

Reversible spinel to rock salt transition in LiCoMnO_δ by oxygen (de) intercalation

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LiCoMnO_4 with the spinel structure loses oxygen on heating in air above $\sim 570^\circ\text{C}$ and by $\sim 1050^\circ\text{C}$ reaches the approximate stoichiometry ' LiCoMnO_3 ' which has the cation-disordered rock salt structure. On cooling, the transformation is fully reversible.

LiCoMnO_4 is the parent material for a potential new generation of cathodes in rechargeable Li batteries^{1,2} which charge (by deintercalation of Li from LiCoMnO_4) and discharge reversibly at a record voltage of $\sim 5\text{ V}$ for 90% of the charge-discharge range. For the remaining 10%, the voltage drops to $\sim 4\text{ V}$; the reason for this is not known.

A second unusual feature² of LiCoMnO_4 is that, after synthesis by solid state reaction at $\sim 800^\circ\text{C}$, it is necessary to give samples a final heat treatment² at $\sim 600^\circ\text{C}$ in order to obtain samples with high quality powder X-ray diffraction, XRD, patterns; these correspond to the cubic spinel structure. The reasons for this are also unknown.

In the present work, we have investigated the thermal stability of LiCoMnO_4 using a combination of *in situ* thermogravimetry, TG, and isothermal annealing followed by quenching to room temperature and XRD analysis. TG results show that LiCoMnO_4 begins to lose weight above $\sim 570^\circ\text{C}$; weight loss is complete by $\sim 1050^\circ\text{C}$ and is essentially recovered on cooling, Fig. 1. On rapid cooling, the original weight is not fully recovered, Fig. 1, but with slower cooling rates, the recovery is more complete.

Separate experiments showed that the loss and gain of weight is associated with oxygen. The total weight loss in the range of $570\text{--}1100^\circ\text{C}$ for a sample that had been synthesised at 800°C , 48 h followed by a slow cool to 550°C and isothermal anneal at

550°C for 12 h was $\sim 7.15\%$ of the original weight, corresponding to ~ 0.8 oxygens per formula unit. Preliminary XRD results on material quenched from high temperature indicated a simple, rock salt-like pattern. For a rock salt phase with a cation: oxygen ratio of 1:1 to form, the weight loss should be 8.66%, corresponding to the loss of one oxygen atom per formula unit.

Since only ~ 0.8 oxygen was lost, it was not clear at this stage whether the initial sample was oxygen deficient, with $\delta = 3.8$, or the final product was oxygen-rich with $\delta \sim 3.2$. A sample was therefore heated under high pressure O_2 [100 atm at 700°C , with a slow cool under pressure at 2°C min^{-1}] in a Morris High Pressure Furnace. By subsequent TG analysis, the weight loss up to 1100°C had increased to 8.15%, close to the theoretical value of 8.66%. We conclude, therefore, that the original samples, prepared in air/ O_2 at 1 atmosphere, were oxygen-deficient.

In order to characterise the materials obtained at high temperature, samples were heated isothermally, quenched to room temperature and analysed by XRD; it was assumed that with rapid quenching, the high temperature stoichiometry and structure were preserved to room temperature. On quenching from 550, 600 and 700°C , the face centred cubic spinel pattern was retained. At 800 and 900°C , some line splittings were observed, indicating a possible structural distortion to give a non-cubic, defect spinel or, alternatively, a mixture of phases. The TG results, Fig. 1, show evidence of an intermediate temperature inflexion or plateau which could correspond to a stable intermediate phase; the temperature range over which this occurs, $\sim 750\text{--}850^\circ\text{C}$, corresponds to the temperatures over which quenched samples showed complex XRD patterns, with line splittings. At 1000 and 1100°C , the pattern reverted to a very simple pattern that could be indexed on a face centred cubic cell, $a = 4.1983(7)\text{ \AA}$, Table 1.

The XRD data of the high temperature phase were not in an appropriate form for Rietveld analysis, but intensity calculations showed good agreement with a simple rock salt structure containing a disordered arrangement of octahedrally coordinated Li, Mn and Co, consistent with the 1:1 cation to

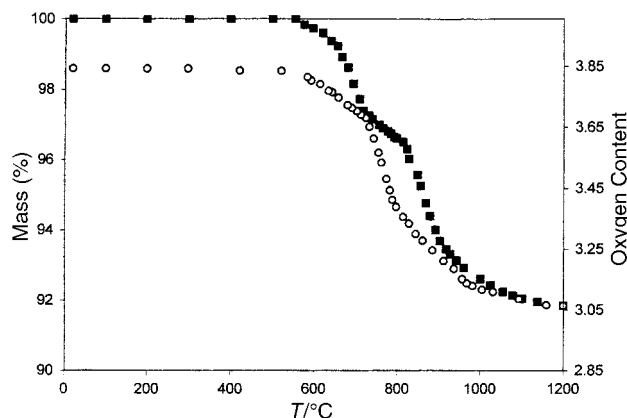


Fig. 1 TG data for LiCoMnO_δ (■ = heating cycle data, ○ = cooling cycle data), in an air atmosphere. A heating rate of $10^\circ\text{C min}^{-1}$ was used. The cooling rate was programmed at $10^\circ\text{C min}^{-1}$ at the higher temperatures, but became slower than this during the cooling cycle.

Table 1 XRD data for LiCoMnO_δ quenched into Hg from 1100°C

$d_{\text{obs}}/\text{\AA}$	$d_{\text{calc}}/\text{\AA}$	I_{obs}	I_{calc}	hkl
2.4212	2.4239	45	37	111
2.0973	2.0991	100	100	200
1.4838	1.4843	51	52	220
1.2655	1.2658	11	14	311
1.2121	1.2119	13	19	222
1.0498	1.0496	4	12	400

Lattice parameter, $a = 4.1983(7)\text{ \AA}$.

oxygen ratio in 'LiCoMnO₃', Table 1. Determination of the cation oxidation states is still required.

Further work is also required to determine the structure(s) of the material with intermediate oxygen content in the general formula LiCoMnO_δ and also whether LiCoMnO₄ itself contains ordering of Co and Mn on the octahedral sites of this structure, which is a normal spinel, Li^{tet}(Co,Mn)^{oct}O₄. Recent electron spin resonance results³ on LiCoMnO₄ gave evidence of local order of Co/Mn, but in light of the present results, the oxygen content of the materials under study may have been $\delta < 4$.

The rapidly reversible nature of the oxygen exchange and the spinel to rock salt transformation arises partly because spinel and rock salt have the same cubic close packed oxide arrangement and Co, Mn occupy octahedral sites in both. Hence, the transition involves primarily the migration of Li from tetrahedral to octahedral sites. Nevertheless, since 25% of the oxygens are lost/gained in the transformation a very considerable diffusion of all cations is required to retain structural integrity. The question remains as to whether the original spinel crystals retain their structural integrity and convert to a rock salt phase in which 25% of both cation and anion sites are vacant or whether fully dense rock salt crystals form by a complete reorganisation of the cation and oxygen positions. Further work on this is in progress.

These results are also of significance for the possible use of LiCoMnO₄ as a cathode in Li batteries. It is probably essential for the oxygen content to be maximised to $\delta=4$ so as to

optimise the contents of Co³⁺ and Mn⁴⁺; the electrochemical data on delithiation and lithiation showed that while ~90% of the overall reaction occurred at ~5 V, the remaining 10% occurred at ~4 V.^{1,2} It now seems plausible that the material used for these tests was not fully oxygenated and that this may have been the cause of the residual 4 V redox process.

As far as we are aware, a fully reversible spinel to rock salt transformation, of the kind reported here and driven by a change in oxygen content, has not been reported previously. It will be of considerable interest to determine whether a similar transition occurs in other spinels such as Li₂CoMn₃O₈⁴ and especially, LiMn₂O₄, which is a candidate material for the next generation of 4 V lithium batteries, and indeed, in a much wider range of spinels.⁵

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Notes and references

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