

## chemistry and structure

Effect of doping  $\text{LiMn}_2\text{O}_4$  spinel on its use as cathodes in Li-ion batteries

$\text{LiMn}_2\text{O}_4$  spinel is a promising cathode material for Li-ion batteries, and doping it with small amounts of other metal ions has a remarkable effect on its electrochemical properties. In order to elucidate the relationship between structure and the electrochemical performance of doped compounds, with the general formula  $\text{Li}_{1-y}\text{Mn}_{2-x}\text{M}'_x\text{O}_4$  ( $x \leq 0.1$ ;  $y \leq 0.02$ ,  $\text{M}' = \text{dopant metal ion}$ ), powder neutron diffraction experiments have been coupled with electrochemical data. Whereas the capacity of the spinels doped with trivalent metal ions is much greater, cyclic fading properties are much enhanced with the use of divalent metal ions. It is suggested that the occupancy of the tetrahedral sites is critical to the improved structural stability on Li insertion/extraction, but that this ultimately hinders the movement of Li.

## The lithium rechargeable

battery based on  $\text{LiCoO}_2$  as a cathode, is today enjoying a great deal of commercial success as an energy storage device, particularly in the field of high performance portable electronics [1]. However, the search for enhanced cost-performance cathode materials represents an important goal, as  $\text{LiCoO}_2$  is relatively expensive and produces some environmental issues. In this respect,  $\text{LiMn}_2\text{O}_4$  has attracted considerable interest. Even though the performance of  $\text{LiMn}_2\text{O}_4$  based batteries remains inferior to other systems, they offer benefits in cost/performance characteristics.  $\text{LiMn}_2\text{O}_4$  crystallises in a cubic spinel structure,  $Fd-3m$  space group, where the lithium and manganese occupy the tetrahedral (8a) and the octahedral sites (16d), respectively, and the oxygen ions are located to the (32e) sites. Recent research has showed that the substitution of various trivalent ion dopants into the  $\text{LiMn}_2\text{O}_4$  framework makes significant improvements to the electro-

chemical performance [2-4].

In order to correlate the reduction of capacity on de/re-intercalation (cyclic fading profile) and structural parameters, we have studied a series of doped compounds of formula  $\text{Li}_{1-y}\text{Mn}_{2-x}\text{M}'_x\text{O}_4$  ( $x \leq 0.1$ ;  $y \leq 0.02$ ) by a combination of neutron diffraction measurements and electrochemical experiments [5]. The powder neutron diffraction technique is particularly sensitive to cation distribution in the crystalline lattice and the large contrast between the scattering length of transition metal ions and both lithium and manganese allows accurate location of the doping ions in the lattice despite their low concentration. The diffraction powder patterns were collected at room temperature on

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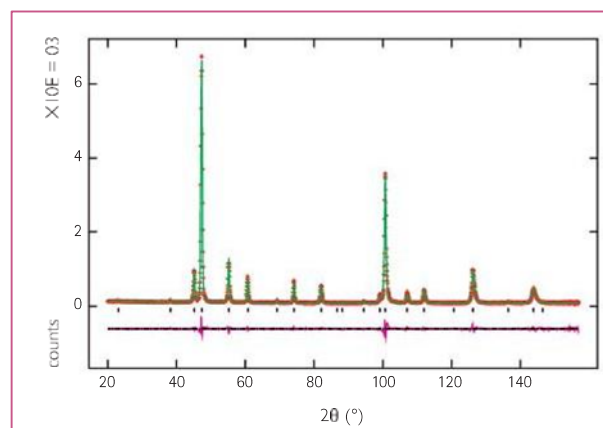
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the D1A diffractometer and the structural and profile analyses refinements were carried out by the Rietveld method (GSAS), (figure 1).

Doping the  $\text{LiMn}_2\text{O}_4$  spinel with small amounts of trivalent (figure 2) and divalent metal ions (figure 3) has a remarkable effect on the electrochemical characteristics. The Ni- and Ga/Cr doped systems show the best performance and at the same time they possess low fade rates ( $4.5 \cdot 10^{-2}$  mAh/g cycle) and higher capacities (111 and 117 mAh/g, respectively). However, whereas the absolute capacity of the Zn- and the Mg-doped spinel is lower (95 and 103 mAh/g, respectively), the cyclic fading performance is significantly better. This is thought to be associated with the occupancy of the tetrahedral sites by Zn and Mg [6].

Neutron diffraction analysis has confirmed the presence of Zn(II) ion on the tetrahedral sites of the spinel lattice, while all the other doping ions, irrespective of

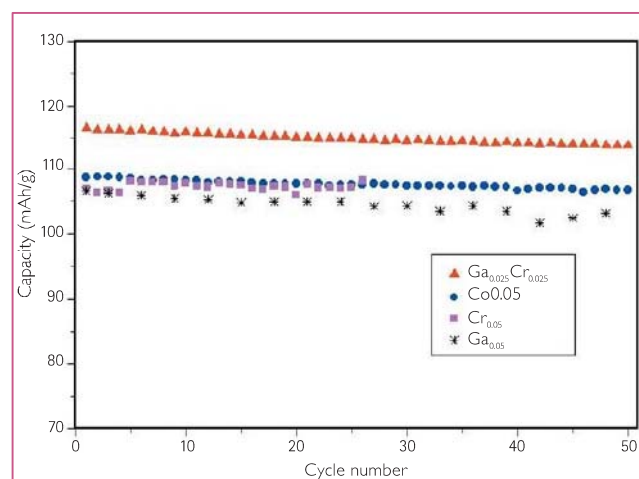


**Figure 1:** Neutron powder diffraction of  $\text{Li}_{1.02}\text{Mn}_{1.95}\text{Ni}_{0.05}\text{O}_4$  taken at room temperature, showing the (+) experimental data, calculated (solid line) and the difference.

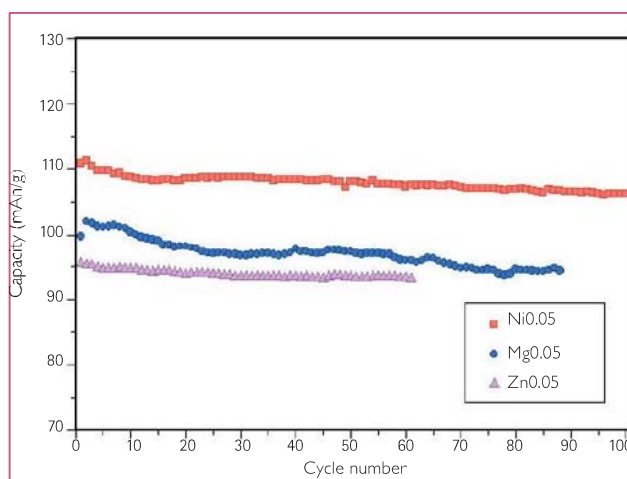
charge, are located on the octahedral sites ( $16d$ ). Incorporation of all of the doping ions, with the exception of the Ti(IV) ion, reduces the lattice parameter  $a$  with respect to the undoped one, while remaining in the  $Fd-3m$  space group. The A-site of the spinel is fully occupied by  $\text{Li}^+$  in all samples, except for those doped with Zn. In the latter, the Zn ions are confirmed to

remaining on the A site during electrochemical cycling and therefore acting as pillars supporting the lattice framework during Li removal. The capacity fading is lower for samples with the lower unit-cell parameters  $a$ . Divalent ions (Zn, Ni) provide the lowest cyclic fading, followed by trivalent ions (Co, Cr), and by Ga-doped material. The underlying reason behind

ordering of Zn ions occurs in the empty tetrahedral ( $8a$ ) site, which then hinders full Li re-insertion. The electrochemical behaviour of the Ti(IV)-doped material is similar to that observed in the undoped Mn spinel. This suggests that  $\text{Ti}^{4+}$  ion substitutes the  $\text{Mn}^{4+}$  ion in the spinel structure, and this accounts for the larger  $a$  parameter of Ti-doped spinel over that



**Figure 2:** Discharge capacities of M(III) ion doped spinels  $\text{Li}_{1.02}\text{Mn}_{2-x}\text{M}_x\text{O}_4$  ( $x < 0.05$ ), M(III) = Co, Cr, Ga and Ga/Cr; measured at room temperature and at  $C/2$  discharge-charge rate.



**Figure 3:** Discharge capacities of M(II)-ion doped spinels  $\text{Li}_{1.02}\text{Mn}_{2-x}\text{M}_x\text{O}_4$  ( $x < 0.05$ ), M(II) = Zn, Ni, Mg, measured at room temperature and at  $C/2$  discharge-charge rate.

reside also on the ( $8a$ ) sites [6]. For these Zn samples the excess Li is displaced on the octahedral ( $16d$ ) site. The substitution of Li in ( $8a$ ) with such divalent ions as Zn(II) and Mg(II) does bring about significant structural stability during electrochemical cycling. The average charge on the A-sites increases while the charge of the B-site decreases compared with the undoped sample. As each oxygen ion is coordinated with one A cation and three B cations, creating a distorted octahedron, then the increase in charge on the A site can alleviate the distortion. A second factor relates to the doping ions

the improved electrochemical properties with reduced lattice parameters may be related to the increased stability in the more compact and undistorted lattice, which is more resilient to the volume changes occurring during Li extraction/insertion. It should also be noted that the samples with the most attractive capacity properties have a 1<sup>st</sup>-cycle charge/discharge efficiency of 97-99%, indicating an easy reinsertion of extracted  $\text{Li}^+$ . However, the Zn containing samples have an efficiency of only 90%, thereby causing reduced capacity. It is probably that as  $\text{Li}^+$  is extracted, some

of the undoped one, and the ratio  $\text{Mn}^{3+}/\text{Mn}^{4+} \geq 1$  causes increased prominence of the Jahn-Teller effect and a poorer electrochemical performance.

In conclusion, with a combination of neutron powder diffraction and electrochemical experiments we have shown the relationship between the metal-ion site occupancy of doped  $\text{LiMn}_2\text{O}_4$  spinels and the electrochemical performance of these cathode materials in term of capacity and stability to the charge-discharge cycling.

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