OCTAHEDRAL SITE OCCUPATION OF LITHIUM IN Li₄Mn₂O₄

E.M. Kelder and J. Schoonman,
Lab. Appl. Inorg. Chem., Delft Univ. of Technology, Julianalaan 136,
2628 BL. Delft, The Netherlands,
phone: +31 (0)15 2783262, fax: +31 (0)15 2788047, e-mail: E.M.Kelder@stm.tudelft.nl

H. Berg and J.O. Thomas,
Institute of Chemistry, Dept. of Inorganic Chemistry, Uppsala University, Sweden,
phone: +46 18 183763, fax: +46 18 508542, e-mail: josh.thomas@kemi.uu.se

ABSTRACT Several lithium manganese oxides are synthesized. Practical and theoretical phase diagrams are discussed. The compositions synthesized at 600 °C and characterized by X-Ray Diffraction (XRD) and Neutron Diffraction (ND) are determined by the Li/Mn input ratio r. These are α-Mn₂O₃, Li[LiₓMn₁₋ₓO₄] for r<0.5 and z is small, Li[LiₓMn₁₋ₓO₄] for 0.5<z<0.65 and 0<z<0.17, and LiₓMn₂O₄ for r>0.5 and z=0.17. Infra Red (IR) spectroscopy along with ND and XRD reveal LiₓMn₂O₄ to contain about 0.25 lithium ions on octahedral sites. These octahedral lithium ions are not extractable at 4 Volt, and, hence, are an undesired source for capacity reduction. The number of octahedral lithium ions depends on the synthesis process conditions. The potential curve of LiₓMn₂O₄ versus x is explained along with reported results. The single-phase regime, i.e. 0.6<z<1, is explained analogous to a titration of a weak acid with a strong base, or vice versa. The dual phase regime, i.e. 0.27<z<0.6 is explained by a precipitate of a spinel LiₓMn₂O₄ with a=0.27, containing only lithium ions on octahedral sites, and a spinel LiₓMn₂O₄ with b=0.6. Below x<0.27, i.e. only lithium ions occupy octahedral sites, an increase in the potential is expected. A same behaviour is observed as for 0.6<z<1.

INTRODUCTION

Lithium manganese oxide LiₓMn₂O₄ with the spinel structure is a promising cathode material for Li-ion batteries and has potential use in 4 Volt batteries. Besides its use for 4V batteries upon lithium ion extraction, LiₓMn₂O₄ can be used also for 3V Li-ion batteries upon lithium ion insertion. Ohtsuka et al. (1) described the potential curve of LiₓMn₂O₄ in the x range of 0.27 up to 2. These authors found several regimes which can be assigned as follows (see also Fig.1):
I \(0<x<2.0\) two coexisting phases of cubic LiMn_2O_4 and tetragonal Li_xMnO_4, resulting in a flat potential of 2.957V (here taken as 3V vs Li/Li\(^+\) for simplicity).

II \(0.60<x<1.0\) a single-phase system, which is characterized by an S-shaped open circuit voltage, with mid-point at 3.94V (here taken as 4V vs Li/Li\(^+\) for simplicity).

III \(0.27<x<0.6\) two coexisting phases of cubic Li_{1/3}MnO_4 and cubic Li_{2/3}MnO_4, resulting in a flat voltage plateau near 4.110V (here taken as 4.2V vs Li/Li\(^+\) for simplicity).

IV \(0<x<0.27\) not specified explicitly.

It is also found that LiMn_2O_4 often reveals only 70% to 80% of its theoretical capacity. Recently, the remaining 20% to 30%, 27% according to Ohzuku et al. (1), are frequently attributed to lithium ions staying on octahedral sites of the spinel host (2,3). However, clear evidence has still not been found. The octahedral lithium ions can be extracted only at elevated potentials. Furthermore, the number of octahedral lithium ions is also depending on the synthesis process conditions, such as gas atmosphere and reaction temperature. Octahedral lithium ions are observed in the inverse spinels LiNiVO_4 and LiCoVO_4 (4) having high potential for lithium ion extraction at 4.8V and 4.2V vs Li/Li\(^+\), respectively (5).

Also, teaching experiments of LiMn_2O_4 with concentrated sulphuric acid (6), and even with stronger chemicals (7) did not reveal pure \(\alpha\)-MnO_2. The minimum amount of lithium ions reported in these references is still about 10% of the initial amount present, i.e. leading to approximately Li_{0.8}Mn_2O_4.

Unfortunately, addition of extra lithium in the synthesis process did not improve the capacity for the 4V level. On the contrary, spinels with the stoichiometry of Li[Li_{1/3}Mn_2/3]O_4 were characterized recently (8), resulting in a dramatic loss of Mn\(^{3+}\) ions, and, hence, theoretical capacity. It should be borne in mind that the ions between square brackets in Li[Li_{1/3}Mn_2/3]O_4 occupy the octahedral sites.

Therefore, the domain in which lithium ions can be extracted and inserted in the 4V level is limited by the number of lithium ions that reside on the tetrahedral sites and that number is determined by the synthesis process conditions. Furthermore, addition of extra lithium in the synthesis process will also reduce the capacity for the 4V level.

Here, we report on the octahedral site occupation of lithium ions in LiMn_2O_4 and on precipitation of a spinel phase that contains only octahedral lithium ions. In addition, several models are presented in order to describe the potential curve of LiMn_2O_4, as observed by Ohzuku et al. (1), in more detail.
EXPERIMENTAL ASPECTS

Powders of lithium manganese oxide compounds were synthesized by using mixtures of manganese acetate tetrahydrate (Mn(CH₃COO)₂·4H₂O) and appropriate amounts of lithium hydroxide (LiOH·H₂O) (9). Calcination was performed at 600 °C. Leaching of LiMn₂O₃ was performed according to Hunter's method (6). The concentration of sulphuric acid was between 2 and 4M. The value of x in Li₃Mn₂O₄ is derived from accurate weighed amounts of powder and sulphuric acid of known concentration, and by measuring the final pH. The mass of the final product after leaching is weighed, which also provides information about the x-value, since the mass reduction is directly coupled to the final x-value as will be shown. Monitoring the pH during such a leaching experiment in which sulphuric acid (3.00M) is added dropwise, leads to a complete overview of the x-value as a function of the pH.

Flame Atomic Absorption Spectroscopy (AAS) is performed in order to obtain the lithium and manganese content. Infra Red (IR) spectra, using an FTIR, were recorded on KBr pellets (approximately 1mm thick and 10mm diameter, 200mg KBr) in which 0.5 to 1 mg of powder is distributed homogeneously. X-Ray Diffraction (XRD) as well as Neutron Diffraction (ND) patterns were recorded. The latter was fitted using Rietveld refinement.

RESULTS AND DISCUSSIONS

Fig. 2 shows three representative XRD patterns of the powders obtained for various manganese over lithium ratios r at a calcination temperature of 600 °C. Below r=0.5, the main composition is α-Mn₃O₄ and LiMn₂O₃. Fig. 3 shows the lattice parameters as calculated from these spectra. It appears that the lattice parameters depend slightly on the ratio r.

For 0.5<r<0.65, only a spinel structure is found with a lattice parameter decreasing upon increasing r (viz. Fig. 3). The structure in this regime can be well described by Li₃[Mn₁₋ₓLiₓ]O₄ with x ranging from 0 to 0.17. However, if proper process conditions are chosen, x can reach a value of 0.33, i.e. Li₃[Mn₁₋ₓLiₓ]O₄ that represents Li₃Mn₂O₄ having only Mn⁴⁺ ions. The lattice parameters show a similar behaviour on going to higher y values as reported (8,10). For r>0.65, i.e. where the results strongly deviate from the reported ones, a new impurity phase Li₃Mn₂O₄ shows up. This impurity phase was also observed by neutron diffraction, and Rietveld refinement reveals that the powder contains 10 w/o of Li₃Mn₂O₄ and 90 w/o of Li₃Mn₂O₄, which matches well with the nominal concentration. Furthermore, the lattice parameter derived from neutron diffraction agrees with that obtained by XRD. The composition Li₃[Mn₁₋ₓLiₓ]O₄ with the impurity phase Li₃Mn₂O₄ for r>0.65 at 600 °C was also observed by Gao and Dahn (10).

The above compositions can be assigned indistinguishably by using the overall manganese content and oxidation state (11). Fig. 5 contains these parameters for compositions Li₃Mn₂O₄ + LiMn₂O₄, Li₃[Mn₁₋ₓLiₓ]O₄, α-Mn₃O₄ and α-Mn₂O₃ + LiMn₂O₄. Compositions of either Li₃Mn₂O₄ or α-Mn₂O₃ with Li₃[Mn₁₋ₓLiₓ]O₄ can be found within the triangles Li₃Mn₂O₄ - LiMn₂O₄ - α-Mn₂O₃, respectively.
It is likely to assume that the dependence of the observed lattice parameter of the spinel present at values of r<0.5 could be explained by the presence of Li\([Li_xMn_{3-x}]_2\)O. Hence, it seems very difficult to obtain very pure LiMn\(_2\)O\(_4\).

Since lithium ion extraction is only related to the number of Mn\(^{3+}\) in the spinel phase material, the actual capacity of the powders is fully determined by their compositions. Fig. 6 depicts the capacity of the aforementioned compositions, normalised to LiMn\(_2\)O\(_4\). Obviously, in terms of capacity, the synthesis of pure LiMn\(_2\)O\(_4\) is heavily desired.

So far, the capacity of the spinel phase LiMn\(_2\)O\(_4\) is only 70 to 80% of the theoretical capacity. The remaining 20 to 30% was attributed to lithium ions on octahedral sites (2,3). In order to obtain materials with only octahedral lithium ions, LiMn\(_2\)O\(_4\) is acid-treated following Hunter's method. A titration of LiMn\(_2\)O\(_4\) with 3.00M H\(_2\)SO\(_4\) is presented in Fig. 7. The x-value is determined from the H\(^+\) consumption of added acid and the remaining H\(^+\) as derived from the pH. Since H\(_2\)SO\(_4\) is used, the second dissociation step

\[ \text{HSO}_4^- \rightarrow \text{SO}_4^{2-} + \text{H}^+ \]  

with

\[ K_{\text{H}_2\text{SO}_4} = 0.012 \text{M} \]  

is taken into account for the calculations, where \( K_{\text{H}_2\text{SO}_4} \) is the equilibrium constant at room temperature (12). The reaction upon leaching is described in Ref. (6):

\[ \text{LiMn}_2\text{O}_4 + 2y\text{H}^+ \rightarrow (1-0.25y)\text{Li}_{1+y}\text{Mn}_{3+y} + 0.5y\text{Mn}^{2+} + y\text{Li}^+ + y\text{H}_2\text{O} \]  

AAS measurements demonstrate indeed the given ratio of Li\(^{+}\)/Mn\(^{2+}\) determined by reaction [3] in the wash water. The results obtained from these calculations are gathered in Fig. 8. In addition, several experiments were performed in order to isolate powders formed after equilibrium was established. The approach of obtaining the x-value was used as given above. However, from those isolated materials the remaining mass also provides the x-value by using reaction [3]. Furthermore, AAS reveals similar results (see Fig. 9). Data of Hunter (6) and Mostbah (7) are given in this figure for comparison.

Even in preboiled de-ionized water (pH=6.24) LiMn\(_2\)O\(_4\) shows activity. Table 1 lists the final pH-values obtained from adding 1 gram of LiMn\(_2\)O\(_4\) to various amounts of water.

The reaction taking place in pure water is derived from reaction [3] and can be written as:

\[ \text{LiMn}_2\text{O}_4 + y\text{H}^+ + y\text{H}_2\text{O} \rightarrow (1-0.25y)\text{Li}_{1+y}\text{Mn}_{3+y} + 0.5y\text{Mn}^{2+} + y\text{Li}^+ + 2y\text{OH}^- \]  

The lithium amount in the spinel was calculated on the basis of LiMn\(_2\)O\(_4\) and is plotted in Fig. 8 together with the results of the titration from Fig. 7. Although a strong increase in the pH is measured on adding LiMn\(_2\)O\(_4\) to water, the calculated decrease in lithium content is marginal. However, this marginal decrease in lithium content in LiMn\(_2\)O\(_4\) has a dramatic increase in electric potential in a battery as was illustrated already in Fig. 1.
Furthermore, it should be stressed that the equilibrium pH is not the only parameter deciding the final x-value. Also, the amount of water and added amount of powder plays an important role, as is obvious from the data in Table 1. This result might be expected on the basis of the equilibrium reactions [1], [3] and [4]. Fig.8 as well as Fig.9 reflect very well the potential curve of Fig.1, and, indeed the same points of inflection are observed.

<table>
<thead>
<tr>
<th>ml water</th>
<th>final pH</th>
<th>x in Li₃Mn₂O₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>10.72</td>
<td>0.99964</td>
</tr>
<tr>
<td>25</td>
<td>10.36</td>
<td>0.99961</td>
</tr>
<tr>
<td>50</td>
<td>10.21</td>
<td>0.99957</td>
</tr>
<tr>
<td>100</td>
<td>9.86</td>
<td>0.99951</td>
</tr>
<tr>
<td>250</td>
<td>9.58</td>
<td>0.99951</td>
</tr>
</tbody>
</table>

IR spectra of various powders are presented in Figure 10. Two main peaks around 610 and 510 cm⁻¹ are visible, but for x-values below x=0.6 a clear peak shows up near 495 cm⁻¹, and is attributed to the formation of the second spinel phase. The peaks can be explained by vibrational frequencies of MnO₆, MnO₄, LiO₆ or LiO₃ groups (or more complex motions of the lattice that will not be considered here). In order to show which basic group motions determine the vibrational frequencies, the absorbance per O₆-unit (Figure 11) is plotted for several x-values in Li₃Mn₂O₄ and Li[(Li₁₋ₓMnx)₂]O₄ (z=(2x−2)/(x+2)).

Above x=1, i.e. z>0 and where Li[(Li₁₋ₓMnx)₂]O₄ exists, the absorbance increases with increasing amount of lithium. This cannot be explained by MnO₆ or MnO₄ group motions, as the number of these groups decreases per O₆-unit. MnO₄ was not even detected with XRD, as MnO₄ would give rise to the diffraction peak (220), which has not been observed. Therefore, it is concluded that the IR absorbance of Li₃Mn₂O₄ cannot be explained by MnO₄ or MnO₄ group motions too.

Below x=1 the IR absorbances of both peaks remain fairly constant down to x=0.6, which makes it impossible to explain these vibrational frequencies by LiO₆, as the number of these groups would be reduced substantially due to lithium ion extraction. The only possibility that remains is the LiO₆ group motion. Usually, MO₆ group motions (M being any metal) are obtained at lower vibrational frequencies than MO₄ group motions (13). For LiO₆, the vibrational frequencies are found between 400 and 500 cm⁻¹ (14). It was already established that lithium ions on octahedral sites require a higher potential to be removed from the host spinel lattice than the tetrahedral lithium ions. A higher potential agrees with a higher binding energy for the octahedral lithium ions, and, therefore, a higher vibrational frequency.
Assuming only LiO\textsubscript{2} group motion, i.e. lithium ions on octahedral sites, it is possible to calibrate the absorbance-axis in terms of a lithium ion octahedral site occupation using the absorbances of the powders of Li\textsubscript{x}(Li\textsubscript{1-x}Mn\textsubscript{2+y})O\textsubscript{2}. From Figure 11 it is derived that Li\textsubscript{x}Mn\textsubscript{3-x}O\textsubscript{2} (0.6<x<1.0) contains about 0.25 lithium ions on octahedral sites, irrespective of the x-value. This value is in accordance with the x-value of regime IV in Fig.1 and with the results presented in both Fig.8 and 9.

In the following part, the different regimes are discussed in further detail on the basis of the results outlined above, except for regime I of Fig.1 because no extra information can be added.

II 0.60<x<1.0
In this single-phase system, the lithium ion activity \(a_\text{Li}^+\) is explained analogous to a titration of a weak acid with a strong base (or a titration of a weak base with a strong acid). Therefore, \(a_\text{Li}^+\) can be written by (15):

\[
a_\text{Li}^+ = K(1-f)/f
\]  

where f represents the fraction of the titration regime (here from 0.60 to 1.0), and \(K\) the equilibrium constant. \(K\) is taken as unity for simplicity, since no accurate data are available to establish \(K\). However, we are currently studying the possibility to derive \(K\) from Eqs.[1], [3], and [4] by varying the activities of Mn\textsuperscript{2+} and Li\textsuperscript{+} ions in solution.

Using the Nernst equation, the potential \(V\) becomes:

\[
V = \frac{R T}{n F} \ln a_\text{Li}^+
\]  

with \(V\) the normal potential (at mid-point, i.e. \(x=0.8\)), \(R\) the gas constant (≈8.314 J/molK), \(T\) the absolute temperature (K), \(n\) the number of electrons involved in the process, and \(F\) the Faraday constant (≈96487 C).

The results of Eq.[6] clearly demonstrate the S-shape curvature as found in the literature for LiMn\textsubscript{3}O\textsubscript{4}. Since the behaviour can be described by this equation, it is assumed that the lithium ions reside on both octahedral as well as tetrahedral sites. But since the octahedral lithium ions can be extracted only at elevated potentials, the extracted lithium ions mainly originate from tetrahedral sites.

III 0.27<x<0.60
Here a dual phase system of cubic Li\textsubscript{x}Mn\textsubscript{3}O\textsubscript{4} and cubic Li\textsubscript{1-x}Mn\textsubscript{2+y}O\textsubscript{2} exists. The first contains lithium ions on both tetrahedral sites and octahedral sites. However, a lithium manganese oxide spinel with lithium ions only on tetrahedral sites cannot be excluded so far. The latter is assumed to have lithium ions only on the octahedral sites, but here too, a precipitation of a spinel compound with both lithium ions on tetrahedral and octahedral sites cannot be excluded at present. However, taking the stoichiometry used by Ohzuku et al. (1), the formation of Li\textsubscript{x}Mn\textsubscript{3}O\textsubscript{4} is interpreted as a precipitation from a solid solution. Since two phases coexist the potential reveals a flat plateau. It is assumed that precipitation is dependent on the number of octahedral lithium ions, the number of Mn\textsuperscript{3+} and Mn\textsuperscript{4+} generated upon lithium ion extraction, and on the composition of the final precipitate.
Therefore, the precipitation reaction can be written as:
\[ y \text{Li}_{10y}^{2+} + y \text{Mn}^{3+} + (2-y)\text{Mn}^{4+} + 4\text{O}^{2-} = \text{Li}_y\text{Mn}_2\text{O}_4 \]  
[7]

with
\[ K_y = a(\text{Li}_{10y}^{2+})^y \times a(\text{Mn}^{3+})^y \times a(\text{Mn}^{4+})^{2y} \times a(\text{O}^{2-})^4 \]  
[8]

where \( a(\text{Li}_{10y}^{2+}) \), \( a(\text{Mn}^{3+}) \), \( a(\text{Mn}^{4+}) \), and \( a(\text{O}^{2-}) \), are the activities of the octahedral lithium ions, the Mn\(^{3+}\) ions, and the Mn\(^{4+}\) ions, the oxygen ions, and \( K_y \) is the solubility product.

In addition, the lithium ion extraction reaction can be written by a disproportionation reaction,
\[ \text{Li}_{0.3} \text{Mn}_2\text{O}_4 = a \text{Li}_{0.3} \text{Mn}_2\text{O}_4 + b \text{Li} \]  
[9]

where \( a \) and \( b \) determine the molar ratio of both spinels formed on extraction, and, hence, the overall x-value in \( \text{Li}_x\text{Mn}_2\text{O}_4 \).

The precipitation product suggested by Ohzuku et al. (1) is \( \text{Li}_{0.27}\text{Mn}_2\text{O}_4 \), however, the real composition could easily be \( \text{Li}_y\text{Mn}_2\text{O}_4 \) with \( 0 < y < 1 \), and with lithium ions only on the octahedral sites. Lithium ions on octahedral sites result in a reduction of the lattice parameter as was observed and shown in Fig.2. Evidence of the composition could be established by careful detection of the onset of precipitation for several starting compositions, such as various \( \text{Li}[\text{Li}_y\text{Mn}_3]\text{O}_4 \) compounds. According to mass balance it is not possible to have a precipitation of compounds with \( \text{Li}/\text{Mn} > 0.5 \), i.e. \( \text{Li}[\text{Li}_y\text{Mn}_{2.2}\text{O}_4] \), without \( \text{O}_2 \) formation,
\[ \text{Li}_{0.8}\text{Mn}_2\text{O}_4 = a \text{Li}_{0.3}\text{Mn}_2\text{O}_4 + b \text{Li}[\text{Li}_y\text{Mn}_{3.3}]\text{O}_4 + c \text{O}_2 \]  
[10]

It should be borne in mind that the coefficients \( a, b, \) and \( c \) are correlated to each other. Since reaction [10] would give rise to an irreversible reaction this is not taken into account, but it could be an explanation for irreversible capacity loss in real batteries during cycling. Moreover, the XRD patterns show a gradual increase of the amount of second phase with \( \text{Li}/\text{Mn} > 0.5 \).

IV 0.0 < x < 0.27 A single-phase system of \( \text{Li}_2\text{Mn}_2\text{O}_4 \) containing lithium ions on octahedral sites only as discussed above. The potential V is written with an analogous argument as described for Regime II. Eq [6] is used in this case with \( V^* \) equal to \( 5V \), which is taken on the basis of the reported and observed high potential required to remove lithium ions from the lattice. However, the potential of \( 5V \) is taken arbitrarily. Again an S-shaped curve is observed, and it might be expected that if more phase transition were to occur the total potential curve can be extended on the same basis as outlined above. Obviously, it should be stressed that the maximum value of this regime is determined by the same argument as outlined for regime III.
CONCLUSIONS

X-Ray Diffraction (XRD) and Neutron Diffraction (ND) reveal several phases of Li-Mn-O compounds. Below Li/Mn=0.5 the composition is mainly α-Mn₂O₄+Li[LiₓMn₁₋ₓ]O₄ with small values of z. For 0.5<Li/Mn<0.65 a spinel structure is found of composition Li[LiₓMn₁₋ₓ]O₄ with 0<x<0.17. Above Li/Mn=0.65 the composition is Li[LiₓMn₁₋ₓ]O₄ + LiₓMnO₂ and x is found to be constant, i.e. 0.17. XRD and ND along with Infra Red (IR) spectroscopy reveal about 25% of lithium ions in LiMn₂O₄ to reside on octahedral sites. These lithium ions are not extractable at 4 Volt. The number of octahedral lithium ions depends on the synthesis process conditions. The amount can be obtained by IR, but also by titration with sulphuric acid and monitoring the pH. The titration curve can be transformed in such a way that it shows a similar behaviour as is observed in well-documented reports of the potential curve. Therefore, the amount of lithium ions that can be extracted at 4 Volt is easily established by the critical point of inflection in the titration curve.

Furthermore, the potential curve of LiₓMn₂O₄ is described by the following regimes, excluding the 3 Volt level.

0<x<α  In this single phase system lithium ions are present on octahedral sites only. α is determined by the number of lithium ions present which is determined by the synthesis process conditions: α is typically smaller than about 0.3. The S-shaped curve is explained analogous to a titration curve of a weak acid with a strong base or vice versa.

α<x<β  This regime represents a dual phase system of two coexisting spinel phases, of which one is described for the regime 0<x<α, and the other by LiₓMn₂O₄ (0.4<β<0.8). Due to the coexisting phases the potential is invariant to x.

β<x<1  Here too, a single phase system exists. The description of the potential curve is in line with the regime 0<x<α with a different potential to be observed.

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**Fig. 1.** Potential $V$ versus $x$ in Li$_x$Mn$_2$O$_4$. The Roman numbers correspond with the regimes as defined in the text.

**Fig. 2.** X-Ray diffraction patterns of various powders as-synthesised with the Li/Mn ratio as indicated in the figure. The diffraction peaks of the spinel phase are assigned by $\blacksquare$, the impurity phases $\alpha$-Mn$_2$O$_3$ and Li$_3$MnO$_4$ by $+$ and $\bullet$, respectively. Note that the peak positions of the spinel phase shift to higher values (i.e. lower lattice constants) if the lithium content in the spinel increases.

**Fig. 3.** Lattice parameters of the observed spinel phases, and data reported by Gumnon et al. (lower line) (8) and by Gao and Dahm (upper line) (10). The $+$ refers to as-synthesised powders containing $\alpha$-Mn$_2$O$_3$ as impurity, $\blacksquare$ refers to as-synthesised powders of Li(Li$_{1-x}$Mn$_x$)$_2$O$_4$ with or without Li$_3$MnO$_4$. $\bullet$ refers to acid-treated materials with $x$ determined by AAS.

**Fig. 4.** Neutron Diffraction pattern of a powder with a Li/Mn ratio of 0.75, fitted using Rietveld refinement and resulting in 10 w/o Li$_3$MnO$_4$ and 90 w/o Li[(Li$_{1-x}$Mn$_x$)$_2$]O$_4$. 

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**Fig. 5.** Phase diagram of Li-Mn-O compounds based on the manganese oxidation state and manganese content, assuming only Li$^+$ and O$^-$ to exist. a, b, and c refer to dual phase compositions of Li[(Li$_2$Mn$_{3-x}$)O$_x$Li$_{1-x}$Mn$_2$O$_4$]+α-Mn$_2$O$_3$, and Li[(Li$_2$Mn$_{3-x}$)O$_x$Li$_{1-x}$Mn$_2$O$_4$] respectively.

**Fig. 6.** Theoretical capacity normalised to Li$_{1-x}$Mn$_2$O$_4$ for the compositions obtained from the different synthesis. a, b, and c as in Fig.5.

**Fig. 7.** Titration curve of 1.000 gram of Li$_{1-x}$Mn$_2$O$_4$ with 3.00M H$_2$SO$_4$. The starting amount of water was 25 ml, and the pH prior to measurement was 10.29.

**Fig. 8.** Measured pH plotted as a function of the x-value derived from Eqs. [1], [2], and [3]. The 5 points at high pH (i.e. from 9 to 11) are taken from Table 1, whereas the other points are taken from Fig.7.
Fig. 9. $x$ in Li$_{2}$Mn$_{3}$O$_{4}$ as a function of the final pH: $\times$ from [6], $\bullet$ from [7], $\triangle$ from mass, $+$ from pH, and $\diamond$ from AAS.

Fig. 10. Infra Red spectra of pure spinel phases, i.e., Li$_{2}$Mn$_{3}$O$_{4}$ and Li$_{2}$[Li$_{2}$Mn$_{3}$]O$_{4}$. The values in the figure represent twice the Li/Mn ratio. The curves are shifted subsequently 25% transmission units per curve.

Fig. 11. Absorbance plotted as a function of twice the Li/Mn ratio. The dotted vertical line roughly indicates the expected number of lithium ions on the octahedral sites calibrated to Li$_{2}$[Li$_{2}$Mn$_{3}$]O$_{4}$. 