

Short communication

Variable oxygen stoichiometry in layered rock salt cathodes, $\text{Li}_x(\text{Mn,Ni})\text{O}_2$, depending on synthesis conditions

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Abstract

The oxygen content in a selection of layered rock salt phases in the system Li–Mn–Ni–O has been investigated by thermogravimetry. Phases that are oxygen-stoichiometric, such as Li_2MnO_3 and $\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$, may lose up to 1% of their oxygen reversibly, on heating to $\sim 1000^\circ\text{C}$. Cation-deficient phases, such as $\text{Li}_{2/3}(\text{Mn}_{2/3}\text{Ni}_{1/3})\text{O}_2$, however, are capable of much greater reversible oxygen loss, leading eventually to an oxygen-stoichiometric cubic rock salt phase with a cation-disordered structure. The oxygen contents of such layered rock salt phases are determined directly by their synthesis conditions and have a direct effect on the charge/discharge capacity during lithium deintercalation.

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1. Introduction

The occurrence of variable oxygen stoichiometry during synthesis is now well-established in spinel-structured lithium cathode materials such as LiMn_2O_4 , LiCoMnO_4 and $\text{Li}_2\text{NiMn}_3\text{O}_8$ [1–5]. Possible oxygen non-stoichiometry in layered rock salt structure cathodes has been given much less attention although there are many examples of the importance of synthesis and/or processing conditions on subsequent electrochemical performance. The possibility of variable oxygen stoichiometry during electrochemical lithium deintercalation has, however, received consideration, since oxygen loss appears to occur during the deintercalation of lithium from certain layered rock salt phases at high voltages, $\geq 4.6\text{ V}$ [6–9].

Oxygen non-stoichiometry is potentially significant, since reduction in average transition metal oxidation state is required to balance any oxygen deficiency; any such changes must influence electrochemical performance, either adversely or beneficially. Our studies into possible oxygen non-stoichiometry in layered rock salt structures were initiated by the discovery that Li_2MnO_3 is capable of reversible oxygen loss by simply heating in air to temperatures above $\sim 900^\circ\text{C}$. The maximum oxygen loss was small, $\sim 1\%$ at 1100°C , but, nevertheless, was

sufficient to cause reduction of some Mn^{4+} to Mn^{3+} and led to a small amount of charge/discharge capacity associated with the $\text{Mn}^{3+/4+}$ redox couple. This result also explained the unexpected electrochemical activity found in Li_2MnO_3 prepared under our experimental conditions [10].

Numerous layered rock salt materials in the system Li–Mn–Ni–O have been considered as potential lithium deintercalation cathodes, in particular $\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$. In this paper, we summarise our recent work, some of which has already been published, on a selection of compositions within this system in order to seek possible correlations between oxygen non-stoichiometry, composition, processing conditions and electrochemical performance.

Compositions in the system Li–Mn–Ni–O may be represented in terms of an equilateral composition triangle, Fig. 1; this triangle refers to the cation contents only and forms the base of a composition pyramid with oxygen at the apex. Hence, although the oxygen contents of the various phases are not given directly from this composition triangle, the cationic contents of each phase are determined by projection of their compositions onto this composition base. This triangle contains several rock salt-related phases that have already been considered as potential cathodes: Li_2MnO_3 , LiNiO_2 , LiMnO_2 and $\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$ as well as spinels such as LiMn_2O_4 and $\text{Li}_2\text{NiMn}_3\text{O}_8$ (not shown).

The oxygen non-stoichiometry of phases such as these can be readily assessed by thermogravimetry (TG) in different atmospheres. In cases where reversible oxygen loss occurs during

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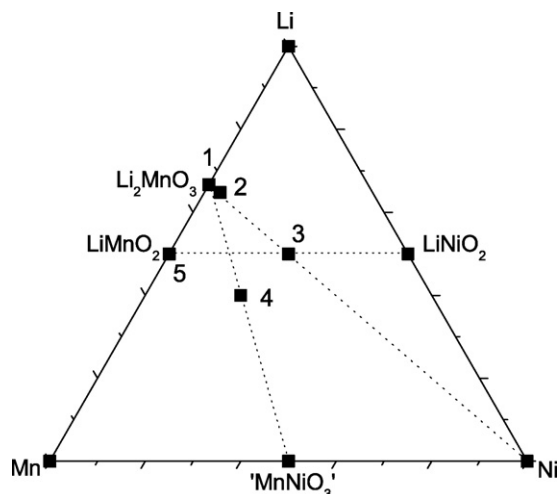


Fig. 1. Composition triangle Li–Mn–Ni–O showing phases (1) Li_2MnO_3 , (2) $\text{Li}_{1.93}\text{Ni}_{0.1}\text{Mn}_{0.97}\text{O}_3$, (3) $\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$, (4) $\text{Li}_{2/3}(\text{Mn}_{2/3}\text{Ni}_{1/3})\text{O}_2$ and (5) LiMnO_2 .

heating in air, this can be characterised by heat–cool cycles of TG. Heating samples in H_2/N_2 atmospheres (H_2 -reduction TG) provides a direct method of chemical analysis, provided the nature of the reduction products is known. Results are summarised here for five compositions.

2. Experimental

For the $\text{Li}_2\text{MnO}_{3-\delta}$, $\text{Li}_{1.93}\text{Ni}_{0.1}\text{Mn}_{0.97}\text{O}_{3-\delta}$ and LiMnO_2 samples, stoichiometric mixtures of dried starting materials Li_2CO_3 , $\text{Ni}(\text{CH}_3\text{COOH})_2 \cdot 4\text{H}_2\text{O}$ and MnO_2 (Sigma–Aldrich), all reagent grade, were ground intimately in an agate pestle and mortar and fired in air, initially at 650°C for 2 h to expel CO_2 , followed by 900°C for 3 days with intermittent regrinding. $\text{Li}_{2/3}(\text{Mn}_{2/3}\text{Ni}_{1/3})\text{O}_{2-\delta}$ and $\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_{2-\delta}$ samples were prepared using a mixed-acetate synthesis method adapted from Julien et al. [11]. The resulting powder was decarbonated at 560°C , ground, heated to 950°C for 6 h and slow-cooled in the furnace. These samples are referred to as “as-prepared”. Portions of the as-prepared samples were reheated in a high O_2 pressure furnace (Morris) at 120 bar for 6 h then 500°C for 3 h followed by a slow-cool under pressure to room temperature (hereafter referred to as the HOP samples). Other portions of the as-prepared samples were heated isothermally at various temperatures and quenched into liquid N_2 . Thermogravimetry (TG) used a Perkin-Elmer Pyris 1 instrument in air with heat–cool rates of $10^\circ\text{C min}^{-1}$; hydrogen-reduction TG was carried out in a $\text{H}_2:\text{N}_2 = 5:95$ mixture.

3. Results and discussion

3.1. $\text{Li}_2\text{MnO}_{3-\delta}$

TG data in air show that approximately 1% of the oxygen content may be lost by heating to 1000°C , Fig. 2; on cooling in air, most of this oxygen is regained during cooling at $10^\circ\text{C min}^{-1}$, but to achieve fully oxygenated samples, it is necessary to cool

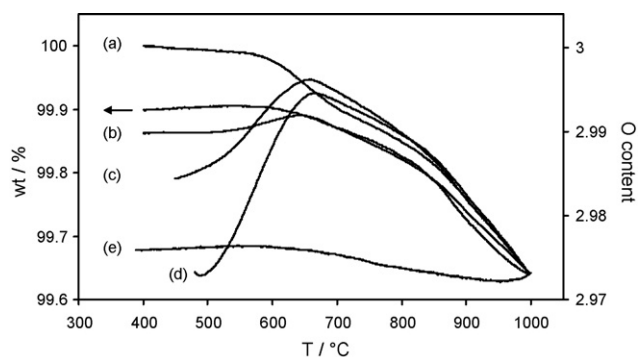


Fig. 2. TG data in air for $\text{Li}_2\text{MnO}_{3-\delta}$ samples (a) in HOP at 120 atm O_2 , 700°C for 3 h, (b) prepared at 900°C and slow-cooled in air, (c) quenched from 1000°C , and (d) quenched from 1100°C . All cooling curves for (a)–(d) were similar (\leftarrow). Data in (e) are for a sample that was heated in air by TG but then, the atmosphere was switched to N_2 for cooling. It is assumed that sample (a) had stoichiometry $\delta = 0$ at 25°C and that all samples have the same δ value when heated in air at 1000°C .

the samples slowly in high-pressure O_2 . If, after heating to 1000°C , the samples are cooled in N_2 , then very little weight gain associated with oxygen uptake occurs (curve e). Curves c and d show that samples prepared at, e.g. 1000 or 1100°C , followed by quenching to room temperature, are O_2 -deficient in their as-prepared conditions and that they pick up O_2 during the TG heating cycle at temperatures in the range ~ 500 – 650°C , following which they then follow the same reversible O_2 loss/gain cycle shown by other compositions.

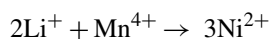
These collective results show that samples of $\text{Li}_2\text{MnO}_{3-\delta}$ can be prepared in which the oxygen content varies over the range 2.97–3.00. It is possible that δ could be increased by heating to temperatures $\geq 1000^\circ\text{C}$.

For TG studies, such as these, it is necessary to have a reference point in order to be able to add an oxygen content scale to the results, as shown on the right hand vertical axis. For Li_2MnO_3 , treatment in high-pressure oxygen was shown to give oxygen stoichiometric material with $\delta = 0$, using a combination of techniques such as H_2 -reduction TG and chemical titration.

It is also useful to note that at high temperatures, e.g. 1000°C , samples quickly reach thermodynamic equilibrium and, for a given atmosphere, all samples rapidly arrive at the same oxygen content. It can, therefore, be useful to normalise TG curves to the data obtained at 1000°C . This then provides a relative measure of oxygen contents, although additional analyses, such as chemical titration, are required in order to determine absolute oxygen contents.

3.2. $\text{Li}_{1.93}\text{Ni}_{0.10}\text{Mn}_{0.97}\text{O}_{3-\delta}$

This composition also has the Li_2MnO_3 -layered rock salt structure and is obtained from the parent Li_2MnO_3 phase by the replacement mechanism:



We do not know the precise location of the Ni^{2+} ions, but it is presumed that they occupy statistically Li and Mn sites and either may be confined to the Li,Mn-mixed layers in the

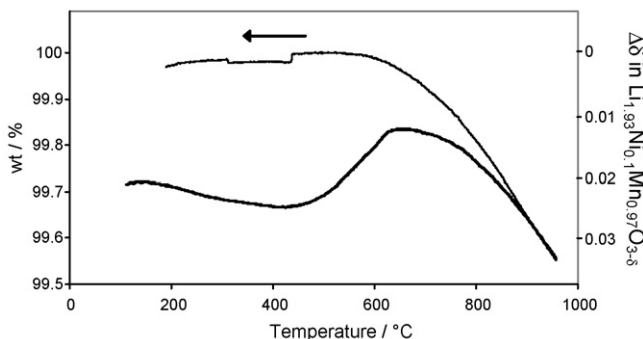


Fig. 3. TG data in air for sample $\text{Li}_{1.93}\text{Ni}_{0.1}\text{Mn}_{0.97}\text{O}_{3-\delta}$ prepared by quenching from $1000\text{ }^\circ\text{C}$. A relative oxygen content scale is shown on the right hand axis.

monoclinic Li_2MnO_3 structure, or may be distributed over both the Li,Mn-mixed layers and the alternating Li layers. TG data are shown for one composition in Fig. 3 and show similar behaviour to that of $\text{Li}_2\text{MnO}_{3-\delta}$: the sample, which was quenched from $1000\text{ }^\circ\text{C}$, picked up some oxygen during heating at $500\text{--}600\text{ }^\circ\text{C}$, followed by reversible loss at higher temperatures. This sample was not treated in high-pressure oxygen and therefore, only the relative variation in the oxygen content is demonstrated in Fig. 3. To a first approximation, the oxygen content is variable over a similar or more probably, slightly larger range than for undoped Li_2MnO_3 .

3.3. $\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_{2-\delta}$

This phase is reported to have alternating Li and Mn,Ni layers and has the rhombohedral space group, $R\bar{3}m$, similar to that of LiCoO_2 . TG data in Fig. 4, for samples quenched from three different synthesis temperatures, all show clear evidence of a small amount of reversible oxygen loss, above $\sim 550\text{ }^\circ\text{C}$. Again, absolute oxygen contents have not been determined, but the total oxygen loss is in the range $0.75\text{--}1.0\%$. Interestingly, the samples reach a constant oxygen content over the temperature range $800\text{--}1000\text{ }^\circ\text{C}$.

3.4. $\text{Li}_{2/3}(\text{Mn}_{2/3}\text{Ni}_{1/3})\text{O}_{2-\delta}$

This phase also has a layered structure related to LiCoO_2 , but its oxygen content is capable of enormous variation, as shown in

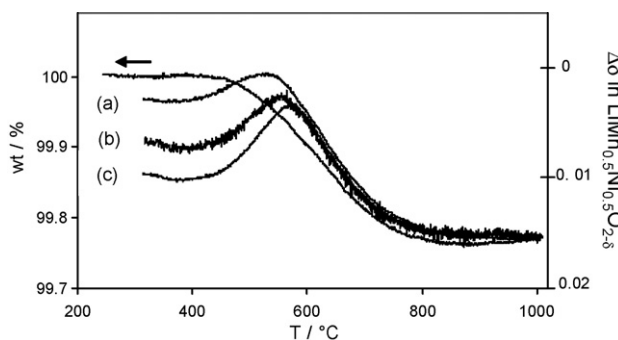


Fig. 4. TG data in air for $\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_{2-\delta}$ samples cooled on a brass-block from (a) $725\text{ }^\circ\text{C}$, (b) $800\text{ }^\circ\text{C}$ and (c) $875\text{ }^\circ\text{C}$. All cooling curves were similar (\leftarrow).

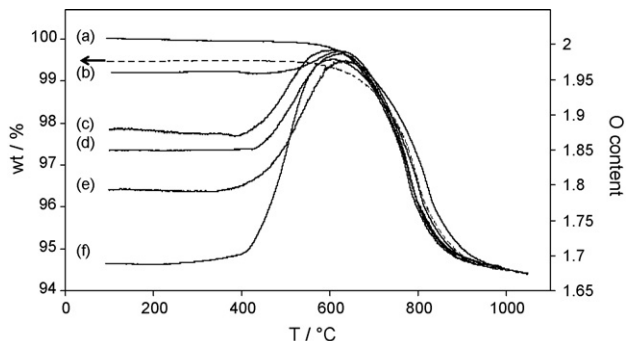


Fig. 5. TG data in air for $\text{Li}_{2/3}(\text{Mn}_{2/3}\text{Ni}_{1/3})\text{O}_{2-\delta}$. Sample (a) was prepared in HOP at 120 atm O_2 , $600\text{ }^\circ\text{C}$ for 6 h then $500\text{ }^\circ\text{C}$ for 6 h. Samples (b)–(f) were quenched from 691 , 790 , 812 , 870 and $1055\text{ }^\circ\text{C}$, respectively. All cooling curves were similar (\leftarrow).

Fig. 5; data for a sample prepared in high-pressure oxygen are shown as a reference (a) and to enable quantification of the oxygen content. All samples lose oxygen rapidly on heating above $\sim 600\text{ }^\circ\text{C}$ and reach an essentially constant oxygen content by $\sim 1000\text{ }^\circ\text{C}$, at which point $\sim 16.7\%$ of the oxygen content has been lost from fully oxygenated starting material. This result is confirmed by TG studies on samples quenched from various temperatures, b–f. Composition f, in particular, has the same oxygen content when quenched from $1055\text{ }^\circ\text{C}$, as that obtained by *in situ* TG at $\sim 1000\text{ }^\circ\text{C}$. This result is also reassuring, since it demonstrates that under the conditions used here, loss of lithium by volatilisation during the TG cycles is not significant and the entire weight changes seen are attributable to variation in oxygen content.

A simple explanation as to why this composition, $\text{Li}_{2/3}(\text{Mn}_{2/3}\text{Ni}_{1/3})\text{O}_{2-\delta}$, should be so susceptible to oxygen loss, is that the parent structure, with $\delta = 0$, is highly cation-deficient compared to a rock salt with cation:anion ratio of 1:1, whereas the material heated at $1000\text{ }^\circ\text{C}$ has, by oxygen loss, achieved this ideal ratio of 1:1 and a structure which is essentially a cation-disordered, cubic rock salt.

3.5. LiMnO_2

This sample has an orthorhombic unit cell with the space group $Pmnm$ and a zig-zag arrangement of the Li cations forming buckled layers. TG data shown in Fig. 6, linked to powder

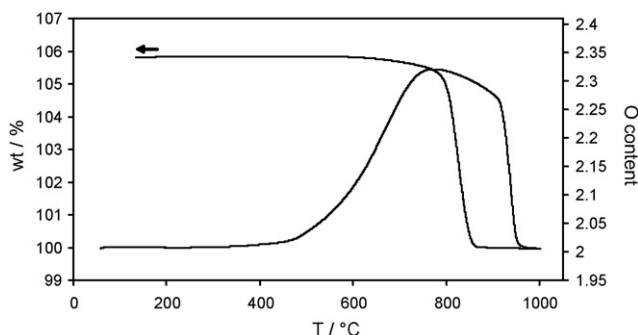


Fig. 6. TG data in O_2 for LiMnO_2 sample.

XRD data to analyse the phases present at various stages, demonstrate quite different behaviour to the above layered rock salt phases. On heating, oxygen uptake occurs above $\sim 600^\circ\text{C}$, followed by a reversible loss above $\sim 900^\circ\text{C}$, reaching a constant value at $\sim 1000^\circ\text{C}$, which is similar to that of the starting LiMnO_2 phase. On cooling, the sample picks up oxygen below $\sim 850^\circ\text{C}$, to reach a constant value below $\sim 700^\circ\text{C}$. However, the products on cooling are two-phase mixtures of Li_2MnO_3 and LiMn_2O_4 . In this case, therefore, we do not detect any reversible oxygen loss from LiMnO_2 but instead, observe reversible reduction of mixtures of Li_2MnO_3 and LiMn_2O_4 to form LiMnO_2 at high temperatures. There is no evidence for O_2 loss from LiMnO_2 at temperatures up to 1000°C .

4. Conclusions

Several types of behaviour are observed in the selection of phases presented above. From these results, which are, admittedly, on a limited number of compositions only, three conclusions may be drawn.

First, phases that have cation:oxygen ratio of 1:1 and therefore have the stoichiometry expected for rock salt-related structures, can lose a small amount of oxygen, reversibly, on heating to $\sim 1000^\circ\text{C}$. This oxygen loss appears to be limited to a maximum of $\sim 1\%$. We do not, at this stage, know the structural consequences of this oxygen loss, i.e. whether the structures at high temperatures contain oxygen vacancies in the crystal lattice, or whether major structural reorganisation occurs so as to maintain a fully dense oxygen cubic close-packed arrangement, but instead, with some cations displaced to interstitial sites. In the case of orthorhombic LiMnO_2 , there is no evidence of oxygen loss but instead the sample fully oxidises to give a mixture of Li_2MnO_3 and LiMn_2O_4 .

Second, samples that are oxygen-deficient as a consequence of their preparation conditions are able to rapidly absorb oxygen over the range $500\text{--}600^\circ\text{C}$, but subsequently lose O_2 on heating to higher temperatures.

Third, compositions whose cation:oxygen ratio is much less than the 1:1 ratio expected for rock salt phases exhibit a high level of reversible oxygen loss at high temperatures and may

transform into a fully cation-disordered rock salt structure with cation:oxygen ratio of 1:1. Hence, the large variation in oxygen content possible in $\text{Li}_{2/3}(\text{Mn}_{2/3}\text{Ni}_{1/3})\text{O}_{2-\delta}$, is attributed to the high cation deficiency (or oxygen excess) in the parent phase with $\delta=0$.

Associated with the variable oxygen content of the phases, a variation in oxidation state of certain cations is required to preserve electroneutrality, leading to a variation in electrochemical performance during lithium (de)intercalation. The structural consequences of oxygen deficiency, i.e. whether oxygen vacancies or cation interstitials are created, accompanied by other possible structural changes, require further evaluation. It is known that certain phases lose O_2 during delithiation at high charging voltages, 4.6 V; it remains to be seen whether there is a correlation between phases that exhibit oxygen loss at high voltages and oxygen loss at high temperatures.

Acknowledgement

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