

Figure 3. Cyclic voltammogram of Li/LiFe<sub>x</sub>Mn<sub>2-x</sub>O<sub>4</sub> (y=0.0, 0.25, 0.5) cell.

of Mn<sup>3+</sup> ( $t_{2g}^3 e_g^1$ ) in the  $e_g$  orbital is repulsing 2O<sup>2-</sup> ions along the z-axis and then Jahn-Teller distortion occurs in spinel LiMn<sub>2</sub>O<sub>4</sub>. If high spin ( $t_{2g}^3 e_g^2$ ) of Fe<sup>3+</sup> which does not induce Jahn-Teller distortion is substituted for Mn<sup>3+</sup>, total Jahn-Teller distortion of the host structure may be reduced. Therefore, the cubic structure will be stabilized by Fe<sup>3+</sup> substitution.

The phase transition of cathode material due to lithium intercalation/deintercalation was investigated by cyclic voltammetry. The cyclic voltammogram is acquired 10 mV/h scan rate in the voltage range of 3.5-4.3 V. The cyclic voltammogram for Li/LiFe<sub>x</sub>Mn<sub>2-x</sub>O<sub>4</sub> is given in Figure 3. In LiMn<sub>2</sub>O<sub>4</sub>, the oxidation peaks are located near 4.0 and 4.15 V, respectively. The electrochemical peaks become much broader and put together as Fe content increases. The

results of CV curve are shown for both oxidation and reduction process in Li/LiMn<sub>2</sub>O<sub>4</sub> cell biphas gradually becomes single phase as Fe is substituted for Mn. Therefore, the substitution of Fe in LiMn<sub>2</sub>O<sub>4</sub> may enhance the cycling performance of lithium manganese oxides.

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## Electrochemical Performance of Chromium Substituted Spinel Lithium Manganese Oxides

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Spinel LiMn<sub>2</sub>O<sub>4</sub> is the most attractive cathode material for the rechargeable lithium batteries due to good performances such as high specific energy and high voltage (~4 V) and its economical and environmental advantages compared to other cathode materials. When lithium content is  $0 \leq x \leq 1$  in Li/Li<sub>x</sub>Mn<sub>2-x</sub>O<sub>4</sub> cells, the cells discharge at ~4 V for lithium, whereas when  $1 < x \leq 2$ , the cells discharge at ~3 V.<sup>1-3</sup> LiMn<sub>2</sub>O<sub>4</sub> which is prepared at 300-400 °C shows a good performance at 3 V than at 4 V.<sup>4</sup> At 700-900 °C, it shows better at 4 V than at 3 V.<sup>5,6</sup> But the capacity of LiMn<sub>2</sub>O<sub>4</sub> is decreased more rapidly as the charge/discharge cycles are repeated in Li<sub>x</sub>Mn<sub>2-x</sub>O<sub>4</sub> ( $0 \leq x \leq 1$ ) than that of LiCoO<sub>2</sub>, which is competitive cathode material.<sup>7</sup>

Tarascon *et al.* reported that the cations of valence 2 or 3 substituted LiM<sub>x</sub>Mn<sub>2-y</sub>O<sub>4</sub> reduced the capacity of the cells at 4.1 V, but did not affect their cycling performance.<sup>8</sup> Another researcher reported that the cobalt-doped LiCo<sub>x</sub>Mn<sub>2-x</sub>O<sub>4</sub> improved cycling behavior.<sup>9</sup>

For a long time, it was impossible to charge LiMn<sub>2</sub>O<sub>4</sub> at high voltage (~4.4 V) due to oxidation of electrolytes. However, recent discovery of a high voltage oxidation-resistant electrolyte, ethylene carbonate(EC)-propylene carbonate(PC)-dimethyl carbonate(DMC)-lithium hexafluoro phosphate (LiPF<sub>6</sub>) opened a way to study high voltage performance.<sup>10,11</sup> This work report the performance of Cr substituted spinel manganese oxide in a range of 3.4-5.2 V.

## Experimental

$\text{LiCr}_x\text{Mn}_{2-x}\text{O}_4$  ( $0 \leq x \leq 0.5$ ) compounds were prepared from stoichiometric mixtures of  $\text{Cr}_2\text{O}_3$ , chemically prepared  $\text{MnO}_2$  (CMD), and  $\text{Li}_2\text{CO}_3$ . The mixtures were calcined at  $600^\circ\text{C}$  in air for 5 hrs. and reground. The powder was pelleted and sintered at  $750^\circ\text{C}$  in air for 24 hrs, followed by slow cooling at the rate of  $1^\circ\text{C}/\text{min}$  in furnace. The sintering was repeated once more. All compounds which have spinel structure were confirmed by X-ray diffraction analysis. Unit cell parameters were obtained from powder X-ray diffraction data which was collected by a X-ray diffractometer 18 kW (MAC-Science Co. Ltd.) with  $\text{Cu-K}\alpha$  radiation.

Electrochemical properties of  $\text{LiCr}_x\text{Mn}_{2-x}\text{O}_4$  were investigated using a galvanic cell, which consists of lithium metal anode, 1M  $\text{LiPF}_6$  in EC(ethylene carbonate)+DMC (dimethyl carbonate) (2:1 in volume ratio) electrolyte, and lithium metal oxide cathode. The cathode was mixture of 89% (wt.%)  $\text{LiCr}_x\text{Mn}_{2-x}\text{O}_4$ , 10% acetylene black for improving conductivity, and 1% PTFE (polytetrafluoroethylene) as binder. The MacPile II Galvanostatic system was used for galvanic measurement. Galvanic data were obtained under condition of constant current, 265  $\mu\text{A}$  and voltage range of 3.4-5.2 V.

## Results and Discussion

The unit cell parameters of each compound were obtained from X-ray diffraction data using least-square method. The cubic lattice parameter  $a(\text{\AA})$  of  $\text{LiCr}_x\text{Mn}_{2-x}\text{O}_4$  decreases slightly as the substituted Cr contents increase (Figure 1). Shannon and Prewitt reported that the crystal radii of  $\text{Cr}^{3+}$ ,  $\text{Mn}^{3+}$ , and  $\text{Mn}^{4+}$  are 75.5 pm, 78.5 pm, and 67 pm, respectively.<sup>12</sup> This fact support that  $\text{Cr}^{3+}$  can be substituted for  $\text{Mn}^{3+}$  in general. Also the substitution  $\text{Cr}^{3+}$  for  $\text{Mn}^{3+}$  reduced the Jahn-Teller effect related with  $\text{Mn}^{3+}$  in high spin state of  $d^4$  electron configuration, and then the local distortion of spinel  $\text{LiMn}_2\text{O}_4$  may be reduced.

Figure 2 shows the voltage variation as a function of capacity for  $\text{Li}/\text{LiCr}_x\text{Mn}_{2-x}\text{O}_4$  cell. Usually the first charge of electrochemical cell shows a non-equilibrium state originating from the condition of test-cell, sample, and so on. This is a main factor that the electrochemical properties of

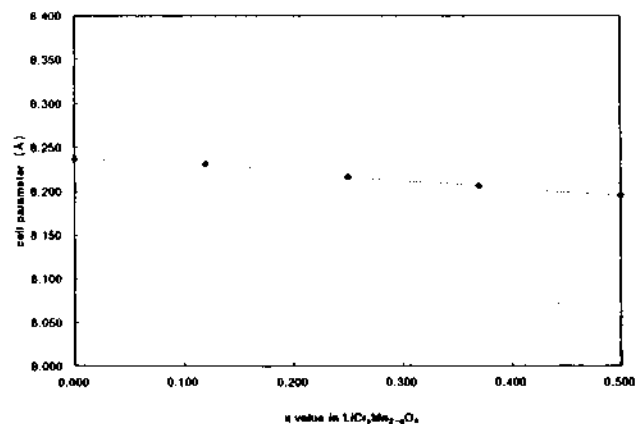


Figure 1. The lattice parameters for  $\text{LiCr}_x\text{Mn}_{2-x}\text{O}_4$  ( $0.0 \leq x \leq 0.5$ ).

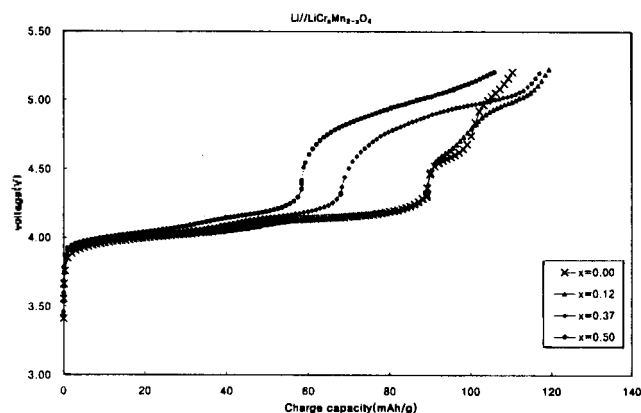


Figure 2. The charge capacities of  $\text{Li}/\text{LiCr}_x\text{Mn}_{2-x}\text{O}_4$ .

pure spinel compound are hardly investigated. Therefore, the first discharge and second charge were selected for the observation of the characteristics for the pure compounds.

As shown in Figure 2, ~82% of the observed capacity in  $\text{LiMn}_2\text{O}_4$  was appeared in a range of 3.5-4.3 V. Two plateaus were observed at 4.05 V and 4.15 V in agreement with literature.<sup>13</sup> Another plateau observed at 4.5 V, which implies the applicability in higher voltage range (above 4.0 V). As Cr content increases, the capacity in a range of 3.4-4.3 V decreases, while the capacity in a range of 4.3-5.2 V increase. The variation of total capacities for  $\text{LiCr}_x\text{Mn}_{2-x}\text{O}_4$  between 3.4 V and 5.2 V is very small. The capacity of high voltage range (4.3-5.2 V) are increased with  $x$  and saturated at  $x \geq 0.37$ .

The plateau in high voltage range was moved from 4.5 V in  $\text{LiMn}_2\text{O}_4$  to about 5 V in  $\text{LiCr}_x\text{Mn}_{2-x}\text{O}_4$ . To prove this phenomenon, the detailed structural analysis will be executed. The same behavior appeared in discharge when lithium is intercalated into metal oxide (Figure 3). This confirms that the electrochemical reaction of  $\text{Li}/\text{LiCr}_x\text{Mn}_{2-x}\text{O}_4$  in 3.4-5.2 V range is reversible. But for  $x=0.5$ , voltage drop is larger than those of other compounds and then the discharge voltage in case of  $x=0.5$  was lower than that of  $x=0.37$ . Especially when the substituted Cr contents is 0.12, it shows larger capacity than that of  $\text{LiMn}_2\text{O}_4$  in 4.3-5.2 V range, but the capacity in 3.4-4.3 V range was almost the same as that of  $\text{LiMn}_2\text{O}_4$ .

Consequently, substitution of Cr for Mn in  $\text{LiMn}_2\text{O}_4$  reduced a unit cell parameter and increased the capacity of

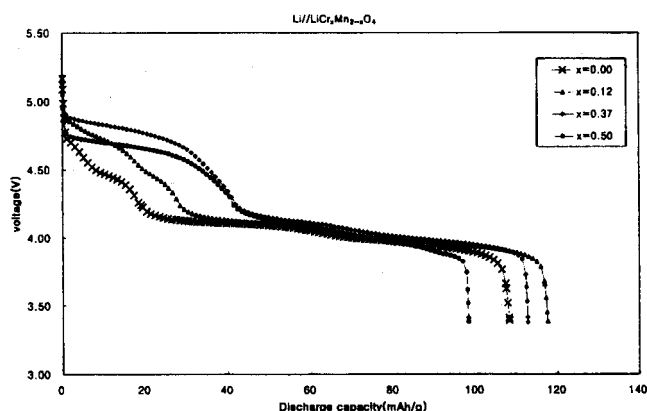


Figure 3. The discharge capacities of  $\text{Li}/\text{LiCr}_x\text{Mn}_{2-x}\text{O}_4$ .

high voltage range. In addition, the plateau between 4.3 V and 5.2 V raised from 4.5 V to ~5 V.

### References

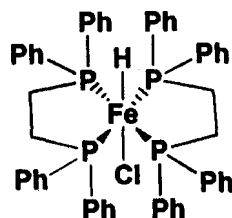
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## Structure of *trans*-Chlorohydrido-bis(diphenylphosphinoethane)iron(II)

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Reductive elimination of hydrogen chloride from chlorohydrido transition metal complexes of the type  $L_nMHCl$  has got continuous interest, because it leads to generation of electron-rich, coordinatively unsaturated complexes with a metal in a low oxidation state.<sup>1</sup> Although the title complex, which is shown below, was prepared a couple of decades ago<sup>2</sup> and its reactions have been extensively studied,<sup>3</sup> its 3-dimensional crystal structure has not been reported yet. Herein we report the molecular structure of *trans*-chlorohydrido-bis(diphenylphosphinoethane)iron(II), *trans*-FeHCl(dppe)<sub>2</sub>, [dppe = Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>].



### Experimental

The title compound was prepared by the literature method.<sup>2</sup> This compound was recrystallized from benzene/diethyl ether. X-ray data were collected with use of a Mac Science MXC diffractometer equipped with an Mo X-ray tube and a graphite crystal monochromator. Details on crystal data and intensity data are given in Table 1. The orientation matrix and unit cell parameters were determined by least-squares analyses of the setting angles of 20 reflections in the range  $20.0^\circ < 2\theta < 30.0^\circ$ . Two check reflections were measured

**Table 1.** X-ray data collection and structure refinement for *trans*-FeHCl(dppe)<sub>2</sub>

Formula	C <sub>22</sub> H <sub>40</sub> P <sub>4</sub> ClFe
Fw	889.09
Temperature (K)	293
Crystal system	Monoclinic
Space group	P2 <sub>1</sub> /n
a, Å	17.209(6)
b, Å	24.425(7)
c, Å	10.696(4)
β, deg	99.98(4)
V, Å <sup>3</sup>	4428(3)
Z	4
d <sub>calc</sub> , g cm <sup>-3</sup>	1.334
μ, mm <sup>-1</sup>	0.581
F(000)	1856
Scan speed	Variable
2θ range (°)	3.4-46.0
Range of hkl	0 ≤ h ≤ 18, 0 ≤ k ≤ 26, -11 ≤ l ≤ -11
No. of reflections measured	5427
No. of reflections with I > 2σ(I)	5266
No. of parameters refined	523
Max. Δ/σ	0.004
Max., min. in Δρ (eÅ <sup>-3</sup> )	0.701, -0.341
S (goodness-of-fit on F <sup>2</sup> )	1.024
R	0.0535
wR <sub>2</sub> <sup>a</sup>	0.1148

$$^a wR_2 = \{[\sum (w(F_o^2 - F_c^2)^2)] / \sum (w(F_o^2)^2)\}^{1/2}$$