{Cr}_x\text{O}_4$  ( $x = 0, 0.01, 0.05, 0.1, 0.2$ ).

Table 1  
The real Li/Mn/Cr ratio and lattice constant of  $\text{LiMn}_{2-x}\text{Cr}_x\text{O}_4$

Nominal chemical formula	$\text{LiMn}_2\text{O}_4$	$\text{LiMn}_{1.99}\text{Cr}_{0.01}\text{O}_4$	$\text{LiMn}_{1.95}\text{Cr}_{0.05}\text{O}_4$	$\text{LiMn}_{1.9}\text{Cr}_{0.1}\text{O}_4$	$\text{LiMn}_{1.8}\text{Cr}_{0.2}\text{O}_4$
Real ratio of (Li/Mn/Cr)	0.952/2/–	0.913/1.990/0.010	0.935/1.954/0.046	0.930/1.907/0.093	0.952/1.809/0.191
Lattice constant $a$ (Å)	8.2442	8.2400	8.2379	8.2341	8.2282

The size of the single granule for  $\text{LiMn}_{2-x}\text{Cr}_x\text{O}_4$  is in nanometer and sub-micrometer scale by TEM result.

The composition of five samples of  $\text{LiMn}_{2-x}\text{Cr}_x\text{O}_4$  analyzed by ICP is also listed in Table 1. Li/Mn are all less than nominal  $1/(2-x)$ , but the Mn/Cr is very near  $(2-x)/x$ . It shows that the samples synthesized in this study are lithium-deficient.

The fading of discharge capacity with cycle number at about 0.5 C ( $0.78 \text{ mA/cm}^2$ ) is presented in Fig. 2. As shown in Table 2, for the pure spinel, the initial specific discharge capacity is 121 mAh/g (it reaches to 130 mAh/g at 0.2 C), but after 100 cycles it decreases to 93 mAh/g, losing about 23%. For  $\text{LiMn}_{1.95}\text{Cr}_{0.05}\text{O}_4$ , it drops from 117 to 95 mAh/g while losing 19%;  $\text{LiMn}_{1.8}\text{Cr}_{0.2}\text{O}_4$  has the best ability to keep capacity, losing only 8% during the first 100 cycles, though its initial capacity is only 108 mAh/g. It is obvious that the cycleability is improved with the substitution Cr for Mn, though the initial discharge capacity is decreased in a certain extent. The improvement of cycleability is related to the more stabilized spinel structure with Cr substitution because of stronger Cr–O bond. The bond energy of Cr–O is 1142 kJ/mol, larger than that of Mn–O, 946 kJ/mol. Also the electron configuration of  $\text{Cr}^{3+}$  with low spin  $3d^3[(t_{2g})^3(e_g)^0]$  is beneficial for forming a stable octahedral  $\text{CrO}_6$  [5]. For  $\text{Mn}^{3+}$ , its  $3d^4[(t_{2g})^3(e_g)^1]$  is relatively instable for octahedral structure.

The discharge curves of the first and 100th cycle for  $\text{LiMn}_2\text{O}_4$ ,  $\text{LiMn}_{1.95}\text{Cr}_{0.05}\text{O}_4$  and  $\text{LiMn}_{1.8}\text{Cr}_{0.2}\text{O}_4$  are plotted in Fig. 3, respectively. Usually there are two discharge plateaus in the discharge curve at about 4.10 and 3.97 V in  $\text{LiMn}_2\text{O}_4$ . However, the clear boundary between two

Table 2  
Discharge capacity and its loss distribution for  $\text{LiMn}_{2-x}\text{Cr}_x\text{O}_4$  ( $x = 0, 0.05, 0.2$ )

		Discharge capacity above 4 V (mAh/g)	Discharge capacity below 4 V (mAh/g)	Total discharge capacity (mAh/g)
$\text{LiMn}_2\text{O}_4$	1st	58	63	121
	100th	36	57	93
	Loss	22	6	28
$\text{LiMn}_{1.95}\text{Cr}_{0.05}\text{O}_4$	1st	48	69	117
	100th	35	60	95
	Loss	13	9	22
$\text{LiMn}_{1.8}\text{Cr}_{0.2}\text{O}_4$	1st	37	71	108
	100th	36	63	99
	Loss	1	8	9

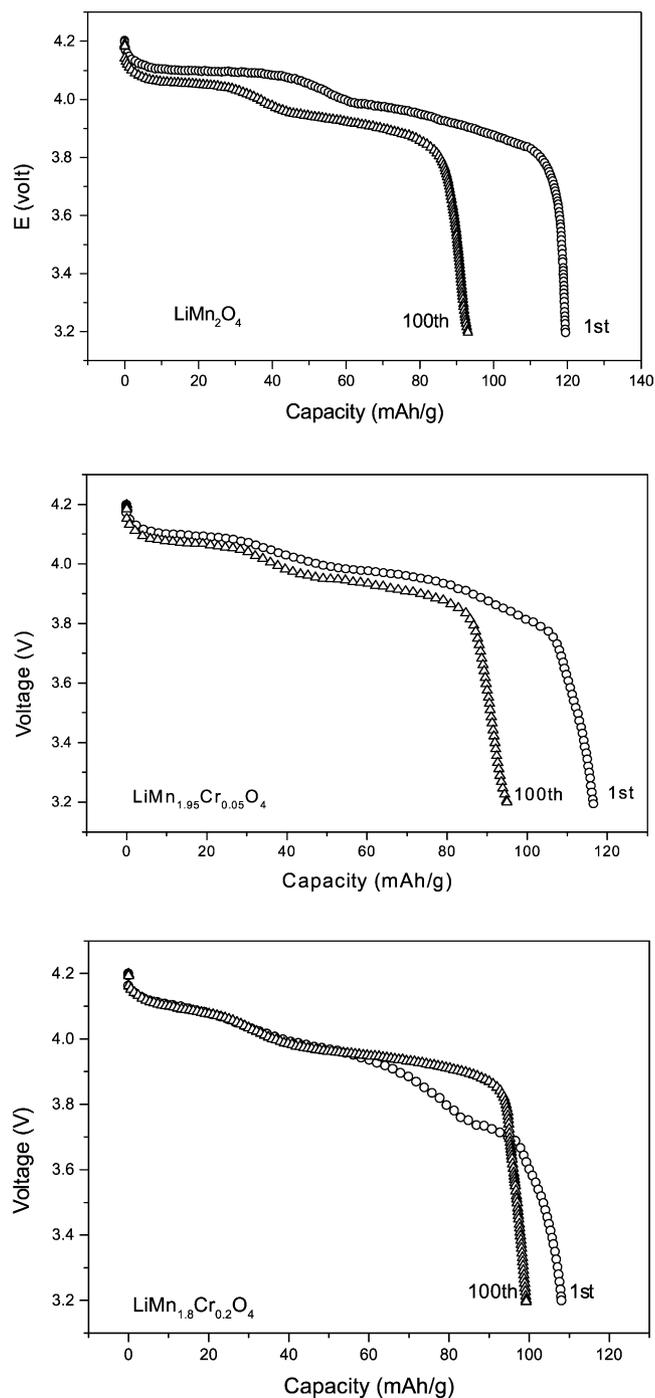


Fig. 3. Discharge curve of 1st and 100th cycle for  $\text{LiMn}_{2-x}\text{Cr}_x\text{O}_4$  ( $x = 0, 0.05, 0.2$ ).

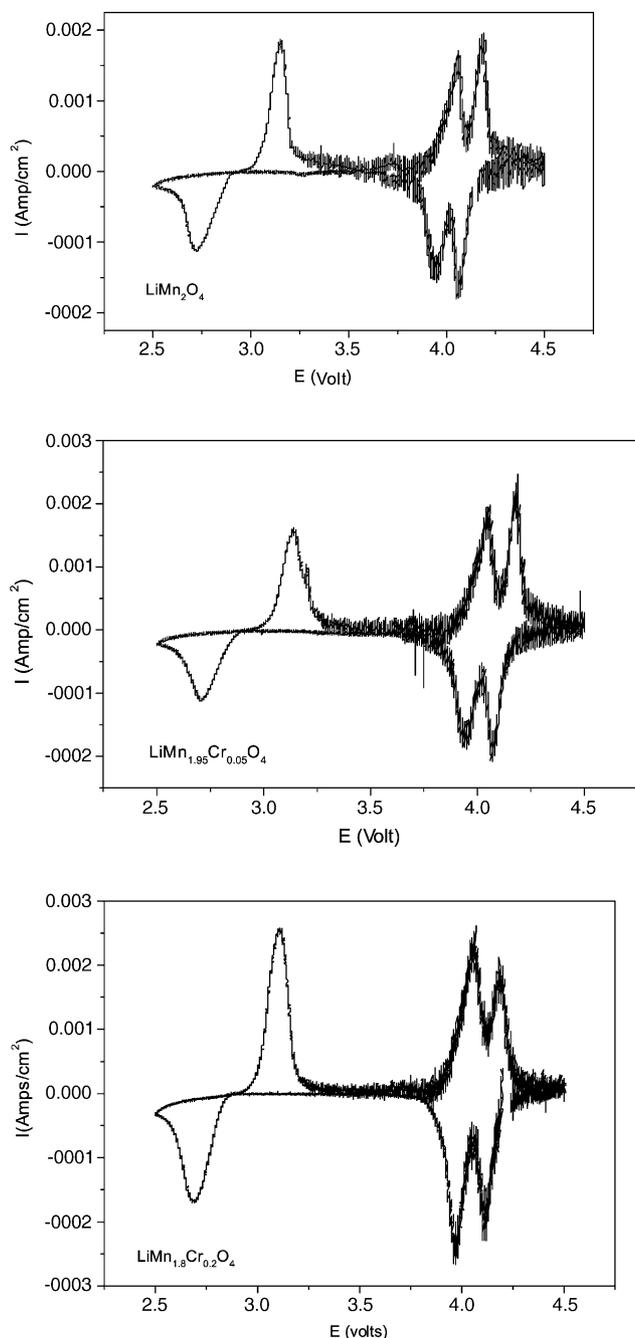


Fig. 4. Cyclic voltanimogram of  $\text{LiMn}_{2-x}\text{Cr}_x\text{O}_4$  ( $x = 0, 0.05, 0.2$ ).

voltage plateaus is smeared out with increasing of Cr substitution.

In this study, it is found that the capacity-discharging distribution is changed with Cr doping (see Table 2). The capacity discharged above 4.0 V is about 58, 48 and 37 mAh/g for the first cycle in  $\text{LiMn}_2\text{O}_4$ ,  $\text{LiMn}_{1.95}\text{Cr}_{0.05}\text{O}_4$  and  $\text{LiMn}_{1.8}\text{Cr}_{0.2}\text{O}_4$ , and decreases to 36, 35 and 36 mAh/g in the 100th cycle. Correspondingly, the capacity discharged below 4.0 V is 63, 69, 71 mAh/g for the first cycle in  $\text{LiMn}_2\text{O}_4$ ,  $\text{LiMn}_{1.95}\text{Cr}_{0.05}\text{O}_4$  and  $\text{LiMn}_{1.8}\text{Cr}_{0.2}\text{O}_4$  and they are decreased to 57, 60 and 63 mAh/g. It indicates that the

most of capacity loss due to cycling occurs at the higher voltage. Similar results were reported and attributed to the electrochemical oxidation of electrolyte solvent molecules at the end of charging period ( $>4.1$  V), causing capacity failing of  $\text{LiMn}_2\text{O}_4$  [14–16]. Therefore, substitution of Cr reduces such a loss and improves the cycleability of  $\text{LiMn}_2\text{O}_4$ .

Fig. 4 gives the cyclic voltammetry of  $\text{LiMn}_2\text{O}_4$  and  $\text{LiMn}_{1.8}\text{Cr}_{0.2}\text{O}_4$ . There is not clear difference for  $\text{LiMn}_2\text{O}_4$  with and without Cr-doping. It is consistent with the result for the same kind of material by normal sol-gel method [17]. However, from discharge characteristics mentioned above, it seems that the two sets of redox peaks around 4 V should be also certainly smeared. The different influence of Cr in cyclic voltammetry and discharge experiments needs to be examined further.

#### 4. Conclusion

The spinel  $\text{LiMn}_{2-x}\text{Cr}_x\text{O}_4$  ( $x = 0, 0.01, 0.05, 0.1, 0.2$ ) with nanometer and sub-micrometer size can be synthesized by a modified citrate route with combustion, which is time- and cost-saving. Cr-doped samples show better cycleability than pure  $\text{LiMn}_2\text{O}_4$ , because it depresses the capacity loss of  $\text{LiMn}_2\text{O}_4$  at high voltage plateau.

#### References

- [1] G.G. Amatucci, N. Pereira, T. Zheng, I. Plitz, J.M. Tarascon, J. Power Sources 81/82 (1999) 39–43.
- [2] G. Pistoia, Solid State Ion. 58 (1992) 285–292.
- [3] Yo. Xia, N. Kumada, M. Yoshio, J. Power Sources 90 (2000) 135–138.
- [4] S.-H. Kang, J.B. Goodenough, J. Electrochem. Soc. 147 (2000) 3621–3627.
- [5] A.D. Roberston, S.H. Lu, W.F. Averill, W.F. Howard Jr., J. Electrochem. Soc. 144 (1997) 3500–3512.
- [6] L. Guoha, H. Ikuta, T. Uchida, M. Wakihara, J. Electrochem. Soc. 143 (1996) 178–182.
- [7] H. Park, J. Kim, C. Lee, J. Power Sources 92 (2001) 124.
- [8] E.I. Santiago, S.T. Amancio-Filho, P.R. Bueno, L.O.S. Bulhoes, J. Power Sources 97/98 (2001) 447–449.
- [9] W. Yang, Q. Liu, W. Qiu, S. Lu, L. Yang, Solid State Ion. 121 (1999) 79–84.
- [10] W. Liu, G.C. Farrington, F. Chaput, B. Dunn, J. Electrochem. Soc. 143 (1996) 879–884.
- [11] Y.K. Sun, Solid State Ion. 100 (1997) 115–125.
- [12] J.M. Tarascon, W.R. Mckinnon, F. Coowar et al., J. Electrochem. Soc. 141 (1994) 1421–1431.
- [13] V. Manev, A. Momchilov, A. Nassalevska, A. Sato, J. Power Sources 54 (1995) 323–328.
- [14] D.H. Jang, Y.J. Shin, S.M. Oh, J. Electrochem. Soc. 143 (1996) 2204–2211.
- [15] D.H. Jang, S.M. Oh, J. Electrochem. Soc. 144 (1997) 3342–3348.
- [16] J.H. Lee, J.K. Hong, D.H. Jang, J. Power Sources 89 (2000) 7–14.
- [17] G.X. Wang, D.H. Bradhurst, H.K. Liu, S.X. Dou, Solid State Ion. 120 (1999) 95–101.