

**STRUCTURAL AND IONIC BOND STRENGTH INVESTIGATION USING  
PAULING ESB RULES OF NONSTOICHIOMETRIC SPINEL  
COMPOUNDS  $\text{Li}_x\text{Mn}_2\text{O}_4$  AND STOICHIOMETRIC  
 $\text{Li}_{1+y}\text{Mn}_{2-y}\text{O}_4$ , AS CATHODE MATERIALS FOR  
RECHARGEABLE LITHIUM-ION  
BATTERIES\***

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**Abstract** – In this paper we present our studies using Pauling electrostatic bond strength (ESB) rules for structural behaviour, cation vacancies, relation between  $x$ ,  $y$ , and the valence of cations and coordination in spinel compounds  $\text{Li}_x\text{Mn}_2\text{O}_4$ ,  $0 < x < 1$  and  $\text{Li}_{1+y}\text{Mn}_{2-y}\text{O}_4$ ,  $0 < y < 1/3$ , which are of interest as the positive electrodes for rechargeable lithium-ion batteries.

**Keywords** – Lithium-ion battery, pauling's E. S. B. rules, spinel

## 1. INTRODUCTION

In order to have a large initial capacity and a low capacity fading, the spinel phases of lithium manganese oxide has been one of the most promising cathode materials for high energy density lithium batteries [1, 2] due to its high electrode potential and low molecular weight. Manganese dioxide ( $\text{MnO}_2$ ) was developed as a cathode material for primary lithium batteries, but the lithiated spinel version ( $\text{Li}_x\text{Mn}_2\text{O}_4$ ) has been studied during the last few years for rechargeable lithium batteries of high energy density utilised in cellular phones, Lap-Top computers and portable cameras.  $\text{LiMn}_2\text{O}_4$ , or actually  $\text{Li}_x\text{Mn}_2\text{O}_4$ , can intercalate lithium at a high voltage (4V vs  $\text{Li}/\text{Li}^+$ ) with a good reversibility [3, 4], hence the spinel system is being developed for 4V rechargeable lithium cells. However, the material often shows a capacity loss during extended cycling [5, 6]. Rechargeability of this spinel phase strongly depends on both the stoichiometry and the preparation conditions of the spinel [7, 8]. It has been reported that the capacity retention during cycling can be improved by adding a small excess of Li to the stoichiometric  $\text{LiMn}_2\text{O}_4$  in order to form  $\text{Li}_{1+y}\text{Mn}_{2-y}\text{O}_4$  ( $y \sim 0.05$ ). Note that this is still a stoichiometric spinel, but here the extra ( $y$ ) Li-ions reside on octahedral sites. Also note that the Mn valency changes upon exchanging Mn by Li.  $\text{LiMn}_2\text{O}_4$  has a theoretical capacity value of 148 mAh/g, based on full de-intercalation of the Li, i.e. down to  $\text{Mn}_2\text{O}_4$ , but the practically obtained values are close to 105-115 mAh/g [9, 10]. Lithium insertion into  $\text{Li}_{1+y}\text{Mn}_{2-y}\text{O}_4$ , i.e. leading to  $\text{Li}_2\text{Li}_{1+y}\text{Mn}_{2-y}\text{O}_4$ , induces a phase transition from spinel to a tetragonal phase. Particularly at low  $y$ -values, the insertion of extra lithium may cause the transition which is a

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significant problem causing fading [11-13]. The formation of the tetragonal phase will not be discussed here.

## 2. EXPERIMENTAL

Various samples were prepared from MnO or MnO<sub>2</sub> (Alfa) and Li<sub>2</sub>CO<sub>3</sub> (Carlo Erba). Thereto, the stoichiometric mixtures were fired in air at temperatures from 600 to 1000 °C. Successive treatments for 8h at 900 °C and 1h at 1100 °C were performed.

X-ray Diffraction powder data were obtained at room temperature using a Philips PW 1710 powder diffractometer with CuK<sub>α</sub> radiation monochromated by graphite crystal. Patterns were collected in the range  $12^\circ \leq 2\theta \leq 100^\circ$  and the scanning rate was  $2^\circ (2\theta)/\text{min}$ . The electrochemical test cells used were as reported in previous papers [14, 15].

## 3. RESULTS AND DISCUSSION

X-ray diffraction data reveal the cubic system with spinel structure, i.e. the space group Fd3m, lattice constants 8.05 and 8.25 Å, for both Li<sub>x</sub>Mn<sub>2</sub>O<sub>4</sub>,  $0 < x < 1$  and LiLi<sub>y</sub>Mn<sub>2-y</sub>O<sub>4</sub>,  $0 < y < 1/3$ . The unit cell contains 8 formula units; 32 Oxygen, 64 tetrahedral sites (8a, 8b, Mn  $\frac{1}{8}, \frac{1}{8}, \frac{1}{8}$  48f) and 32 octahedral sites (16c, 16d) having atomic positions: Li(8a), 0.26. A typical unit cell part of the spinel is  $\cong$ , and O (32e), u, u, u, and u  $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$  (16d), given in Fig. 1.

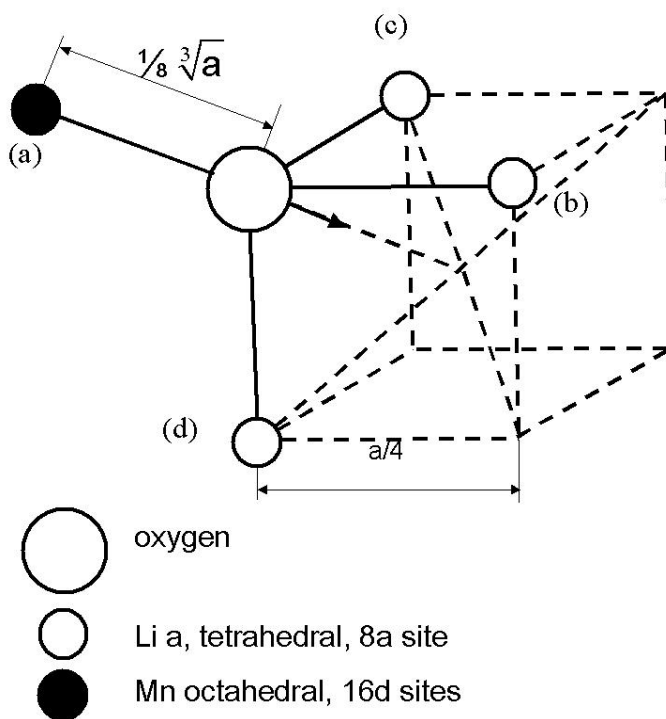


Fig.1. Elementary part of the unit cell of a spinel

The atomic configuration and atomic position for a spinel structure is as follows:

Extracted form:  $(Li_x^I)[4]8a(Mn^{III}_{1-x} Mn^{IV})[6]16dO_{32e}$   $0 < x < 1$

Exchanged form:  $(Li_x^I)[4]8a(Li_y^I Mn^{III}_{x-3y} Mn^{IV}_{2+2y-x})[6]16dO_{32e}$   $0 < y < 1/3, 0 < x < 1-3y,$

In the case of  $y=1/3$ , all the Mn-ions on the octahedral site are tetravalent.

The Pauling electrostatic valency rules and bond strength for ionic crystals for the spinel according to the extracted form are as follows:

$$ESB = \frac{\text{Charge of cation}}{\text{coordination number}}, p = \frac{z}{n}, \text{ Charge of anion} = \sum \frac{z}{n}, [16] \quad (1)$$

$$\frac{Li_{8a}}{1 - (1-x)} + \frac{Mn^{III}_{16d}}{3 + (1-x)} + \frac{Mn^{III,VI}_{16d}}{3 + (1-x)} \left[ \frac{(+)}{2} \right] + \frac{Mn^{III}_{16d} O_{32e}^{cep}}{4} + \frac{4}{6} = 2 \quad (2)$$

(c)                      (d)                      (b)                      (a)

Typical Pauling ESB rules for  $x=0, 0.5,$  and  $1$  are given in Table 1.

Table 1. Relation between  $x$ , charge of cation and coordination of  $Li_xMn_2O_4$ ,  $x=0, 0.5, 1$

Material	$x$	Pauling ESB rules	Charge of oxygen
$\lambda Mn_2O_4$	0	$0 + \frac{4}{6} + \left[ \left( \frac{4}{6} + \frac{4}{6} \right) / 2 \right] + \frac{4}{6}$	2
$Li_{0.5}Mn_2O_4$	0.5	$\frac{0.5}{4} + \frac{3.5}{6} + \left[ \left( \frac{3.5}{6} + \frac{4}{6} \right) / 2 \right] + \frac{4}{6}$	2
$LiMn_2O_4$	1	$\frac{1}{4} + \frac{3}{6} + \left[ \left( \frac{3}{6} + \frac{4}{6} \right) / 2 \right] + \frac{4}{6}$	2

With this hypothesis the voltage profile from 3.5 to 4.2 V as shown in Fig. 2 could be interpreted in terms of the extracted  $Li_xMn_2O_4$  electrode type, of which  $0 < x < 1$ .

In the formation of  $Li_xMn_2O_4$  spinel products, the extracted form, in which Li ions occupy only the tetrahedral 8a sites of the spinel and all the Mn-ions occupy the octahedral 16d sites (viz. Eq. (2)) with the cation distribution, a, b, c and d, the Pauling bond strength for this configuration is:

$$ESB (a) < ESB (b) < ESB (c) < ESB (d)$$

During extraction,  $Li^+$  ions are removed from the tetrahedral sites, over a voltage range from 3.8 to 4.2. The  $Mn^{III}$  ions on the octahedral sites, position b and c in Eq. (2), are oxidised to  $Mn^{IV}$ , and clearly, the ESB of  $Mn^{IV}$  is stronger than that of  $Mn^{III}$ . The structure shrinks, and lithium tetrahedral vacancies remain,  $V_{Li}^{\cdot}$  (note that Kröger Vink notation has been used to describe the defects), and so a decrease of the lattice parameter is expected. Therefore, the amount of lithium ions, represented by  $x$  in the notation  $(Li_x^I)[4]8a(Mn^{III}_{1-x} Mn^{IV}) [6]16dO_{32e}$ , is analysed by the lattice constant. Fig. 3 reports the X-Ray (331) peaks of  $Li_xMn_2O_4$  with different lithium amounts,  $0 < x < 1$ , during the first charge. Cation vacancies are related to the cathode potential [12], and therefore the potential behaviour of Fig. 2 can be explained.

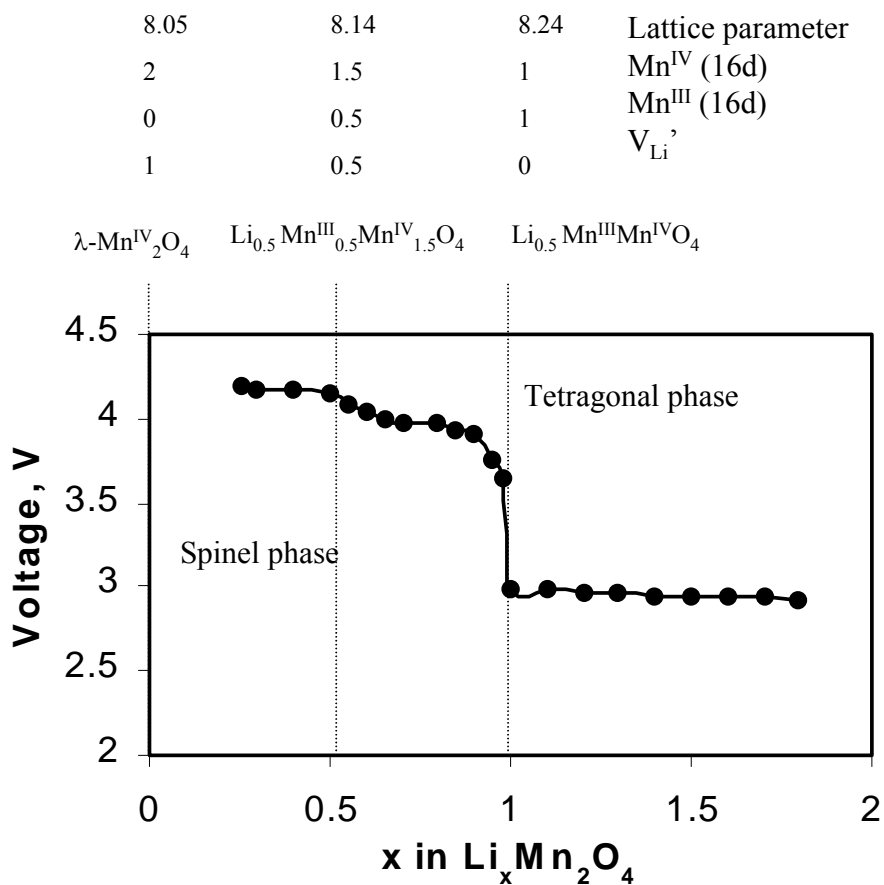


Fig. 2. Electrochemical Voltage profile of the  $\text{Li}_x\text{Mn}^{\text{III}}_{1-x}\text{Mn}^{\text{IV}}_{1+x}\text{O}_{32e}$

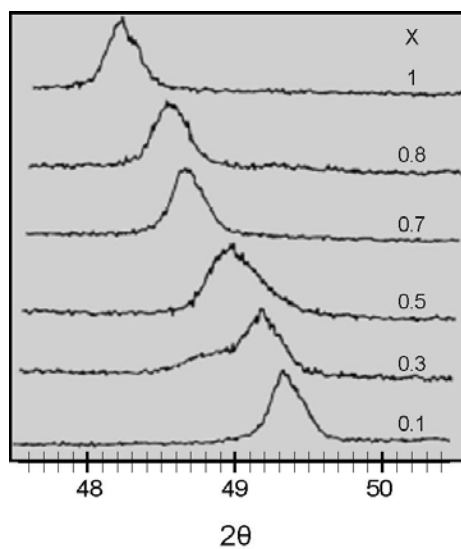


Fig. 3. XRD pattern of the (331) peak of  $\text{Li}_x\text{Mn}^{\text{III}}_{1-x}\text{Mn}^{\text{IV}}_{1+x}\text{O}_{32e}$  for various x

Paulings ESB rules for the spinel  $\text{LiLi}_y\text{Mn}_{2-y}\text{O}_4$ , i.e. the exchanged form, can be represented by:

$$\frac{1}{4} + \frac{(4-3y)-(1-3y)}{6} + \left[ \left( \frac{(4-3y)-(1-3y)}{6} + \frac{4}{6} \right) / 2 \right] + \frac{4}{6} = 2 \quad (3)$$

In Eq. (3) the relationship between the charge of Li,  $\text{Mn}^{\text{III}}$  ( $1-3y$ ),  $\text{Mn}^{\text{IV}}$  ( $1+2y$ ), the position and the coordination are shown. Table 2 lists the results of the ESB rules for the exchanged form.

Table 2. Relation between  $y$ , charge of cations and coordination of  $\text{Li}(\text{Li}_y\text{Mn}_{2-y})\text{O}_4$ ,  $y=0.1$  and  $0.2$

$y$	Li 8a		LiMn <sup>III,IV</sup> 16d		LiMn <sup>III</sup> Mn <sup>IV</sup> 16d		Mn <sup>IV</sup> 16d
0.1	$\frac{1}{4}$	+	$\frac{(4-0.3)-(1-0.3)}{6}$	+	$\left[ \frac{(4-0.3)-(1-0.3)}{6} + \frac{4}{6} \right] / 2$	+	$\frac{4}{6}$
0.2	$\frac{1}{4}$	+	$\frac{(4-0.3)-(1-0.3)}{6}$	+	$\left[ \frac{(4-0.6)-(1-0.6)}{6} + \frac{4}{6} \right] / 2$	+	$\frac{4}{6}$

In this configuration, Li ions are distributed over both tetrahedral and octahedral sites. For  $x=1$ , all the Li ions occupy the 8a tetrahedral sites, thus there is no lithium vacancy on the 8a sites. In the case of  $y>0$ , this fraction of lithium reside on the octahedral 16d sites, i.e. exchanging a Mn-ion, and in order to maintain charge balance, two  $\text{Mn}^{\text{III}}$  ions are oxidised to two  $\text{Mn}^{\text{IV}}$ . Figure 4 shows the dependences of the  $\text{Mn}^{\text{III}}$ ,  $\text{Mn}^{\text{IV}}$  concentrations on the  $y$  fraction of lithium calculated using the exchanged form formula.

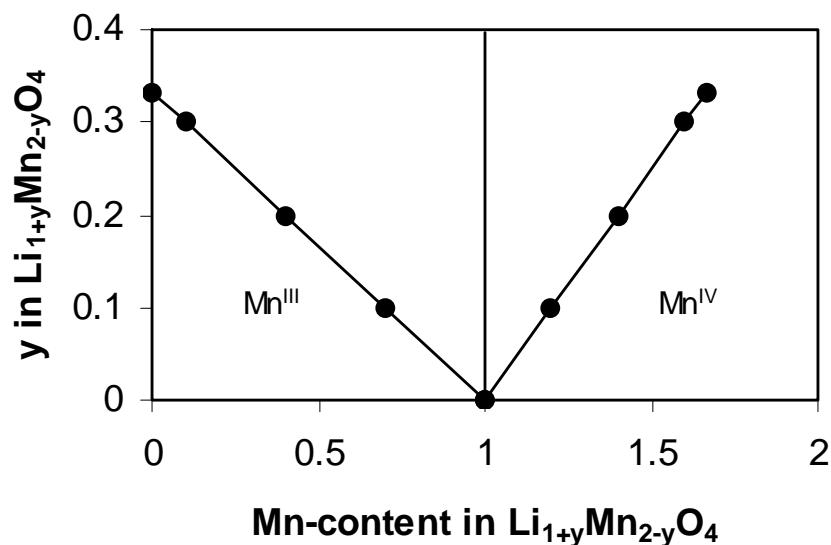


Fig. 4.  $\text{Mn}^{\text{III}}$  and  $\text{Mn}^{\text{IV}}$  content as a function of  $y$  in  $\text{Li}(\text{Li}_y\text{Mn}_{2-y})\text{O}_4$

For the Pauling ESB rules we can derive:

$$\text{ESB} \frac{\text{Mn}^{\text{IV}}}{6} > \text{ESB} \frac{\text{Mn}^{\text{III}}}{6}$$

It is clear that the trivalent  $\text{MnO}_6$  volume is higher than the tetravalent  $\text{MnO}_6$  volume, which results in a contraction of the structure. Substitution/exchanging the 16d octahedral Mn-ions for Li, i.e. in  $\text{Li}[\text{Li}_y(\text{Mn}^{\text{III}}\text{Mn}^{\text{IV}})_{2-y}]\text{O}_4$ , results in a decrease of the lattice parameter with increasing  $y$ . The amount of lithium exchanged is presented in Fig. 5 and Fig. 2 by the lattice parameter obtained by XRD; lithium concentrations of  $x=1$  and  $0.2 > y > 1$  are shown.

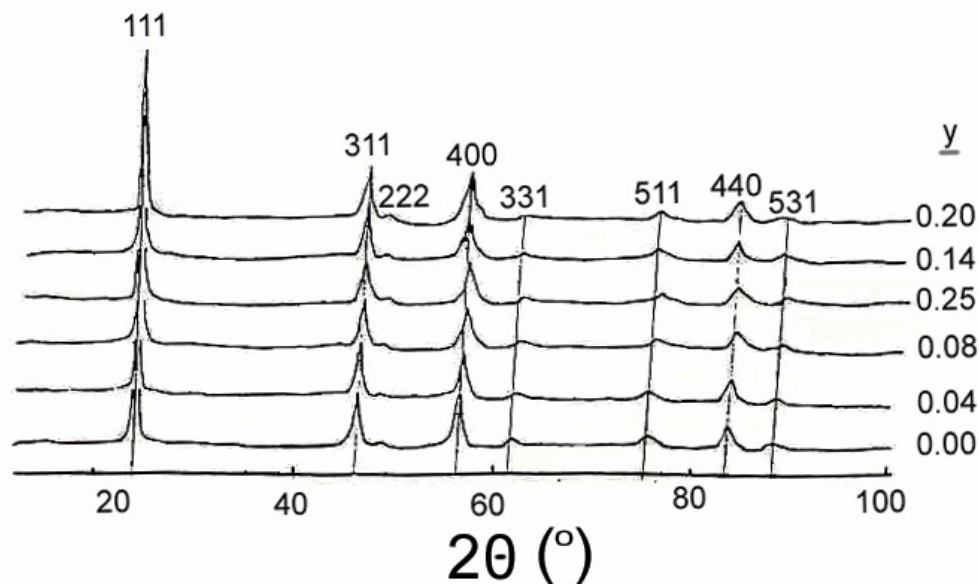


Fig. 5. XRD patterns with different  $y$  values in  $\text{Li}(\text{Li}_y\text{Mn}_{2-y})\text{O}_4$

A Li/electrolyte/spinel cell operates at approximately 4V over the range of  $0 < x < 1$  and at approximately 3V if  $1 > x > 2$ . In the case of  $y > 0$ , the theoretical capacity drops significantly as the  $\text{Mn}^{\text{III}}$  concentration drops rapidly, i.e. the average Mn-valency  $Z$  can be calculated by  $Z = \frac{7-y}{2}$ .

The present results show two different behaviours in the two composition ranges in  $(\text{Li}_x^{\text{I}})^{[4]}_{8a}(\text{Li}_y^{\text{I}}\text{Mn}^{\text{III}}_{1-x-3y}\text{Mn}^{\text{IV}}_{2y})^{[6]}_{16d}\text{O}_{32e}$ ;

1:  $0 < x < 1$  and  $y=0$ , the lattice parameter depends on  $x$  and refers to vacancies on the tetrahedral 8a sites, with the Li vacancy concentration  $V_{\text{Li}} = 1-x$ , and which can be understood by the Pauling ESB rules.

2:  $x=0$  and  $0 > y > 1/3$ , a lattice contraction is explained by an increase of  $\text{Mn}^{\text{IV}}$ , which can also be understood from the Pauling ESB rules.

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