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Disproportionation of stoichiometric LiMn_2O_4 on annealing in oxygen

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Abstract

The evolution of stoichiometric LiMn_2O_4 upon annealing under oxygen pressures in the range 0.2–5 atm at moderate temperature (450°C) was studied with a combination of thermogravimetry, X-ray and neutron diffraction. It is shown that such treatments result in a slight, but significant mass increase. Structural analyses show that the resulting spinel is a manganese-deficient spinel phase with lower cell parameter and higher manganese valence, and that the expelled manganese forms Mn_2O_3 . The presence of this second phase, which was not identified in a recent study of oxygen annealing on this compound (Nakamura and Kajiyama, *Solid State Ionics* 133 (2000) 195), is compatible with the initial stoichiometry and does not require any oxygen vacancies in the initial LiMn_2O_4 , as supposed earlier. The most likely formula of the resulting lithium-rich spinel with increased manganese valence is $\text{Li}(\text{Mn}_{2-\varepsilon}\square_\varepsilon)\text{O}_4$ with ε in the range 0.02–0.03 at 5 atm O_2 .

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1. Introduction

The Li–Mn–O spinel system possesses a rich crystal chemistry. Without considering vacancies (cation/anion ratio strictly equal to 3/4), the formula of the spinel phase can vary along a solid solution $\text{Li}_{1+\alpha}\text{Mn}_{2-\alpha}\text{O}_4$ with $0 \leq \alpha < 1/3$, where a fraction of lithium replaces manganese on the 16d (octahedral) site of the spinel structure. This substitution range is actually limited not by crystal chemistry, but by the fact that manganese reaches the oxidation state +4 when $\alpha = 1/3$. The exact stoichiometry of $\text{Li}_{1+\alpha}\text{Mn}_{2-\alpha}\text{O}_4$ samples (α value) of Li–Mn–O samples annealed in air has been shown to be determined by the annealing temperature [1,2].

The basic, strictly stoichiometric compound LiMn_2O_4 , which has an average manganese valence +3.5, also undergoes a structural transition to an orthorhombic supercell on cooling at a temperature close to room temperature. Rousse et al. [3,4] showed that this symmetry lowering is due to partial charge

ordering. To make matters more complex, LiMn_2O_4 is known to accommodate vacancies on all sites: (i) on the lithium 8a sites, in the well-known delithiation reaction which has been widely studied in view of lithium battery applications [5,6], (ii) on the manganese 16d site for specific low-temperature syntheses [7,8], (iii) on the oxygen 32e sites, in samples quenched from temperatures $\geq 800^\circ\text{C}$ [9,10].

In this context, it is interesting to investigate the evolution of LiMn_2O_4 when annealed under oxygen pressures larger than that in air. This study was also prompted by a report by Nakamura and Kajiyama, who found a significant lattice constant decrease on annealing LiMn_2O_4 in oxygen pressures up to 5 atm [11]. This effect was ascribed by these authors to an increase in average manganese valence, which could only occur in a single-phase spinel phase assuming the presence of oxygen vacancies in the initial, “stoichiometric” compound. Such a mechanism is in disagreement with numerous structural studies on LiMn_2O_4 prepared by the classical solid state route in air at high temperature with furnace or slow cooling, where no vacancies were found [12–14]. We will show here that the behaviour of

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LiMn_2O_4 when annealed in oxygen is more complex: it actually corresponds to a disproportionation of stoichiometric LiMn_2O_4 into a spinel with higher manganese valence on one hand, and the trivalent manganese oxide Mn_2O_3 on the other. Unlike the reaction mechanism proposed by Nakamura et al. [11], this reaction does not require the presence of oxygen vacancies in the initial material and is supported by X-ray and neutron data analyses.

2. Experimental

LiMn_2O_4 was prepared by solid-state reaction of appropriate mixtures of reagent-grade lithium carbonate with (a) manganese carbonate or (b) a specially ground $\beta\text{-MnO}_2$ oxide. The reactions were carried out in air at 800–850°C with furnace-cooling.

The reaction on annealing in the 400–500°C range was first studied by thermogravimetry in air with 2°C/min heating/cooling rate, using a Setaram CS 92 apparatus.

Annealing under 1 atm oxygen were carried out by flowing 99.9% oxygen on LiMn_2O_4 samples placed in a tubular furnace for ≥ 24 h at 450–470°C (optimum temperature according to thermogravimetric results). For annealing at pressures > 1 atm, the sample was placed in a gold crucible in a stainless steel autoclave and submitted to oxygen pressure at 470°C for 14–24 h. The oxygen pressure was maintained until the autoclave was cooled to at least 100°C.

The initial LiMn_2O_4 samples used were characterized by X-ray diffraction (Siemens D-5000 diffractometer with $\text{CuK}\alpha$ radiation) and by volumetric determination of the manganese oxidation state. Annealed samples were investigated using low-noise X-ray diffractometry (0.02 step size, ≥ 10 s counting time). The most oxidized sample (with lowest unit cell parameter) was measured on the high-resolution neutron powder diffractometer D2B at I.L.L., Grenoble with a wavelength of 1.594 Å.

Structural refinements were carried out by the Rietveld method using the Fullprof program [15].

3. Results

3.1. LiMn_2O_4 characterization

Both LiMn_2O_4 batches made from manganese carbonate and from ground $\beta\text{-MnO}_2$ were phase-pure within the sensitivity of X-ray diffraction. Their characteristics are summarized in Table 1. Structural refinements from neutron data on data recorded above the orthorhombic–cubic transition temperature ($T_{\text{tr}} \approx 294$ K on cooling, 300 K on heating [3]) are given in Table 1. They are in excellent agreement with Refs. [4,12] and do not reveal any significant vacancy fraction as conjectured by Nakamura et al. [11]

3.2. Thermogravimetric study

A 2°C/min thermogravimetric curve of stoichiometric LiMn_2O_4 in air is shown in Fig. 1. Even in air [$p(\text{O}_2) \approx 0.2$ atm], a small, but significant mass uptake is observed in the range 400–500°C. In Li–Mn–O spinel thermogravimetric studies, this phenomenon was usually masked by the much larger mass loss observed at temperatures $> 750^\circ\text{C}$, corresponding to the appearance of oxygen vacancies as established previously [9,16].

Further gravimetric measurements in oxygen up to 450°C confirmed the occurrence of an irreversible mass uptake, equal to 0.19 mass% in 1 atm oxygen.

3.3. X-ray diffraction studies

Fig. 2 shows powder diffraction patterns of pristine and oxygen-annealed LiMn_2O_4 . A shift in peak positions towards higher diffraction angles can be observed. This corresponds to a decrease in unit cell parameter, in agreement with an increase in manganese valence.

Table 1

(a) Characterization of initial LiMn_2O_4 samples				
Reagent	Synthesis temperature (°C)	Cell parameter (Å)	Mn valence (from redox titration)	
MnCO_3	800	8.247(2)	3.50(2)	
Ground MnO_2	850	8.246(2)	3.51(2)	
(b) Structural data for LiM_2O_4 prepared at 850°C (neutron data)				
Atom	Site	Atomic coordinates	B_{iso} (Å ²)	Occupation
Space group $Fd\bar{3}$, $a = 8.2474(2)$ Å				
Li	8a	$x, y, z = 1/8$	1.15(8)	1 (fixed)
Mn	16d	$x, y, z = 1/2$	0.87(5)	1 (fixed)
O	32e	$x, y, z = 0.2630(1)$	1.48(3)	1.01(1)

$R_p = 3.75$, $R_{\text{wp}} = 4.93$, $R_{\text{exp}} = 1.93$, $N - P + C = 2774$.

R_{Bragg} (spinel phase) = 3.44.41 spinel reflections used.

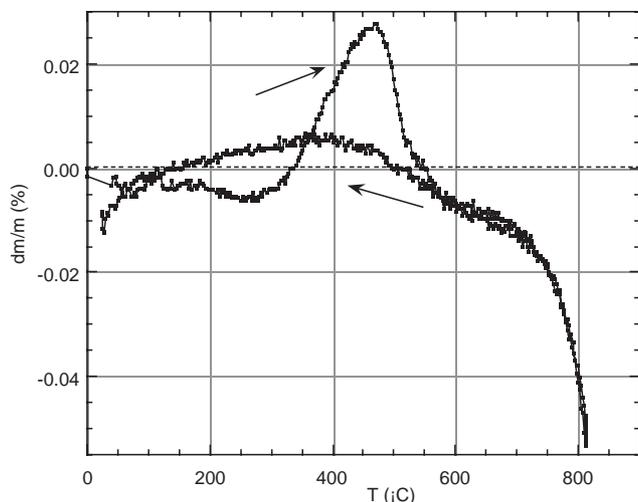


Fig. 1. Thermogravimetric behaviour of stoichiometric LiMn_2O_4 in air (heating/cooling rate $2^\circ\text{C}/\text{min}$).

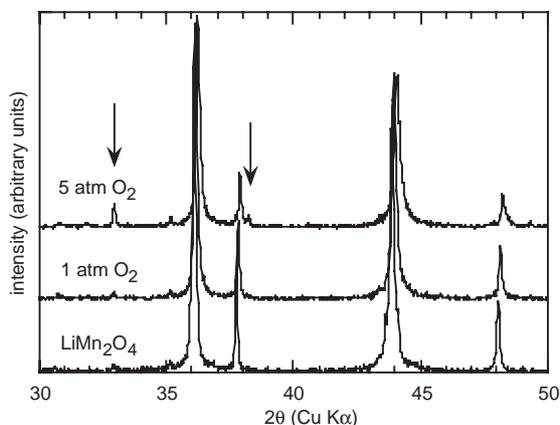


Fig. 2. X-ray diffraction patterns of initial LiMn_2O_4 and of samples obtained at increasing oxygen pressures at 470°C (from bottom to top). Mn_2O_3 reflections are marked with arrows.

A plot of the evolution of cell parameter with oxygen pressure (see Fig. 3) shows that this effect varies with oxygen pressure and tends to saturate at $p(\text{O}_2) > \approx 3 \text{ atm}$, in agreement with previous measurements [11].

A closer look at the diffraction patterns reveals the appearance of significant extra lines in oxygen-annealed samples. These new reflections reveal the presence of Mn_2O_3 in annealed samples. The presence of such a second phase, which was not at all considered in the previous work on oxygen-annealed LiMn_2O_4 [11], changes completely the reaction scheme of LiMn_2O_4 with oxygen.

The manganese valence increase in the spinel phase can be explained by two mechanisms:

- (i) Formation of a Mn-cation vacant spinel $\text{LiMn}_{2-\varepsilon}\text{O}_4$, with expelled manganese forming Mn_2O_3 as a

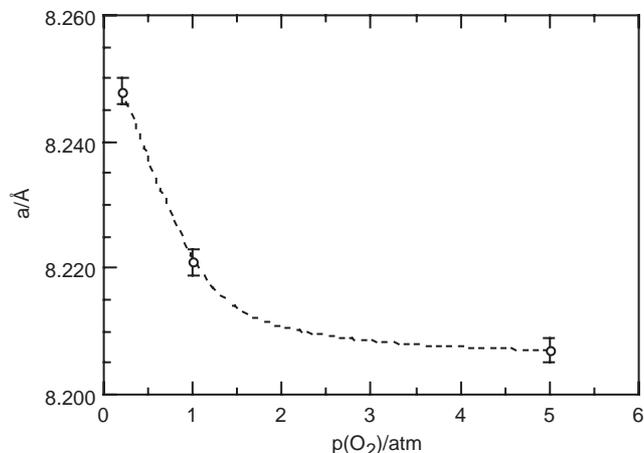
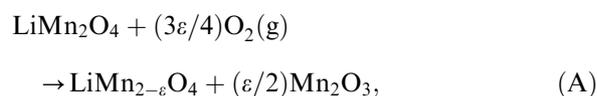


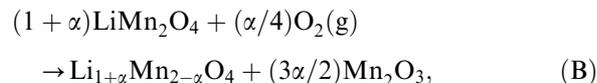
Fig. 3. Evolution of the cubic cell parameter of spinel phase with oxygen pressure after 470°C annealing.

second phase:



where the manganese valence in the spinel phase increases from 3.5 to $7/(2-\varepsilon)$.

- (ii) Migration of a fraction of lithium cations in the octahedral sites, resulting in a manganese-poorer spinel. Again, this frees manganese which can form Mn_2O_3 as a second phase:



where the manganese valence in the spinel phase increases from 3.5 to $(7-\alpha)/(2-\alpha)$.

In addition, it should be noted that an oxidative mechanism including the migration of lithium and manganese cations has been proposed for the formation of cation-deficient spinels with formula close to $\text{Li}_2\text{Mn}_4\text{O}_9$ [7].

3.4. Neutron diffraction refinement

A neutron diffraction pattern has been collected on diffractometer D2B of ILL, Grenoble, on the 5 atm O_2 sample. Refinements results (see Fig. 4) are summarized in Table 2. This confirms the assumption of a slight manganese deficit on the spinel $16d$ site after oxygen annealing. However, such a refinement is unable to distinguish between reactions A and B: since Mn and Li both have negative Fermi lengths, similar solutions can be found with the $16d$ site occupied by either $(0.98\text{Mn} + 0.02\text{Li})$ or a $(0.99\text{Mn} + 0.01\Box)$ combination.

4. Discussion

At first sight, it seemed rather surprising to observe the formation of *trivalent manganese* oxide Mn_2O_3 on annealing a compound with initial manganese valence 3.5 in *oxidating conditions*. But it was systematically observed, and the structural analysis shows that it is more than compensated by the increase in manganese valence in the majority spinel phase: equilibrating reactions A and B actually requires extra oxygen, and the overall reaction is indeed a manganese oxidation. Because of the formation of a second, manganese-rich phase, no oxygen vacancies need to be postulated in the initial phase to explain the mass uptake reaction of LiMn_2O_4 in oxygen, unlike in the mechanism proposed previously [11].

The composition of the resulting spinels (defined by ε or α , see reactions A and B above) can be inferred from (i) mass uptake measurements, (ii) 2-phase structural

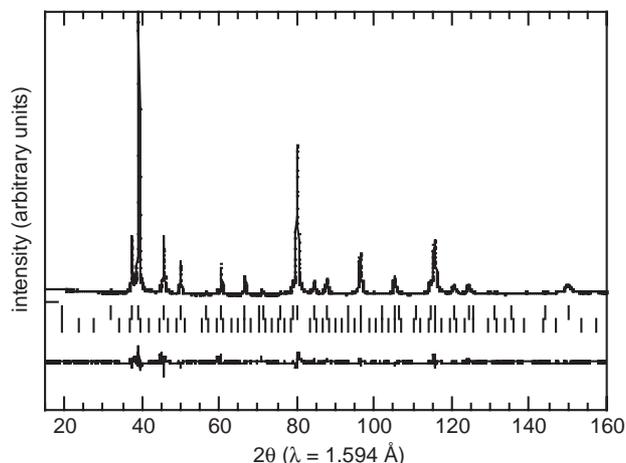


Fig. 4. Observed (points) and calculated (continuous line) intensities of a sample annealed under 5 atm oxygen at 470°C. The bottom line shows $I_{\text{obs}} - I_{\text{calc}}$. Upper ticks: spinel phase, lower ticks: Mn_2O_3 .

refinements. However, all these methods are rather inaccurate in the present case, due to the small fraction of the second phase. An independent determination of α in case B can also be provided from the evolution of the cell parameter a , which has been determined in the $\text{Li}_{1+\alpha}\text{Mn}_{2-\alpha}\text{O}_4$ solid solution by several authors [1,17–19]. Unfortunately, literature data for the $a = f(\alpha)$ dependence are rather scattered, especially at low α value (even cell parameter values for $\alpha = 0$ quoted in these papers differ by $\approx 0.01 \text{ \AA}$), again resulting in a poor accuracy.

Table 3 summarizes values of ε , α and manganese valence calculated from available experimental data. For reaction A, they give ε values of 0.014 and 0.02–0.03 for oxygen pressures 1 and 5 atm, respectively. For reaction B, the results (α values) are more scattered. Going back to structural considerations, it should be pointed out that reaction B requires a much more complex rearrangement of the spinel network content than reaction A. Firstly, reaction B involves not only manganese loss from the 16d sites, but partial migration of lithium atoms to these empty octahedral sites. Secondly, a fraction of the initial spinel phase [(1+ α) formula units] is also lost [1 spinel unit remaining]. Whereas the gaseous oxygen uptake in reaction A exactly matches the quantity required to form $\varepsilon/2 \text{ Mn}_2\text{O}_3$, the oxygen needed to form $3\alpha/2 \text{ Mn}_2\text{O}_3$ in reaction B comes partly from the gaseous oxygen uptake, partly from the initial solid phase. Such a complex mechanism seems less likely to occur at relatively low temperatures such as 450°C. Note that the temperature range used here is similar to that used to prepare other cation-deficient spinels with formulas more or less close to “ $\text{Li}_2\text{Mn}_4\text{O}_9$ ”, i.e., $(\text{Li}_{8/9}\square_{1/9})[\text{Mn}_{16/9}\square_{2/9}\text{O}_4]$ in spinel formula notation [8,20]. All these considerations support reaction A, i.e., disproportionation of LiMn_2O_4 into a Mn-vacant spinel with higher manganese valence and Mn_2O_3 .

Table 2

Results of Rietveld refinement from neutron powder data of LiMn_2O_4 annealed in 5 atm O_2 for 24 h

Atom	Site	Atomic coordinates	B_{iso} (Å^2)	Occupation	Interatomic distances (Å)
(1) Spinel phase, space group $Fd-3m$, $a = 8.209(1) \text{ \AA}$					
Li	8a	$x, y, z = 1/8$	1.18(14)	1 ^a	Li–O
Mn	16d	$x, y, z = 1/8$	0.78(6)	0.965(5) Mn + 0.0365(5) Li or 0.98(1) Mn	1.959(1) Mn–O
O	32e	$x, y, z = 0.2628(4)$	1.51(3)	1 (fixed)	1.923(1)
(2) Mn_2O_3 , space group: $Ia-3^b$, $a = 9.409(3) \text{ \AA}$					
Mn1	8b	$x, y, z = 1/4$	B_{overall}		
Mn2	24d	0, 0, 1/4	1.32	Mass fraction 1.3(3) %	
O	48e	0.375, 0.162, 0.400 ^b			

15 variables, $R_p = 5.83$, $R_{\text{wp}} = 8.80$, $R_{\text{exp}} = 2.25$, $N - P + C = 2885$.

R_{Bragg} (spinel phase) = 6.46. 41 spinel reflections used.

^aNot refined simultaneously with B; refined value 1.02(1) with B fixed.

^bCubic model [21]; the actual symmetry is $Pbca$ with a/b 0.9994, c/b 1.0005 [22]; atomic parameters not refined.

Table 3
Stoichiometric parameters and manganese valence for reactions A and B

$p(\text{O}_2)$ atm	Measurement	A case		B case	
		ε	v (Mn)	α	v (Mn)
1	Gravimetry	0.014(1)	3.525	0.042(3)	3.55
	Cell parameter: $a = 8.223(1)$ Å	na ^a		≈ 0.04	
5	Cell parameter: $a = 8.208(1)$ Å	na ^a		≈ 0.08	
	16d site occupation ^b	0.02(1)	3.535	0.036(5)	3.545
	Fraction of 2nd phase ^b	0.029(4)	3.55	0.010(2)	3.52

^aSolid solution model: applicable to B case only.

^bFrom 2-phase neutron diffraction data refinement.

Finally, the oxidation of manganese in the spinel phase is substantiated not only by the decrease in cell parameter, but also by a decrease in Mn–O bond length. The value obtained for the 5 atm sample (Table 3) is intermediate between those in LiMn_2O_4 (1.958 Å) and in a cation-vacant spinel with manganese valence 3.82 (1.942 Å) (see Fig. 6 in Ref. [8]).

5. Conclusions

In this study, we show that annealing stoichiometric LiMn_2O_4 under oxygen pressures in the range 1–5 atm results in a slight oxidation and introduction of manganese vacancies in the spinel phase, the manganese lost forming Mn_2O_3 . This mechanism, which is actually a disproportionation of the initial $\text{Mn}^{+3.5}$ present in LiMn_2O_4 into Mn^{3+} and $\text{Mn}^{3.5+\delta}$, is quite compatible with the stoichiometry for the initial compound and does not require any undocumented assumption of oxygen vacancies in the initial, high-temperature-made LiMn_2O_4 , unlike the mechanism recently proposed by Nakamura et al. [11].

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