Investigation on the Phase Stability and Defect Structure of Li-Mn-O and Li-Me-Mn-O Spinel (Me=Mg, Ni, Co)

Von der Fakultät für Mathematik, Informatik und Naturwissenschaften der Rheinisch-Westfälischen Technischen Hochschule Aachen zur Erlangung des akademischen Grades eines Doktors der Naturwissenschaften genehmigte Dissertation

vorgelegt von
Master-Ingenieur Chunhui Luo
aus Gansu, V. R. CHINA

Berichter: Univ.-Prof. Dr. Manfred Martin
Priv.-Doz. Dr. Michael Schroeder

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1 Introduction

1.1 Lithium ion batteries and its relative

1.1.1 Lithium ion batteries
1.1.1.1 Rechargeable batteries

Nowadays, “mobility” has become the key word in the modern society. Portable phones, camera as well as camcorder, portable multimedia player, notebook, electric vehicles etc. supply great versatility and convenience for the “mobile life”. However, all of the electric products mentioned above demand a continuous, sufficient and clean energy provision to function perfectly, which promotes the improvement of the energy storage – battery technology. Due to world-wide shortage of the natural resources and serious environmental pollution, a kind of recyclable energy provider has been urgently demanded, where only the primary batteries are not fit for the consuming needs any more.\[^{[1]}\] Furthermore, with the electric products developing to smaller and lighter the battery manufactures, in the same, are required to meet these demands of small volume with higher energy storage and cheaper price.

In the last decades, since the first lead acid battery was invented in 1859, the rechargeable batteries have developed significantly and played more and more important roles in the battery field. Compared to the primary batteries, use of rechargeable batteries helps to achieve several of the objectives of the order, including waste reduction, toxicity reduction, waste prevention, and reuse of product. Moreover, the rechargeable batteries have another excellent advantage of low internal resistance, which allows high current on demand, an attribute that is essential for digital devices and instruments needing high inrush currents. Table 1.1.1 shows the world-wide use of different types of rechargeable batteries, covering consumer and original equipment manufacturer (OEM) markets. Presently, the global battery market is about $50 billion US, of which roughly $5.5 billion is allocated to rechargeable (secondary) batteries. The growth is estimated at 6% annually through 2006. A new generation of energy-hungry...
electronic devices, such as digital cameras, camera phones and high performance portable computing devices, will drive the growth.

Due to quite different types of batteries and battery uses it is difficult to give a common standard to evaluate the performance of the rechargeable batteries. Three main aspects are generally mentioned to evaluate the performance of rechargeable batteries: cost, performance for a given application, and environmental friendliness. A comparison of several most conventional rechargeable batteries is given in table 1.1.2. It is shown that Li-ion batteries are the most promoting technology compared to the other rechargeable batteries, especially suitable for the application in higher operating voltage range at higher temperature.

**Table 1.1.1.** World-wide use of consumer-rechargeable batteries [million batteries]^2[^]

<table>
<thead>
<tr>
<th>Battery type</th>
<th>1995</th>
<th>1997</th>
<th>2001</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nickel-cadmium</td>
<td>1560 (81%)</td>
<td>1710 (65%)</td>
<td>1940 (42%)</td>
</tr>
<tr>
<td>Nickel-metal hydride</td>
<td>310 (16%)</td>
<td>600 (23%)</td>
<td>1716 (37%)</td>
</tr>
<tr>
<td>Lithium</td>
<td>30 (2%)</td>
<td>250 (9%)</td>
<td>700 (15%)</td>
</tr>
<tr>
<td>Rechargeable alkaline</td>
<td>20 (1%)</td>
<td>70 (3%)</td>
<td>284 (6%)</td>
</tr>
<tr>
<td>Total</td>
<td>1960</td>
<td>2360</td>
<td>4640</td>
</tr>
</tbody>
</table>

**Table 1.1.2.** Comparison of several secondary batteries[^2]

<table>
<thead>
<tr>
<th></th>
<th>PbO$_2$/Pb</th>
<th>NiO$_x$/Cd</th>
<th>NiO$_x$/MH</th>
<th>Li-ion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific energy [Wh kg$^{-1}$]</td>
<td>30</td>
<td>50</td>
<td>60</td>
<td>100</td>
</tr>
<tr>
<td>Energy density [Wh l$^{-1}$]</td>
<td>50</td>
<td>100</td>
<td>180</td>
<td>200</td>
</tr>
<tr>
<td>Open-circuit voltage [V]</td>
<td>2.1</td>
<td>1.3</td>
<td>1.3</td>
<td>4.1</td>
</tr>
<tr>
<td>Operating range [V]</td>
<td>2.0–1.8</td>
<td>1.2–1.0</td>
<td>1.2–1.0</td>
<td>3.8–3.0</td>
</tr>
<tr>
<td>Peak charge/discharge rate [C]</td>
<td>6</td>
<td>10</td>
<td>5</td>
<td>1</td>
</tr>
<tr>
<td>Temp. operating range [°C]</td>
<td>–30 to +50</td>
<td>–20 to +45</td>
<td>–10 to +40</td>
<td>–20 to +60</td>
</tr>
<tr>
<td>Temp. charge range [°C]</td>
<td>0 to +45</td>
<td>0 to –45</td>
<td>0 to +40</td>
<td>0 to +45</td>
</tr>
<tr>
<td>Final charge voltage [V]</td>
<td>2.4</td>
<td>1.5</td>
<td>1.5</td>
<td>4.5</td>
</tr>
<tr>
<td>Charging time range [h]</td>
<td>2–20</td>
<td>1–3</td>
<td>2–5</td>
<td>3–20</td>
</tr>
<tr>
<td>Overcharge permitted</td>
<td>Limited</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>Overdischarge (reversal)</td>
<td>No</td>
<td>Yes</td>
<td>Limited</td>
<td>No</td>
</tr>
<tr>
<td>Charge efficiency, W [%]</td>
<td>90</td>
<td>85</td>
<td>80</td>
<td>90</td>
</tr>
<tr>
<td>Cycle life x 30% DOD$^*$</td>
<td>500</td>
<td>2000</td>
<td>800</td>
<td>2000’</td>
</tr>
<tr>
<td>80% DOD$^*$</td>
<td>200</td>
<td>800</td>
<td>600</td>
<td>800</td>
</tr>
<tr>
<td>100% DOD$^*$</td>
<td>20–50</td>
<td>500</td>
<td>200</td>
<td>200</td>
</tr>
<tr>
<td>Calendar life [year]</td>
<td>3</td>
<td>5</td>
<td>3</td>
<td>3–5</td>
</tr>
<tr>
<td>Discharge [%/month]</td>
<td>At 20 °C</td>
<td>3–5</td>
<td>15–20</td>
<td>20–30</td>
</tr>
<tr>
<td></td>
<td>At 45 °C</td>
<td>50</td>
<td>60</td>
<td>80</td>
</tr>
<tr>
<td></td>
<td>At 65 °C</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Component toxicity</td>
<td>High</td>
<td>High</td>
<td>Medium</td>
<td>Medium</td>
</tr>
<tr>
<td>Cost per cycle [$] (Reference)</td>
<td>0.10</td>
<td>0.04</td>
<td>0.12</td>
<td>0.14</td>
</tr>
</tbody>
</table>

DOD: Depth of Discharge
1.1.1.2 Working principle of lithium ion batteries

Lithium ion batteries are generally composed of a lithium containing transition metal oxide as the positive electrode material, a carbon material as the negative electrode material and an electrolyte in between. Figure 1.1.1 illustrates the working principle of the lithium-ion battery, which is based on the intercalation of Li in the active material. During charging lithium ions diffuse from the positive electrode through the electrolyte to the negative electrode, at the same time, equivalent number of electrons moves from the positive electrode to the negative electrode through the external circuit of the charger. As the potential of the positive electrode rises and that of the negative electrode is lowered by charging, the voltage of the cell becomes higher and the electrical energy is stored. Discharge reverses the process of charge, where the lithium ions and electrons move in the opposite directions by connecting a load between the positive and negative electrodes.

![Fig. 1.1.1. Schematic description of charge/discharge mechanism of a Li-ion battery](image)

[3]
The electrochemical charge/discharge reactions are described by equations 1.1.1 and 1.1.2, where M denotes a transition metal such as Co, Ni or Mn, and CLi\(_x\), the graphite materials intercalated with \(x\) moles of Li.

\[
(+, \text{ positive electrode}): \quad \text{LiMO}_2 \leftrightarrow \text{Li}_{1-x}\text{MO}_2 + x\text{Li}^+ + xe^- \quad 1.1.1
\]

\[
(-, \text{ negative electrode}): \quad \text{C} + x\text{Li}^+ + xe^- \leftrightarrow \text{CLi}_x \quad 1.1.2
\]

The active materials can accommodate Li in the interior of the solid phase by intercalation or insertion. The positive active material accommodates Li during the discharging of the battery, and the negative active material accommodates Li during the charging. Thus, lithium ion rechargeable batteries function by repeatedly cycling Li\(^+\) between two host materials with different chemical potential, so called “rocking chair batteries”.[4]

**1.1.2 Li-Mn-O spinel as the cathode of Li-ion batteries**

**1.1.2.1 Characteristics as the cathode of Li-ion batteries**

The characteristic of the materials used as the active cathode in Li-ion batteries is one of the decisive factors to affect the performance of a Li-ion battery, which should generally satisfy the following requirements:[5]

- Must be an intercalation host for lithium
- Low Fermi level and Li\(^+\) site energy \(\rightarrow\) high open-circuit voltage
- Electrode potential varies little with lithium content \(\rightarrow\) cell voltage varies little with state of charge
- Capable of accommodating large quantities of lithium per formula unit \(\rightarrow\) high capacity
- Low formula mass \(\rightarrow\) high gravimetric energy density
- Low molar volume \(\rightarrow\) high volumetric energy density
- Sustain high rates of lithium intercalation and Deintercalation \(\rightarrow\) high cell discharge/charge rates
- Highly reversible lithium intercalation and Deintercalation \(\rightarrow\) many charge-discharge cycles
- Avoid co-intercalation of solvent
- Stable in contact with candidate electrolytes
Chapter 1. Introduction

- Adequate electronic conductivity
- Low cost
- Easily fabricated into electrode
- Environmentally friendly

Since 1990 Sony introduced the first lithium ion battery with LiCoO\(_2\) cathode for the market, the lithium battery industry is undergoing rapid expansion. Presently three main compounds are investigated as the positive electrode for Li-ion batteries, two-dimensional layered Li-CoO\(_2\), LiNiO\(_2\) and three-dimensional spinel LiMn\(_2\)O\(_4\). The performance of various cathode materials for lithium ion rechargeable batteries was shown in table 1.1.3.

The components of the Li-ion batteries used currently are mostly expensive and toxic Co and Ni, which are not suitable for the rash growth of the consumption in the future. Therefore, LiMn\(_2\)O\(_4\) becomes the most attractive candidate of the cathode materials due to lower cost, nontoxicity and high working voltage, although compared to the other two cathode materials LiMn\(_2\)O\(_4\) has a smaller energy density.

**Table 1.1.3. Comparison of Various Cathode Materials for Li-Ion Batteries\[^{[6]}\]**

<table>
<thead>
<tr>
<th>Cathode material</th>
<th>LiCoO(_2)</th>
<th>LiNiO(_2)</th>
<th>LiMn(_2)O(_4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Theoretical specific capacity (mAh/g)</td>
<td>274</td>
<td>274</td>
<td>148</td>
</tr>
<tr>
<td>Density of cathode (g/cc)</td>
<td>5.16</td>
<td>4.78</td>
<td>4.28</td>
</tr>
<tr>
<td>Nominal average voltage (vs. Li)</td>
<td>4.0</td>
<td>3.7</td>
<td>4.0</td>
</tr>
<tr>
<td>Operating voltage range (V)</td>
<td>3.0–4.3</td>
<td>2.8–4.1</td>
<td>3.5–4.3</td>
</tr>
<tr>
<td>Practical specific capacity (mAh/g)</td>
<td>&gt;140</td>
<td>&gt;140</td>
<td>~110</td>
</tr>
<tr>
<td>Cycle ability</td>
<td>Good</td>
<td>Good</td>
<td>Good</td>
</tr>
<tr>
<td>Environmental</td>
<td>Contains toxic Co</td>
<td>Contains Ni</td>
<td>Green</td>
</tr>
<tr>
<td>Cost</td>
<td>Very high</td>
<td>Moderate</td>
<td>Low</td>
</tr>
</tbody>
</table>

1.1.2.2 Working principle of a LiMn\(_2\)O\(_4\) cathode

The use of LiMn\(_2\)O\(_4\) spinels as positive electrode materials was first reported in 1983. LiMn\(_2\)O\(_4\) is quite distinct from the layered oxides in that it is a three-dimensional Li-ion host. The spinel structure consists of cubic close-packed oxide ions with Mn ions in one half of the octahedral sites and Li\(^+\) in one eighth of the tetrahedral sites. The Mn\(_2\)O\(_4\) framework of the spinel structure is highly stable, and defines a series of channels formed by the face-sharing of tetrahedral lithium (8\(a\)) and empty octahedral (16\(c\)) sites. The interstitial octahedral sites (16\(c\)) are interconnected three-dimensionally by sharing common edges with six like near neighbors exactly as the 16\(d\) sites, which are shifted by half a lattice parameter in space. They provide
Chapter 1. Introduction

3D conduction pathways for Li\(^+\) intercalation in the cathode materials for electrochemical cells and rechargeable lithium batteries.\(^7\) These channels intersect in three dimensions and support rapid lithium diffusion, but unlike the layered compounds the spinels, because of the greater structural rigidity, are selective for lithium ions over solvent molecules or other large cations.

Another distinction of LiMn\(_2\)O\(_4\) as electrode material is that it offers the possibility of both lithium extraction and insertion. Li may be fully extracted to form a polymorph of \(\lambda\)-MnO\(_2\) with spinel structure, which cannot be prepared by other means. Such deintercalation refers to a potential of 4 V vs. Li\(^+\)/Li with oxidation of the Mn\(^{3+}\) to Mn\(^{4+}\). Lithium may also be intercalated into LiMn\(_2\)O\(_4\) up to a maximum composition to transform in a first-order reaction to the rock-salt phase Li\(_2\)Mn\(_2\)O\(_4\). This is associated with the insertion of lithium into the octahedral (16c) sites and a potential of 3 V vs. Li\(^+\)/Li, accompanied by a simultaneous reduction of Mn\(^{4+}\) to Mn\(^{3+}\) of the host. The origin of this large voltage difference between lithium removal and insertion is believed to be related to the difference in the site energy of Li\(^+\) in the tetrahedral (8a) and octahedral (16c) positions. In both cases the redox couple is Mn\(^{4+/3+}\). Thus the operating capacity of the Li-Mn-O spinel electrode covers a wide range as shown in figure 1.1.2. The reactions of the two steps Li-ion de- and intercalation are described as

\[
\lambda\text{-MnO}_2 \text{(spinel)} \rightleftharpoons _\text{Li}^{4V} \text{LiMn}_2\text{O}_4 \text{(spinel)} \rightleftharpoons _\text{Li}^{3V} \text{Li}_2\text{Mn}_2\text{O}_4 \text{(rock-salt)}
\]

1.1.3

![Fig. 1.1.2. Open-circuit voltage vs. Li\(^+\)/Li couple as a function of lithium content in Li\(_x\)Mn\(_2\)O\(_4\).\(^5\)](image)
1.1.2.3 Disadvantages of the LiMn$_2$O$_4$ cathode

As one of the most promoting cathode materials used in Li-ion batteries LiMn$_2$O$_4$ spinel shows high theoretical energy density, low cost, and acceptable environmental characteristics, however, exhibits also significant capacity fading during cycling. In deeply discharged Li$_x$Mn$_2$O$_4$ electrodes the increase in the concentration of Mn$^{3+}$ ions decreases the cubic symmetry of the LiMn$_2$O$_4$ spinel phase to irreversible tetragonal symmetry of the Li$_2$Mn$_2$O$_4$ rock-salt phase,\cite{8} where the so called Jahn-Teller effect takes place. The non-homogeneous local structure distortion of the Li$_x$Mn$_2$O$_4$ material is believed to at least partly contribute to the capacity loss. Great efforts have been made to improve the electrochemical performance of the LiMn$_2$O$_4$ spinel. Presently, three main techniques are adopted to overcome this problem, (i) introducing cation defects or vacancies (Li$_{1-x}$Mn$_{2-x}$O$_4$), (ii) doping with excess lithium to form the solid solution Li$_{1+x}$Mn$_{2-x}$O$_4$, (iii) doping different metals (for example, Mg, Ni, Co, Cu, Zn, Cr, and Al) on the manganese octahedral 16$d$ sites. The efforts are made to increase the amount of Mn$^{4+}$ by increasing the value of the atomic ratio Li/Mn slightly, where the Jahn-Teller effect becomes less severe, therefore, the structural stability increases and the cyclability is improved. Some of the measures have improved the cyclability of the Li-ion batteries to a great extent but accompanied by significant loss of capacity. Furthermore, the choice of substitutional ion and its oxidation state may modify the electrode in other ways, depending on the chemical characteristics of the doped ion.\cite{9–11}

1.2 Li-Mn-O spinel

1.2.1 Crystal structure of a LiMn$_2$O$_4$ spinel

1.2.1.1 Cubic spinel

The crystal structure of spinel was firstly determined by Bragg\cite{12} and Nishikawa\cite{13} separately in 1915. The normal spinel structure of the general chemical formula (A)$_{tet}$[B$_2$]$_{oct}$O$_4$ belongs to the space group $Fd\bar{3}m$, which has A cations on the tetrahedral sites and B cations on the octahedral sites, respectively. The atomic arrangement of a conventional spinel is illustrated in Fig. 1.2.1. Four primitive units at the front side with atomic position are indicated in the diagram. This cell consists of eight molecular AB$_2$X$_4$ units and is represented by four octants. The distribution of the primitive unit cubic is indicated in figure 1.2.2. Consequently, there are $Z = 8$ primitive units per cubic unit cell consisted of 32 anions and 24 cations, for a
Chapter 1. Introduction

Fig. 1.2.1. Structure of LiMn$_2$O$_4$ Spinel

Lithium 8$a$ tetrahedral sites
Manganese 16$d$ octahedral sites
Oxygen 32$e$ sites
Vacancy 8$b$ tetrahedral sites
Vacancy 16$c$ octahedral sites

Fig. 1.2.2. Distribution of the primitive unit cubic in spinel
(Same color refers to the same ion-distribution.)

Total: Li$_4$Mn$_3$O$_{16}$

4 × Green cubic
4 × Blue cubic
Chapter 1. Introduction

Vacancy 16c
Octahedral sites

Lithium 8a
Tetrahedral A site

Oxygen 32e sites

Fig. 1.2.3. Schematic illustration of lattice surroundings and nearest neighbors for the lithium 8a tetrahedral A site

Lithium 8a
Tetrahedral A sites

Manganese 16d Octahedral B sites

Oxygen 32e sites

Vacancy 8b
Tetrahedral sites

Vacancy 16c
Octahedral sites

Fig. 1.2.4. Schematic illustration of lattice surroundings and nearest neighbors for the manganese octahedral B sites
total 56 atoms. Oxygen located at 32e sites are arranged in close-packed cubic array and construct a face-centred cubic (fcc). Total 96 interstices are formed between the oxygen in the cubic unit cell, but only 24 are occupied by cations in AB₂O₄ compounds. Of the 64 tetrahedral interstices that exist between the oxygen, 8 are occupied by A cations (8a), and half of the 32 octahedral interstices are occupied by 16 B cations (16d), respectively.[14]

The nearest surrounding of each lattice site are schematically described in Fig 1.2.3 and 1.2.4 for a ideal cubic close packed spinel, where 8b and 16c represent the vacancies on the tetrahedral and octahedral sites respectively. A-site tetrahedra in spinel are isolated from each other and share corners with neighboring B-site octahedra. No edge sharing occurs between A-site tetrahedra and other A- or B-site polyhedra. B-site octahedra share six of twelve X-X edges with nearest-neighbor B-site octahedra. The other six edges are shared with octahedra that surround 16c vacant sites. The X-X edges that are shared by the B cations form chains in the lattice along the <110> directions. It is generally accepted that the ideal LiMn₂O₄ compound has a spinel crystal structure with Li⁺ ions on tetrahedral sites (8a) and equal amount of Mn³⁺ and Mn⁴⁺ ions on octahedral sites (16d) with an average electric charge of +3.5. The lattice symmetry is cubic with a lattice constant of about 825 pm.[15] The 8a and 16c sites form a three-dimensional pathway for lithium diffusion.

1.2.1.2 Inverse spinel

Many compounds with spinel structure can accommodate great amounts of cation disorder. In an extreme case, when the tetrahedral sites are fully occupied by B cations whereas the octahedral sites are occupied by A and B cations in equal proportions, the crystal structure becomes a “inverse” spinel with formula (B)ₚ[AₜBₜ]ₚO₄, which was introduced by Verwey and Heilmann.[14] Experiments have revealed that cation order is often located somewhere between the extremes of normal and inverse spinel. Some of the principal factors that influence cation inversion include temperature, the electrostatic contribution to the lattice energy, cationic radii, cationic charge, and crystal-field effects. The defect structure of the inverse spinel is an intrinsic defect disorder. In an inverse Li-Mn-O spinel, part or half of the Mn ions on the 16d sites displace the lithium ions on the 8a sites and prevent more facile diffusion of lithium ions from 8a to other 8a sites through vacant octahedral 16c sites.
The formula of the intermediate Li-Mn-O compound, where a fraction of Li$^{+}$ are substituted for Mn$^{2+}$, can be written as \((\text{Li}_{1-x}\text{Mn}_{x}^{2+})_{6d}[\text{Mn}_{1-x}^{4+}\text{Mn}_{x}^{3+}]_{6d}\text{O}_{4}\), which is described as a cubic close-packing of O atoms, with manganese in octahedral positions and either lithium or divalent manganese in tetrahedral positions.\(^{[16][17]}\) Because of the dislocation of lithium and manganese ions, the X-ray diffraction peaks of the spinel that are sensitive to the cation occupancy of the tetrahedral or octahedral sites should change. The [220] Bragg peak \((2\theta = 30.7^\circ)\), which is the indication of Mn$^{2+}$ on the octahedral sites, should increase with increasing cation mixing.\(^{[18][19]}\)

### 1.2.1.3 Tetragonal spinel

In an ideal LiMn$_2$O$_4$ spinel equal number of Mn$^{3+}$ and Mn$^{4+}$ occupy octahedral 16d sites, where the spinel has a face-centred cubic construction. However, most of the Li-Mn-O cathodes using the Mn$^{4+/3+}$ redox couple suffer from large Jahn-Teller (JT) instability. That is essentially caused by the cooperative interaction of the local distortion around trivalent manganese ions (electron configuration: \(t_{2g}^3e_g^1\)) at the octahedral sites, which is suppressed by non-Jahn-Teller ions, Mn$^{4+}$ (\(t_{2g}^3e_g^0\)) and Mn$^{2+}$ (\(t_{2g}^1e_g^2\)). The instability of unequally filled e$_g$ orbitals in a strictly octahedral geometry induces the tetragonal distortion.\(^{[20–22]}\) The average valence of Mn in LiMn$_2$O$_4$ is 3.5, which is just on the critical point. Therefore, even a slight external disturbance to LiMn$_2$O$_4$ induces the Jahn-Teller distortion as a result of the average Mn valence decreasing to keep the charge neutrality.\(^{[22]}\) The local structure of the cubic spinel (space group \(Fd\bar{3}m\)) transforms in a first-order reaction to a tetragonal spinel (space group \(I4_1/amd\)).

Three types of tetragonal structures in LiMn$_2$O$_4$-based materials have been attributed to Jahn-Teller distortion.\(^{[23]}\) The first type was observed when a composition of Li$_2$Mn$_2$O$_4$ was achieved through chemical or electrochemical Li-ion intercalation, which causes a cooperative displacement of the lithium ions in the 8a sites to neighboring vacant 16c sites and a simultaneous reduction of the host transition metal ions.\(^{[20][24]}\) The second was found for the sample heated to a higher temperature,\(^{[17][18]}\) which was described by the general formula LiMn$_{2-\delta}$O$_{4-\delta}$. It was suggested that the tetragonal phase observed in the sample is a result of oxygen extraction, which results also in the increase of Mn$^{3+}$ concentration but different mechanisms from the Li-ion intercalation. The third was reported for a stoichiometric LiMn$_2$O$_4$ sample cooled just below room temperature to about 280K.\(^{[25–27]}\) It was indicated by
Yamada that the temperature change, which is not accompanied by a change in the valence state of Mn, is not a strong driving force in inducing the Jahn-Teller distortion. The tetragonal distortion $c/a$ in the $I4_1/amd$ phase was 1.011, which is much smaller than the room temperature data for $\text{Li}_2\text{Mn}_2\text{O}_4$ ($c/a = 1.158$) and $\text{LiMn}_2\text{O}_{3.86}$ ($c/a = 1.070$). The influence on the performance of a cell containing $\text{LiMn}_2\text{O}_4$ cathode may be negligible.\[22\] Furthermore, the substitution of manganese by lithium would lower the temperature at which the Jahn-Teller distortion occurs.\[28\]

The tetragonal phase, in which the manganese oxidation state is less than 3.5, manifests itself in the XRD pattern at 840°C by the splitting of the [311] peak of the cubic $\text{LiMn}_2\text{O}_4$ phase into the [311] and [113] peaks of the tetragonal phase. The extent of the tetragonal (Jahn-Teller) distortion depends on the amount of oxygen lost from the sample and

Fig. 1.2.5. Comparison of XRD patterns of cubic and tetragonal spinel phases\[18\]
on the concentration of Mn$^{3+}$ cations on the octahedral sites of the spinel structure; at 840°C, the c/a ratio of the tetragonal phase is 1.02, indicative of only a small deviation from ideal cubic symmetry (c/a = 1.00).[17][29] Another study has also identified the transformation of LiMn$_2$O$_4$ from a cubic to a tetragonal lattice. In the transformation to the tetragonal phase, all the hkl peaks split into two, with one roughly twice as intense as the other, except for peaks with $h = k = l$ as shown in figure 1.2.5.[18]

### 1.2.2 Phase diagram of Li-Mn-O system

#### 1.2.2.1 Ternary phase diagram

An isothermal cross section of the ternary Li-Mn-O phase diagram was first reported by Thackeray et al. The position of spinel and rock-salt compositions within $\lambda$-MnO$_2$, MnO and Li$_2$MnO$_3$ tie-triangle is marked by the shade in figure 1.2.6. Stoichiometric spinels fall on the tie line between Mn$_3$O$_4$ (hausmannite) and Li$_4$Mn$_5$O$_{12}$, whereas stoichiometric rock-salt compounds are located on the MnO–Li$_2$MnO$_3$ tie-line.[30] An expanded view of this tie-triangle is shown in figure 1.2.7. The Li-Mn-O spinel can be obtained over a wide compositional range within the Mn$_3$O$_4$–Li$_4$Mn$_5$O$_{12}$–$\lambda$-MnO$_2$ triangle. $\lambda$-MnO$_2$ cannot be synthesized directly from the lithium and manganese salts, which has a same occupation of Mn in the octahedral 16d and O in 32e sites as LiMn$_2$O$_4$, in which all Li$^+$ in the tetrahedral 8a sites is extracted by electrochemical or chemical methods. Therefore, it is preferable to refer to the Li-Mn-O spinel phases of particular interest as insertion cathode locating in the LiMn$_2$O$_4$–Li$_4$Mn$_5$O$_{12}$–Li$_2$Mn$_4$O$_9$ triangle. Apparently, Li$_3$Mn$_5$O$_{12}$ ($x = 1/3$ in Li$_{1+x}$Mn$_{2-x}$O$_4$) is the limiting compound of lithium-rich series and Li$_2$Mn$_4$O$_9$ ($x = 1/9$ in Li$_{1-x}$Mn$_{2-2x}$O$_4$) of the vacancy-rich series, in which the average Mn valence is +4.[15] Li$_2$Mn$_4$O$_9$ and Li$_3$Mn$_5$O$_{12}$ spinels have lower degree of crystalline compared to LiMn$_2$O$_4$.[32]

The stoichiometric Li$_{1+x}$Mn$_{2-x}$O$_4$ compounds ($0 \leq x \leq 1/3$) are located on the tie-line between LiMn$_2$O$_4$ ($x = 0$) and Li$_4$Mn$_5$O$_{12}$ ($x = 1/3$), which have lithium ions in both the tetrahedral A-sites and octahedral B-sites.[33] Increase of the Li:Mn mole ratio for Li$_{1+x}$Mn$_{2-x}$O$_4$ ($0 \leq x \leq 1/3$) leads to composition varying along the tie line from LiMn$_2$O$_4$ to Li$_4$Mn$_5$O$_{12}$, where the Li-Mn-O compounds maintain a cubic spinel construction. The lattice constant $a$ decreasing with increasing $x$ was given in figure 1.2.8, which shows a roughly linear dependence.[34][35] According to the charge neutrality the spinel with lithium excess can be written as Li$_{1+x}$Mn$^{III}_{1-3x}$Mn$^{IV}_{2+3x}$O$_4$, which has 1–3x Mn$^{3+}$ ions and 1+2x Mn$^{4+}$ ions in Li$_{1+x}$Mn$_{2-x}$O$_4$. The
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Fig. 1.2.6. Ternary phase diagram of Li-Mn-O system

Fig. 1.2.7. Extended ternary phase diagram of Li-Mn-O system
end member of lithium rich spinel Li$_4$Mn$_5$O$_{12}$ possesses a cubic spinel structure with a significant smaller lattice constant of about 817 pm,\cite{7,15} in which lithium ions occupy both the whole tetrahedral $8a$ sites, and one third of the octahedral $16d$ sites, while all the manganese ions occupy the residual $16d$ sites.\cite{36} The atomic distribution can be described by formula \((\text{Li})_{8a}[\text{Li}_{1/3}\text{Mn}_{5/3}]_{16d}\text{O}_4\) if neglecting the cation mixing.

The Li-Mn-O compounds located on the tie-line between LiMn$_2$O$_4$ and Li$_2$Mn$_4$O$_9$ can be presented by the general formula Li$_{1-x}$Mn$_{2-2x}$O$_4$ (0 $\leq$ \(x\) $\leq$ 1/9), where Li/Mn mole ratio is equal to 0.5 and cation vacancies exist on both the tetrahedral $8a$ sites and octahedral $16d$ sites.\cite{37} The cation deficient Li-Mn-O phase has a cubic spinel structure.\cite{38} Increasing of oxygen content results in the increasing of Mn$^{4+}$ concentration to maintain the charge neutrality in the spinel. When all Mn$^{3+}$ ions are oxidized into Mn$^{4+}$, the spinel Li$_2$Mn$_4$O$_9$ is obtained, which can be equivalently expressed by \((\text{Li}_{8/9}\text{V}_{1/9})_{8a}[\text{Mn}_{16/9}\text{V}_{2/9}]_{16d}\text{O}_4\). The unit cell parameter of Li$_2$Mn$_4$O$_9$ were determined as 810.92 pm, which is smaller than that of LiMn$_2$O$_4$.\cite{32} The cation deficient spinel Li$_{1-x}$Mn$_{2-2x}$O$_4$ (0 $\leq$ \(x\) $\leq$ 1/9) is unstable at higher temperature and difficult to fully oxidized.\cite{39} The number of the vacancies on the tetrahedral and octahedral sites was reduced when the calcination temperature increasing, where the defect spinel tends to change from the nonstoichiometric to stoichiometric one.\cite{40,41}
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For lithium-rich spinels, actually, it is very difficult to obtain a common formula such as \( \text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_{4} \), in which the total number of Li and Mn atoms is just equal to three per formula unit. The description depends not only on the Li/Mn mole fraction in the starting materials but also on the oxygen content. A formula \( \text{Li}_{1+y}\text{Mn}_{2-x}\text{O}_{4} \) \( (y \geq x) \) was raised by Xia \(^{[37]}\) to present the lithium-rich or/and vacancy-rich spinels, which are located in the \( \text{LiMn}_{2}\text{O}_{4} - \text{Li}_{4}\text{MnO}_{12} - \text{Li}_{2}\text{Mn}_{4}\text{O}_{9} \) triangle on the ternary phase diagram. All compounds in the triangle can be synthesized directly by a reaction in which the Li/Mn mole ratio, reaction temperature, oxygen partial pressure and preparation route are all controlled.

The stoichiometric lithium deficit compounds, \( \text{Li}_{1-x}\text{Mn}_{2+x}\text{O}_{4} \), in which part of the \( \text{Li}^{+} \) ions on the tetrahedral sites are substituted by \( \text{Mn}^{2+} \) ions, have also the spinel crystal structure (belong to inverse spinel), which are located on the line between \( \text{LiMn}_{2}\text{O}_{4} \) and \( \text{Mn}_{3}\text{O}_{4} \) on the ternary phase diagram. The lattice constant of lithium deficit spinel is smaller than that of \( \text{LiMn}_{2}\text{O}_{4} \).\(^{[19]}\) The oxygen deficient compounds with a general formula \( \text{LiMn}_{2}\text{O}_{4-\delta} \) can also be synthesized at higher temperature, which maintain the spinel structure but has the strong tendency to perform the Jahn-Teller distortion as discussed above. \( \text{LiMn}_{2}\text{O}_{4-\delta} \) spinels are located on the extended line of \( \text{Li}_{2}\text{Mn}_{4}\text{O}_{9} \) to \( \text{LiMn}_{2}\text{O}_{4} \). By taking into account both lithium deficiency and oxygen nonstoichiometry an extended spinel region is pointed out in figure 1.2.7 by the blue triangle schematically, in which the spinels were generally considered to have the tetragonal crystal structure.\(^{[19]}\)

Lithium insertion into/extraction from the tetrahedral A-sites of the spinel structure occurs at 4 V, while lithium insertion into/extraction from octahedral sites occurs at 3 V as shown in figure 1.1.2. Generally, the 4 V region lies within the \( \text{LiMn}_{2}\text{O}_{4-\lambda}\text{-MnO}_{2} - \text{Li}_{4}\text{Mn}_{2}\text{O}_{12} \) tie-triangle, and the 3 V region within the \( \text{LiMnO}_{2} - \text{LiMn}_{2}\text{O}_{4} - \text{Li}_{4}\text{Mn}_{3}\text{O}_{12} - \text{Li}_{2}\text{MnO}_{3} \) quadrilateral. The onset of the Jahn-Teller distortion in lithiated-spinel electrodes occurs when the average oxidation state of manganese reaches approximately +3.5.\(^{[8]}\)\(^{[17]}\)\(^{[31]}\)

1.2.2.2 Phase diagram of the second kind

In the ternary Li-Mn-O phase diagram discussed above all the possible composition of the compounds can be described in detail, however, the relationship of the compounds mentioned in the Li-Mn-O system is still ambiguous, because most of the compounds are stable on different conditions, which is not indicated in the diagram. Another kind of phase diagram
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Fig. 1.2.9. Phase diagram of Li-Mn-O system of the second kind\textsuperscript{[19]}

The phase diagram (of the second kind) of the system Li-Mn-O in air was given in figure 1.2.9, where y-axis represents temperature between 350 and 1060 °C and x-axis the mole fraction Li/(Li+Mn), respectively. Li-Mn spinel exhibits several stability regions: LiMn\textsubscript{1.75}O\textsubscript{4} and Li\textsubscript{4}Mn\textsubscript{5}O\textsubscript{12} (with Mn oxidation state $\nu$ = 4.0) are stable below 400 °C; cation-mixed spinels Li\textsubscript{1+x}Mn\textsubscript{2–x}O\textsubscript{4} (with 3.5 < $\nu$ < 4.0) are stable at intermediate temperatures, and tetragonal spinel Li\textsubscript{1–x}Mn\textsubscript{2+x}O\textsubscript{4} (with $\nu$ < 3.5) is stable at elevated temperatures.\textsuperscript{[19]} Apparently, the single phase Li-Mn-O spinel of certain composition is stable only at certain temperature in air. Li\textsubscript{4}Mn\textsubscript{5}O\textsubscript{12}, the end member of Li\textsubscript{1+x}Mn\textsubscript{2–x}O\textsubscript{4} ($x = 0.33$), exhibits a lowest stable temperature at about 400°C, while the spinel with Li/(Li+Mn) < 1/3 (refers to lithium deficit spinel) maintain the spinel structure only at higher temperature with a tetragonal crystal construction. Apparently, the spinel stability region in air given on the diagram is related on the temperature and mole fraction of Li/(Li+Mn).\textsuperscript{[19]} In air atmosphere LiMn\textsubscript{2}O\textsubscript{4} is a high temperature modification and can maintain the single phase composition at room temperature by quenching. Slow cooling decomposes LiMn\textsubscript{2}O\textsubscript{4} into manganese oxide and a Li-rich spinel phase. The single phase Li-rich spinels are a low temperature modification in air and decomposes during heating into Li-poor spinel phase and Li\textsubscript{2}MnO\textsubscript{3}.\textsuperscript{[15][42]}
1.2.3 Thermal stability of the single phase spinel

The wide variety of lithium-manganese-oxide spinel compounds and the existence of large areas of solid solution make it difficult to prepare single-phase compounds with predetermined compositions, particularly in large quantities. The control of preparation procedures, particularly temperature and oxygen partial pressure, to control the oxygen stoichiometry, and the application of the homogeneously mixed starting materials are critically important to fabricate high quality materials. Therefore, many studies have concentrated on investigating the thermal stability of the Li-Mn-O spinel by thermogravimetric analysis (TGA) and differential thermal analysis (DTA) and in situ X-ray diffraction (XRD) methods.

1.2.3.1 Upper critical temperature, $T_{c1}$

The XRD patterns of a heated LiMn$_2$O$_4$ sample given in figure 1.2.10 show that several phase changes occur between room temperature and 1200°C. At moderate temperature below 800°C only the peaks of the single phase spinel were detected. Above this temperature the second phase, a stable rock-salt phase, Li$_2$MnO$_3$ is formed, accompanied by the change of the spinel crystal symmetry from cubic to tetragonal. This result is consistent with the thermogravimetric analysis (TGA) data collected in their work very well (figure 1.2.11). At 780°C the sudden uncontinuous mass decrease found on the TG plot reflects, in general, the onset of a phase transition, which was defined as the upper critical temperature, $T_{c1}$. These combined data provide evidence of the following reaction process at $T_{c1}$:

$$\text{LiMn}_2\text{O}_4 \leftrightarrow \text{Li}_{1-2x}\text{Mn}_{2-x}\text{O}_{4-3x-x'} + x \text{Li}_2\text{MnO}_3 + x'/2 \text{O}_2(g)$$  \hspace{1cm} 1.2.1

During this reaction, the mass decreases continuously due to loss of oxygen from LiMn$_2$O$_4$, where lithium diffuses to the particle surface, resulting in a disproportionation of LiMn$_2$O$_4$ into a tetragonal spinel phase, Li$_{1-2x}$Mn$_{2-x}$O$_{4-3x-x'}$ and a stable rock-salt phase, Li$_2$MnO$_3$.\cite{17, 29, 40, 43}

The second critical temperature, $T_{c2}$, was also discussed by several research groups. At 915°C as shown in figure 1.2.11 the second uncontinuous mass change during heating was observed on the TG plot, which refers to another phase transformation that was described by

$$\text{Li}_2\text{MnO}_3 + \text{LiMn}_2\text{O}_4 \leftrightarrow 3 \text{LiMnO}_2 + \frac{1}{2} \text{O}_2$$  \hspace{1cm} 1.2.2
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The Li$_2$MnO$_3$ and the spinel host react and form a new phase LiMnO$_2$ accompanied by further release of oxygen, where another slope of mass decrease was obtained.$^{[17]}$ The direct evidence of the phase transition around this temperature was shown in the *in situ* XRD plot in figure 1.2.10, where the peaks of Li$_2$MnO$_3$ disappear and those of LiMnO$_2$ appear.

**Fig. 1.2.10.** *In situ* XRD patterns of LiMn$_2$O$_4^{[17]}$

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**Fig. 1.2.11.** TG plot of LiMn$_2$O$_4^{[17]}$
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1.2.3.1.1  $T_{c1}$ dependence on $n_{Li}/n_{Mn}$

The first weight-loss onset-temperature depends on the amount of the Li/Mn mole ratio of the samples. It was shown in figure 1.2.12 that the upper critical temperature, $T_{c1}$, becomes lower as the lithium content in the starting material is increased.\cite{34,35,37,42} In other words, the Li-Mn-O spinel with general formula $Li_{1+x}Mn_{2-x}O_4$ ($0 < x \leq 0.33$) requires lower synthesis temperatures to ensure single-phase products. Tarascon\cite{18} pointed out that materials quenched from temperatures between $T_{c1}$ and $T_{c2}$ have a tetragonal structure, so the inflection at $T_{c1}$ could indicate the onset of the cubic-tetragonal distortion. The strong dependence of $T_{c1}$ on $x$ provides a very important way for determining the lithium to manganese ratio in the spinel phase.\cite{44}

![Fig. 1.2.12. Dependence of $T_{c1}$ on $x$ in $Li_{1+x}Mn_{2-x}O_4$\cite{34}](image)

(Series A, B, G and H refer to different preparation routes)

1.2.3.1.2  $T_{c1}$ dependence on $pO_2$

The dependence of the upper stability line, $T_{c1}$, on the oxygen partial pressure, $pO_2$, is shown in figure 1.2.13 for the Li-Mn-O spinel with different lithium content.\cite{19} $T_{c1}$ increases with $pO_2$ increasing. $T_{c1}$ is the critical temperature, where Li-Mn-O spinel begins to decompose into a two-phase mixture, accompanied with release of oxygen as described in the equation 1.2.1. Apparently, oxygen partial pressure, $pO_2$, plays a very important role in the reaction. Increasing $pO_2$ results in increase of $T_{c1}$. A higher temperature is required to decompose
Fig. 1.2.13. Dependence of $T_c$ on $pO_2$ for the $Li_{1+x}Mn_{2-x}O_4$ spinel with different $x$.\cite{19,45}

1.2.3.2 Lower critical temperature, $T_{cL}$

At lower temperature the existence of the impurity phase manganese oxides for the $Li_{1+x}Mn_{2-x}O_4$ spinel ($0 \leq x < 0.33$) was confirmed by some research groups.\cite{19,40,41,45} The Li-Mn oxide has the single phase spinel composition only at certain temperature region. The critical temperature between the single phase spinel and the two-phase mixture was determined between 600 and 700°C by XRD measurements as shown in figure 1.2.14 for the sample of $n_{Li}/n_{Mn}=0.5$.\cite{40} Below the critical temperature the peaks of $Mn_2O_3$ and spinel phase indicate the coexistence of those two phases. If not taking into account the oxygen non-stoichiometry in the spinel, the reaction at the critical temperature could be written as

$$LiMn_2O_4 + \frac{x}{4(1+x)}O_2 \leftrightarrow \frac{1}{1+x}Li_{1+x}Mn_{2-x}O_4 + \frac{3x}{2(1+x)}Mn_2O_3$$ \hspace{1cm} 1.2.3

where oxygen could be consumed to produce the spinel with lithium excess and manganese oxide.\cite{19}

Furthermore, the coexistence of $Mn_2O_3$ with spinel phase was also verified for the sample with lithium deficit.\cite{19,40–42,46–49} The peaks of $Mn_2O_3$ together with spinel are shown
in figure 1.2.15 on the XRD pattern recorded at room temperature for the Li-Mn-O sample with \( n_{Li}/n_{Mn}=0.45 \) after calcination at 800°C.\(^{[47]} \) It implies that at a certain temperature a critical mole fraction of lithium and manganese exists, which indicates the boundary between single phase spinel and two-phase mixture region.

![XRD patterns](image)

**Fig. 1.2.14.** XRD patterns recorded after the precursor firing in air at given temperature. The precursor was obtained by sol-gel procedure.\(^{[40]} \)

![XRD patterns](image)

**Fig. 1.2.15.** The XRD patterns of Li-Mn-O sample \( n_{Li}/n_{Mn}=0.45 \)\(^{[47]} \)

1.2.4 The defect aspect of Li-Mn-O spinel
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It has been confirmed that the nonstoichiometric defect in the Li-Mn-O spinel plays an important role on the electrochemical performance of the Li-ion batteries with the spinel as the cathode materials. The defect structure has been investigated by some research groups. Sugiyama et al\cite{50,51} have measured the oxygen nonstoichiometry in LiMn$_2$O$_{4-\delta}$ by using thermogravimetric method at certain temperatures when the oxygen partial pressure was changed between $10^{-4}$ and 1 bar. The maximum oxygen deficiency was found to be about 0.2 and the dependence of $\delta$ on $pO_2$ was expressed by $\delta \sim pO_2^{-0.67\pm0.06}$. Three defect models were put forward to explain the nonstoichiometric structure in their work. A complicated cluster model, in which four Mn$^{3+}$ ions were bound to two oxygen vacancies, was considered to be the suitable one. Another point of view was raised by Hosoya’s group.\cite{52} The relationship between $\delta$ and $pO_2$ was determined by measuring the density change of the Li-Mn-O sample under different $pO_2$ at 750°C. The oxygen nonstoichiometry estimated was $0 \leq \delta \leq 0.018$, which is quite smaller than Sugiyama’s results. Furthermore, the nonstoichiometric defect was considered to be the metal-rich defect.

In order to determine the defect structure in Li-Mn-O spinel, Ammundsen\cite{53} and Koyama\cite{54} have investigated the defect models respectively by calculating the defect formation energy on the basis of defect simulation method. The defect formation of vacancies and interstitials of Li, Mn and O as well as Schottky defect was discussed in their works. It was reported by both groups that the formation energy of Li interstitials on the octahedral 16$c$ sites shows the lowest value among the possible defect species, which was determined to be 1.65 and 1.46 eV per defect respectively. Moreover, it was also mentioned by Koyama et al\cite{54} that the defect formation of excess Mn at the 8$a$ by substituting for Li or at the empty 16$c$ by pushing one neighboring Li on the next 16$c$ has the similar low-level energy consumption as that of Li ions on 8$a$ direct occupancy on empty 16$c$ sites.

1.3 Li-Me-Mn-O spinel (Me = Mg, Ni, Co)

In order to improve the cycle performance of the Li-ion batteries with Li-Mn-O spinel cathode, several research groups have investigated the properties of metal substituted Li-Me-Mn-O compounds (Me = Al, Cr, Ga, Ti, Ge, Fe, Co, Zn, Ni, Mg). It was pointed out that the substitution of metal cation for Mn enhances the stability of the spinel structure, where the average Mn valence increases and the Jahn-Teller distortion is suppressed. It is generally ac-
cepted that the metal cation doped stoichiometric Li-Mn-O compounds have the common formula Li$_{8a}$[Me$_{y}$Mn$_{2-y}$]$_{16d}$O$_{4}$, and possess a cubic spinel structure. The doped metal ions substitute for the manganese ions on the octahedral 16$d$ sites, where lithium ions keep the tetrahedral 8$a$ location. The thermal stability of LiMe$_{1/6}$Mn$_{11/6}$MnO$_{4}$ (Me=Co, Mg, Ni) were studied by TG-DTA and in situ high-temperature powder X-ray diffraction measurement. These samples were partially decomposed to monoclinic Li$_2$MnO$_3$ at high temperature, which refers to the same characteristic of the upper critical temperature, $T_{c1}$, for the undoped Li-Mn-O spinels. Similar TG-DTA plots were also recorded for the doped samples.$^{[55]}$

Magnesium doping decreases the specific surface area of the resultant powders. The lattice constant of the spinel decreases with increasing of magnesium doping as shown in figure 1.3.1 due to increase of Mn$^{4+}$ concentration resulting from the substitution of lower valence Mg$^{2+}$ for higher valence Mn$^{3+}$ ions. Electrochemical measurements revealed that LiMg$_x$Mn$_{2-x}$O$_4$ cathode has an initially smaller capacity but more excellent cycling performance with 100% retention of its capacity over the first ten cycles when compared with the undoped spinel LiMn$_2$O$_4$.$^{[56–58]}$

Li-Mn-O compounds with nickel or cobalt dopant is more complicated than that with magnesium dopant, because these two dopants can exhibit different valences in the spinel compounds. Both dopants result in the initial capacity loss but improvement of the cycle performance. Doping increases the average valence of manganese to more than 3.5, where the spinel is more stable to avoid Jahn-Teller distortion during charging-discharging cycling.

Nickel doped spinel has higher thermal stability than LiMn$_2$O$_4$.$^{[59]}$ If heated over the stability limit LiNi$_x$Mn$_{2-x}$O$_4$ loses oxygen and changes disproportionally to a spinel with a smaller Ni content and Li$_2$Ni$_{1-x}$O.$^{[60]}$ Different arguments were given in literature for the nickel valence in the LiNi$_x$Mn$_{2-x}$O$_4$ spinel. It was pointed out by Amon et al. that either Ni$^{2+}$ or Ni$^{3+}$ exist possibly in the Ni-doped spinel phase, the amount of which varies according to the dopant concentration.$^{[61]}$ However, Zhong et al. has indicated that the nickel takes only oxidation state +2 and there are 1–2x Mn$^{3+}$ and 1+x Mn$^{4+}$ in LiNi$_x$Mn$_{2-x}$O$_4$ per formula unit, which can be described as Li$^{1+}$Ni$^{2+}$Mn$_{1-2x}^{3+}$Mn$_{1+x}^{4+}$O$_{4-}$.$^{[60]}$ The lattice constant of Ni-doped spinel decreases with increasing of Ni concentration.$^{[60][62]}$ as shown in figure 1.3.2.
Fig. 1.3.1. Lattice constant as a function of $x$ in LiMg$_x$Mn$_{2-x}$O$_4$\textsuperscript{[58]} 

Fig. 1.3.2. Lattice constant as a function of $x$ in LiNi$_x$Mn$_{2-x}$O$_4$\textsuperscript{[60]}
(Different point forms denote different preparation routes.)

Fig. 1.3.3. Lattice constant as a function of $x$ in LiCo$_x$Mn$_{2-x}$O$_4$\textsuperscript{[63]}
(Different point forms denote different preparation routes.)
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It was suggested that the oxidation state of the cobalt in the Co-doped Li-Mn-O spinel is +3. The Co$^{3+}$ ions replace the Jahn-Teller Mn$^{3+}$ ions in LiMn$_2$O$_4$ on the octahedral sites to formation Li[Co$_x$Mn$_{1-x}$O$_{4-x/2}$]O$_4$, where the electrochemical performance of the Co-substituted Li-Mn-O spinel is improved. The unit cell parameter decreases as the Co-content increases as shown in figure 1.3.3.

1.4 Background of this work

A lot of research has been concentrated on improving the electrochemical performance for the Li-Mn-O spinels by measuring the charge-discharge characteristics. It is reasonable to believe that a good comprehension of the material physical chemical properties is one of the most important aspects to enhance the behavior, and thereafter to overcome the disadvantages exhibited as the cathode materials. Therefore, this work was focus on the investigation on the spinel phase diagram and oxygen nonstoichiometry for Li-Mn-O spinel, which revealed the properties of the spinel thermal stability, defect structure formation as well as the relative characteristics from the view of physical chemistry.

1.4.1 The thermal stability of the spinel phase

The thermal stability of the spinel phase has been investigated by several research groups. The Li$_{1+x}$Mn$_{2-x}$O$_4$ ($0 \leq x \leq 0.33$) spinel with given x has an upper and lower stability temperature. Over the upper stability temperature, $T_{c1}$, the spinel phase is partially decomposed to monoclinic Li$_2$MnO$_3$, while below the lower critical temperature, $T_{cL}$, to Mn$_2$O$_3$. The upper critical temperature was confirmed to be a function of x in Li$_{1+x}$Mn$_{2-x}$O$_4$ ($0 \leq x \leq 0.33$) spinel and oxygen partial pressure $pO_2$. However, the determination of the lower critical temperature was more difficult. At lower temperature due to the quite small driving force of the decomposition a long time is needed to reach the reaction equilibration. Moreover, the second phase, Mn$_2$O$_3$, takes only a small ratio in the two-phase mixture. Very weak peak intensity of Mn$_2$O$_3$ phase was shown on the x-ray diffraction patterns compared to the host spinel phase, which is difficult to be distinguished.

The thermal stability for the lithium deficient spinel Li$_{1-x}$Mn$_{2+x}$O$_4$ was also discussed before. At high temperature the single phase tetragonal spinel was found in some works, but another argument was also put forward that no Jahn-Teller distortion performed and the spinel
possessed the same cubic spinel lattice as the Li$_{1+x}$Mn$_{2-x}$O$_4$ ($0 \leq x \leq 0.33$) spinel. At lower temperature the existence of the impurity phase Mn$_2$O$_3$ for the lithium deficient spinel was also confirmed, which has bigger peak intensity on the XRD patterns than lithium excess spinel, that refers to a higher concentration of Mn$_2$O$_3$ in the two-phase mixture.

The impurity phases, such as Li$_2$MnO$_3$ and Mn$_2$O$_3$, are sources of unwanted capacity loss for Li-Mn-O spinel cathode. Since the Li-Mn-O compounds maintain the single phase spinel composition only when satisfying certain requirements, it is necessary to confirm the stability conditions accurately. In this work the single phase conditions of the undoped Li-Mn-O spinel were determined by \textit{in situ} X-ray diffraction (XRD) and by thermogravimetry (TG). The diffraction patterns and the mass changes were measured as a function of increasing and decreasing temperature and of partial pressure of oxygen. Both upper and lower critical stability were described by temperature as the function of Li/Mn mole ratio (including lithium excess and deficit spinel) and oxygen partial pressure. For the doped Li-Me-Mn-O spinel (Me = Mg, Ni, Co) the thermal stability was studied in the same way. The purpose is to find the single phase spinel regions.

1.4.2 The defect structure of oxygen nonstoichiometric spinel

Oxygen nonstoichiometry and the defect structure in Li-Mn spinel oxide played an important role in the electrochemical capacity and the cycle performance. It was indicated that the cycle performance depends on the oxygen stoichiometry rather than the Li/Mn molar ratio.\textsuperscript{[67]–[68]} The change of oxygen concentration has direct effect on the average oxidation state of manganese ions, and further on the stability of the spinel structure. It was generally accepted that the oxygen-rich or cation-defect spinel has vacancies on the tetrahedral 8\textit{a} and octahedral 16\textit{d} sites, which are disappeared at higher temperature or under lower oxygen partial pressure. If continuing to heating or/and lowering oxygen partial pressure the oxygen deficient spinel is produced. The interpretation of the defect structure for oxygen deficient spinel is quite controversial according to several research groups. One argument is that defect results only from the oxygen vacancies on the 32\textit{e} sites, where the lithium and manganese ions occupy the initial 8\textit{a} and 16\textit{d} sites. The maximum oxygen deficiency of LiMn$_2$O$_{4-\delta}$ was reported to be $\delta_{cr} \approx 0.2$. The dependence of $\delta$ on pO$_2$ was expressed as $\delta \sim pO_2^{(-0.67\pm0.06)}$.\textsuperscript{[50]} Another opinion is that the lithium and manganese ions insertion into 16\textit{c} interstitial sites to compensate the decrease of 8\textit{a} and 16\textit{d} sites due to release of oxygen. The LiMn$_2$O$_{4-\delta}$ was obtained in
range of $0 \leq \delta \leq 0.018$. However, it seems that in both investigations the stability field of the spinel was left. The observed weight losses were probably caused both by the formation of new phases and changes of the oxygen nonstoichiometry in the spinel. Furthermore, it was pointed out that a higher degree of oxygen deficiency was obtained when lower Li/Mn ratios were used for the same synthesis conditions.

In order to investigate the defect structure of the oxygen deficient spinel the oxygen nonstoichiometry of Li-Mn-O and Li-Me-Mn-O (Me = Mg, Co, Ni) spinel was determined. The mass changes were recorded at certain temperatures as the function of oxygen partial pressure jump in the single phase spinel region determined above. The experimental results were discussed in terms of possible defect chemical models of the Li-Mn-O as well as Li-Me-Mn-O spinel. At the temperature investigated the correspondent oxygen partial pressure were estimated for a stoichiometric Li-Mn-O and Li-Me-Mn-O (Me = Mg, Co, Ni) spinel. The dependence of dopants on the oxygen nonstoichiometry will also be discussed in detail.
## Experimental procedure

### 2.1 Sample preparation

#### 2.1.1 Pechini method

At present two methods were used to manufacture Li-Mn-O powder as the cathode in Li-ion batteries: solid-state reaction method and solution method. Compared with the conventional solid-state reaction method, solution method has many advantages: homogeneous mixing, good stoichiometric control and the production of submicron-sized particles with narrow particle-size distribution in relatively shorter processing time at a lower calcination temperature.\(^{[69][70]}\) The powder synthesized by solution method includes few impurities and its morphology can be controlled.\(^{[71–73]}\) The amorphous and crystalline Li-Mn-O powder prepared by solution method shows expectedly an isotropic structure, which implies a large electrochemically active surface area, and a lower density, which suggests a larger number of vacant sites available for lithium-ion intercalation as compared with that manufactured by the solid-state reaction method.\(^{[24][74][75]}\)

The Pechini process is based on the ability of certain weak acids to form polybasic acid chelates with various cations. These chelates can undergo polyesterification when heated in poly-hydroxyl alcohol to form a solid polymeric resin throughout which the cations are uniformly distributed. Thus the resin retains homogeneity on the atomic scale and may be calcined at low temperature to yield fine particulate oxides.\(^{[41][72]}\) Addition of dopant is another advantage of use of solutions during the powder preparation. That characteristic permits better reproducibility and more economy in the fabrication of ceramics.

In this work, modified Pechini process was performed to produce Li-Mn-O samples in which the precursors are pre-ignited in open space before calcination in order to supply sufficient oxygen to the sample.\(^{[76]}\) Reagents of LiNO\(_3\) (99.995\%), Mn(NO\(_3\))\(_2\)·4H\(_2\)O (98.5\%), citric
acid (CA, C₆H₈O₇·H₂O) and ethylene glycol (EG, C₂H₆O₂) were used as starting materials in the modified Pechini method. LiNO₃ and Mn(NO₃)₂·4H₂O with an appropriate mole ratio were dissolved in distilled water separately. Pre-dissolved solution of CA and EG with a molar ratio of CA/EG = 1/4, CA/(Li+Mn) = 1 are added to the cation solution. The mixed solutions were stirred on a hot plate below 90°C, until the solutions became a dark-brown gel. After that the temperature was increased step by step, and at 140°C an esterification reaction occurred between the hydroxyl groups of EG and the carboxylic acid group of CA. At 180°C the system turns into foam or glasslike solid which is stable in air and contains no precipitates. The structure of the produced polymeric precursor is illustrated in figure 2.1.1. Lithium and manganese cations are trapped homogeneously on an atomic scale throughout a polymer matrix. The organic polymer was degraded and charred by self-propagating combustion synthesis (SPCS) route. The puffed precursor was further heated up to about 330°C until the auto-ignition occurred, where most of the organic substances in the precursors were burned out. The ignited powders were pretreated by heating at 350°C for 48h and then calcined at 750°C for 4 h in a furnace in air. A black fine powder of Li-Mn-O samples was obtained. In the same way, the doped Li-Me-Mn-O (Me = Mg, Ni, Co) samples were also prepared. Mg(NO₃)₂·6H₂O (99.9%), Ni(NO₃)₂·6H₂O (99.999%) and Co(NO₃)₂·6H₂O (99%) were used as the source of the doped elements.

![Schematic illustration of the overall structure of the polymeric precursor](image-url)

(Green and blue balls denote Li and Mn ions respectively.)
2.1.2 Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES)

Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) was used to determine the concentrations of Li, Mn as well the doped Mg, Ni and Co elements that the prepared samples contain. In the ICP-OES, plasma is used as an energy source for producing enough heat to ionize and excite analyte atoms. Upon the electron’s decay to its ground state, light is emitted and detected. Because the excited ion only emits light of certain wavelengths, spectral lines dependent on the element are produced. These lines can then be used to qualitatively determine the components of the sample. A calibration curve of spectra intensity and concentration can be used to quantitatively determine the concentration of analyte in the sample. The apparatus for the ICP-OES is schematically illustrated in figure 2.1.2.

![Fig. 2.1.2. ICP-OES schematic diagram](image)

The ICP-OES analysis was carried out at Forschungszentrum Jülich. 10 mg as-prepared sample was dissolved in 10 ml HNO\(_3\) (65%) with additionally a few drops of H\(_2\)O\(_2\) and then diluted into 100 ml water solution. The solution was introduced into the inductively generated argon plasma through a nebulizer system and excited. The spectrum emitted was transferred into a spectrometer where it was decomposed into the individual wavelengths and evaluated. The intensities of the spectral lines were measured by CID semiconductor detectors. Calibration lines were obtained from standard solutions with different concentration. The standard solutions used in this work were provided by two different manufacturers.
2.2 X-ray powder diffraction (XRD)

The wavelengths of X-rays (0.01 nm to 10 nm) are of the same order as the atomic spacing in a crystal (about 0.3 nm). Therefore, they are ideally suited for probing the structural arrangement of atoms and molecules in a wide range of materials. Basically, an X-ray diffractometer involves a source of radiation and an X-ray detector, which are placed on the circumference of a graduated circle centered on the powder specimen (figure 2.2.1). The detector and specimen holder are mechanically coupled with a goniometer so that a rotation of the detector through 20 degrees occurs in conjunction with the rotation of the specimen through 0 degrees, a fixed 2:1 ratio.

![Schematic description of an X-ray diffractometer](image)

Fig. 2.2.1. Schematic description of an X-ray diffractometer

In crystalline substances the atoms are arranged in a regular pattern forming crystal lattices. If an incident X-ray beam encounters a crystal lattice, general scattering occurs. A diffracted beam is produced by such scattering only when certain geometric conditions satisfied, which is illustrated in figure 2.2.2. The relation by which diffraction occurs is known as the Bragg law or equation:

\[ n \lambda = 2d \cdot \sin \theta \]  

2.2.1
where $d$ is the lattice interplanar spacing, $\lambda$ is the wavelength of the incoming X-rays, $\theta$ is the diffraction angle which is equal to the angle of incidence of the incoming X-rays and $n$ is an integer. Because each crystalline material has a characteristic atomic structure, it will diffract X-rays in a unique characteristic pattern. Measurements of the $\theta$ angles were used to determine the lattice interplanar spacing $d$ characteristic of the diffraction crystal. The cubic structure of the Li-Mn-O material studied in this thesis facilitates the determination of the lattice parameter $a$ from one diffraction peak according to:

$$\frac{1}{d} = \frac{\sqrt{h^2 + k^2 + l^2}}{a}$$  \hspace{1cm} 2.2.2$$

Where $h$, $k$, $l$ are the Miller indices of the measured reflection.

**Fig. 2.2.2.** Schematic description of X-rays diffraction in the crystal$^{[79]}$

The crystal structure of the Li-Mn-O and Li-Me-Mn-O (Me = Mg, Ni, Co) samples prepared was firstly checked at room temperature by X-ray diffraction (XRD). The lattice constant $a$ was calculated for the single phase spinel according to the Bragg equation. The relationship between the lattice constant and the cation concentration in the spinel was discussed. Then in order to observe the phase transformation of the Li-Mn-O compounds at higher temperature the XRD patterns of the samples were recorded in situ on a STOE powder diffractometer with copper radiation ($\text{Cu K}_{\alpha 1}=154.056$ pm) between 350°C and 1000°C (50°C intervals) in the atmosphere $pO_2 = 0.2$ bar. Before collection of the intensity data at certain temperature, the samples were held at the temperature for 2 hours to guarantee a complete reaction, which is particularly necessary for the lower temperature measurements.
2.3 Thermogravimetry analysis (TGA)

Thermogravimetry analysis (TGA) is a technique measuring the variation in mass of a substance as a function either of the temperature under a controlled atmosphere or of the atmosphere (partial pressure of certain gas) at a constant temperature. The mass variation can be either a loss of mass or a gain of mass. The thermobalance of Setaram used in this work to record the thermogravimetric curves is illustrated in figure 2.3.1, which has a maximum sensitivity of 0.04 µg mass change. The temperature was adjusted automatically according to the given temperature program. The oxygen partial pressure (pO$_2$) around the sample was controlled by using mass flow controller of MKS (accuracy: 1% full flow) to regulate the gas flow of carrier gas (N$_2$) and auxiliary gas (mixture of N$_2$ and O$_2$) as well as the mole ratio of N$_2$ and O$_2$ in the auxiliary gas. In order to eliminate the effect of the buoyancy effect, which is dependent on the temperature, the volume of the crucible and sample, the atmosphere around

![Schematic illustration of the thermobalance Setaram Setsys 16/18](image-url)
the sample, the heating conditions and so on, calibration measurements are required. The TGA calibration curves were recorded when the similar measuring process was performed with inert materials. Then the real TGA curves were obtained by subtracting the calibration curves from the TGA curves measured with samples.

2.3.1 Isobaric mass change curves

The isobaric mass change curves show the characteristics of the compounds due to unique sequence from physicochemical reactions over specific temperature ranges and heating rates. Qualitatively, if the sample undergoes a discontinuous mass change when heating or cooling through the phase boundary due to the variation of oxygen exchange rate between the sample and the atmosphere, the discontinuous mass changes shown on the isobaric mass change curves refer to exactly the phase transformation occurring at correspondent temperatures if the heating or cooling rate is slow enough to ensure an equilibrated reaction. As a result, the critical temperature of the phase transition for investigated samples could be determined. Qualitatively, by observing the isobaric TG curves the amount of mass change during heating or cooling could be determined, which corresponds to the amount of the released or consumed oxygen, and is associated generally with the concentration and composition of the phases in the sample at the temperature involved. Thereafter, the reaction equations about synthesis or decomposition, reduction or oxidation could be obtained. In order to investigate the thermal stability of the spinel phase, the isobaric mass change curves of the Li-Mn-O and Li-Me-Mn-O (Me = Mg, Ni, Co) compounds were recorded with constant heating and cooling rates between room temperature and 1000°C under 0.2 bar oxygen partial pressure. The dependence of the critical temperature on pO$_2$ was also determined for the Li-Mn-O samples by performing the similar measurements under different pO$_2$.

2.3.2 Isothermal mass change curves

When the mass changes are recorded as the function of oxygen partial pressure changes at constant temperature, the isothermal mass change curves are obtained. The mass change under different pO$_2$ refers to the amount of released or obtained oxygen of the sample, at the same time, gives information of the defect structure due to the variation of oxygen content in the phase. The dependence of oxygen nonstoichiometry change on oxygen partial pressure jump could be determined by using isothermal mass change curves; thereafter the defect
construction is informed. In this work, the isothermal measurements were carried out at 600, 650 and 700°C for the Li-Mn-O and Li-Me-Mn-O (Me = Mg, Ni, Co) samples with different composition, respectively, where pO\textsubscript{2} was changed in the region, where the compounds maintain the single phase spinel composition. The 1500 micro liter quartz crucible and suspension (stable up to 1000°C) were used in the isothermal measurements to provide a bigger volume for the measured sample, and further more remarkable mass changes.

### 2.4 Differential thermal analysis (DTA)

Differential thermal analysis (DTA) is a technique in which the temperature difference between a substance and a reference is measured as a function of temperature while the substance and reference are subjected to the same controlled temperature program. Changes in the sample which lead to the absorption or evolution of heat can be detected relative to the inert reference. The temperature changes are shown as endothermic peaks (negative ΔT) or exothermic peaks (positive ΔT) on the DTA curves. The onset of the peak refers to the temperature at which the transformation of the substance occurs. The area under a DTA peak is associated with the enthalpy change during the substance transformation.\cite{80,81,82} In order to determine the enthalpy change quantitatively, the calibration experiments were carried out by measuring the area under the DTA peak of different metals, of which the fusion energy are

![Fig. 2.3.2. Schematic description of a DTA measurement head](image)
known and the melt points are distributed at different temperatures. The conversion factors between area under the DTA peak and the enthalpy change at different temperatures were obtained. Then, the unknown enthalpy change of the samples could be determined according to the conversion factors and the DTA measurement at correspondent temperature.

In this work, it was attempted to identify the phase transformation of the Li-Mn-O and Li-Me-Mn-O (Me = Mg, Ni, Co) compounds by DTA measurements, which were carried out in the Setaram Setsys 16/18 thermobalance on a TG-DTA coupled measurement head as shown in figure 2.3.2. Both the TGA and DTA signals were recorded simultaneously. The alumina powder was used as the reference material, which is thermally inactive over the temperature range investigated. The DTA curves were obtained when the samples were heated up and cooled down at 1°C/min rate between room temperature and 1000°C. The calibration DTA curves were recorded by performing the similar measurements but replacing the sample by inert alumina powder.
3 Defect chemistry in spinel

3.1 Oxygen nonstoichiometry in Li-Mn-O spinel

In the perfect cubic LiMn$_2$O$_4$ spinel structure, the oxygen anions on the 32$e$ sites construct the face-centered cubic, where the lithium and manganese ions occupy the tetrahedral 8$a$ and octahedral 16$d$ sites, respectively, and the tetrahedral 8$b$ and octahedral 16$c$ sites are empty. If taking only the defect structure aspect into account, there are many possibilities to introduce defects into the spinel structure, which are summarized as cation vacancies (lithium and manganese vacancies), cation interstitials (lithium and manganese interstitials), anion vacancies (oxygen vacancies), anion interstitials (oxygen interstitials) and disordered cation distribution (lithium on octahedral 16$d$ sites or manganese on tetrahedral 8$a$ sites). Generally, in a close-packed cubic spinel structure no places are available for oxygen insertion, thus, the existence of oxygen interstitial is neglected. Moreover, conceivable positions for cation insertion are only the octahedral 16$c$ sites, due to the too short distance between 8$b$ and 16$d$ site (177 pm).\[83]\[84] Furthermore, if considering the defect of a relative small concentration is infinitely diluted in the spinel, the surrounding of the same defect specie could be regarded as identical. Thus, it is reasonable to believe that Mn ions exist on tetrahedral 8$a$ or interstitial 16$c$ sites only with one type of the oxidation state simultaneously, of which the lowest formation energy is required. Therefore, the ion and vacancy distribution in the Li-Mn-O spinel is written as

\[
\begin{align*}
\text{on tetrahedral 8$a$ sites:} & & \text{Li}^{+}_{\text{Tet}} & \text{V}_{\text{Tet}} & \text{Mn}^{m^+}_{\text{Tet}} \\
\text{on octahedral 16$d$ sites:} & & \text{Li}^{+}_{\text{Oct}} & \text{V}_{\text{Oct}} & \text{Mn}^{3^+}_{\text{Oct}} & \text{Mn}^{4^+}_{\text{Oct}} \\
\text{on oxygen 32$e$ sites:} & & \text{O}^{2-}_{\text{O}} & \text{V}_{\text{O}} \\
\text{on interstitial 16$c$ sites:} & & \text{Li}^{+}_{\text{i}} & \text{Mn}^{n^+}_{\text{i}} & \text{V}_{\text{i}}
\end{align*}
\]

where m and n denotes the possible oxidation state of Mn ions on the tetrahedral and interstitial sites in the spinel, respectively.
Chapter 3. Defect chemistry in spinel

Commonly, a nonstoichiometric spinel could be expressed by a general formula LiMn$_2$O$_{4-\delta}$, where the amount of the sites, the ions and the vacancies follow

\[
\begin{align*}
 n_{\text{Li}_{\text{Tet}}} + n_{\text{Mn}^{3+}_{\text{Tet}}} + n_{\text{V}_{\text{Tet}}} &= n_{\text{Tet-sites}} \quad 3.1.1 \\
n_{\text{Li}_{\text{Oct}}} + n_{\text{Mn}^{3+}_{\text{Oct}}} + n_{\text{Mn}^{4+}_{\text{Oct}}} + n_{\text{V}_{\text{Oct}}} &= n_{\text{Oct-sites}} \quad 3.1.2 \\
n_{\text{O}^{2-}_{\text{Tet}}} + n_{\text{V}_{\text{Tet}}} &= n_{\text{O-sites}} \quad 3.1.3 \\
n_{\text{Li}^+} + n_{\text{Mn}^{3+}} + n_{\text{V}_{\text{I}}} &= n_{\text{I-sites}} \quad 3.1.4 \\
\text{and} \\
n_{\text{Li}_{\text{Tet}}} + n_{\text{Li}_{\text{Oct}}} + n_{\text{Li}_{\text{I}}} &= n_{\text{Li}} \quad 3.1.5 \\
n_{\text{Mn}^{3+}_{\text{Tet}}} + n_{\text{Mn}^{4+}_{\text{Tet}}} + n_{\text{Mn}^{4+}_{\text{Oct}}} + n_{\text{Mn}^{3+}_{\text{Oct}}} &= n_{\text{Mn}} \quad 3.1.6 \\
n_{\text{O}^{2-}_{\text{Tet}}} &= n_{\text{O}} \quad 3.1.7
\end{align*}
\]

With definition

\[
\begin{align*}
\frac{n_{\text{Li}_{\text{Tet}}}}{n_{\text{Tet-sites}}} &= [\text{Li}^+_{\text{Tet}}] \\
\frac{n_{\text{V}_{\text{Tet}}}}{n_{\text{Tet-sites}}} &= [V_{\text{Tet}}] \\
\frac{n_{Mn^{3+}_{\text{Tet}}}}{n_{\text{Tet-sites}}} &= [Mn^{3+}_{\text{Tet}}] \\
\frac{n_{\text{Li}_{\text{Oct}}}}{n_{\text{Tet-sites}}} &= [\text{Li}^+_{\text{Oct}}] \\
\frac{n_{\text{V}_{\text{Oct}}}}{n_{\text{Tet-sites}}} &= [V_{\text{Oct}}] \\
\frac{n_{\text{Mn}^{3+}_{\text{Oct}}}}{n_{\text{Tet-sites}}} &= [Mn^{3+}_{\text{Oct}}] \\
\frac{n_{\text{Mn}^{4+}_{\text{Oct}}}}{n_{\text{Tet-sites}}} &= [Mn^{4+}_{\text{Oct}}] \\
\frac{n_{\text{O}^{2-}_{\text{Tet}}}}{n_{\text{Tet-sites}}} &= [O^{2-}] \\
\frac{n_{\text{V}_{\text{Tet}}}}{n_{\text{Tet-sites}}} &= [V_{\text{Tet}}] \\
\frac{n_{\text{Mn}^{3+}_{\text{Tet}}}}{n_{\text{Tet-sites}}} &= [Mn^{3+}_{\text{Tet}}] \\
\frac{n_{\text{Mn}^{4+}_{\text{Tet}}}}{n_{\text{Tet-sites}}} &= [Mn^{4+}_{\text{Tet}}]
\end{align*}
\]

Equation 3.1.1 to 3.1.7 could be written as

\[
\begin{align*}
[\text{Li}^+_{\text{Tet}}] + [\text{Mn}^{3+}_{\text{Tet}}] + [V_{\text{Tet}}] &= 1 \quad 3.1.8 \\
[\text{Li}^+_{\text{Oct}}] + [\text{Mn}^{3+}_{\text{Oct}}] + [\text{Mn}^{4+}_{\text{Oct}}] + [V_{\text{Oct}}] &= 2 \quad 3.1.9 \\
[O^{2-}] + [V_{\text{Tet}}] &= 4 \quad 3.1.10 \\
[\text{Li}^+_{\text{I}}] + [\text{Mn}^{3+}_{\text{I}}] + [V_{\text{I}}] &= 2 \quad 3.1.11
\end{align*}
\]
Chapter 3. Defect chemistry in spinel

and

\[ [\text{Li}_{\text{Tet}}^+] + [\text{Li}_{\text{Oct}}^+] + [\text{Li}_i^+] = \frac{n_{\text{Li}}}{n_{\text{Tet-sites}}} \]  

3.1.12

\[ [\text{Mn}_{\text{Tet}}^{m^+}] + [\text{Mn}_{\text{Oct}}^{3^+}] + [\text{Mn}_{\text{Oct}}^{4^+}] + [\text{Mn}_i^{n^+}] = \frac{n_{\text{Mn}}}{n_{\text{Tet-sites}}} \]  

3.1.13

\[ [\text{O}_{\text{O}}^{2-}] = \frac{n_{\text{O}}}{n_{\text{Tet-sites}}} \]  

3.1.14

Additionally,

\[ \frac{n_{\text{Li}}}{n_{\text{O}}} = \frac{1}{4 - \delta} \]  

3.1.15

\[ \frac{n_{\text{Mn}}}{n_{\text{O}}} = \frac{2}{4 - \delta} \]  

3.1.16

then the nonstoichiometry \( \delta \) could be expressed by a general formula

\[ \delta = [V_{\text{O}}] - \frac{4}{3} ([V_{\text{Tet}}] + [V_{\text{Oct}}]) + \frac{4}{3} ([\text{Li}_i^+] + [\text{Mn}_i^{n^+}]) \]  

3.1.17

where \( \text{Mn}_i^{n^+} \) denotes the Mn interstitial with possible oxidation state.

3.2 Ionic defect in Li-Mn-O spinel

In an ideal LiMn\(_2\)O\(_4\) spinel the ion distribution obey the rules that 8\(a\), 16\(d\) and 32\(e\) sites are filled with lithium, manganese and oxygen ions, respectively, where 8\(b\) and 16\(c\) sites are empty. Apparently, various ionic disorders could be introduced into the spinel structure to build a defect spinel, where the reactions of defect formation are described and the defect concentration could be determined according to the respective reaction mechanism.
Chapter 3. Defect chemistry in spinel

The formation of oxygen vacancies is described by

\[ \text{2Mn}_{\text{Oct}}^{4+} + \text{O}_2^2- \leftrightarrow \frac{1}{2} \text{O}_2 \text{(g)} + \text{V}_0 + \text{2Mn}_{\text{Oct}}^{3+} \] 3.2.1

where the electrons are compensated by valence decrease of manganese ions. The equilibrium constant is defined as

\[ \Rightarrow K_1 = \frac{[\text{V}_0] \cdot [\text{Mn}_{\text{Oct}}^{3+}]^2 \cdot (p\text{O}_2)}{[\text{O}_2^2-] \cdot [\text{Mn}_{\text{Oct}}^{4+}]} \cdot \left( \frac{p\text{O}_2}{p_0} \right)^{1/2} \] 3.2.2

with \( p_0 \) as standard pressure. The defect formation process and the equilibrium constant of the reactions in the spinel are written as following:

**Schottky defect**

\[ \text{nil} \leftrightarrow \text{V}_{\text{Tet}} + 2\text{V}_{\text{Oct}} + 4\text{V}_0 \] 3.2.3

\[ \Rightarrow K_2 = [\text{V}_{\text{Tet}}] \cdot [\text{V}_{\text{Oct}}]^2 \cdot [\text{V}_0]^4 \] 3.2.4

**Cation Frenkel**

\[ \text{Li}_{\text{Tet}}^{3+} + \text{V}_1 \leftrightarrow \text{Li}_{\text{Tet}}^{3+} + \text{V}_{\text{Tet}} \] 3.2.5

\[ \Rightarrow K_3 = \frac{[\text{Li}_{\text{Tet}}^{3+}] \cdot [\text{V}_{\text{Tet}}]}{[\text{Li}_{\text{Tet}}^{3+}] \cdot [\text{V}_1]} \] 3.2.6

\[ \text{Mn}_{\text{Oct}}^{3+} + \text{V}_1 \leftrightarrow \text{Mn}_{\text{Oct}}^{3+} + \text{V}_{\text{Oct}} \] 3.2.7

\[ \Rightarrow K_4 = \frac{[\text{Mn}_{\text{Oct}}^{3+}] \cdot [\text{V}_{\text{Oct}}]}{[\text{Mn}_{\text{Oct}}^{3+}] \cdot [\text{V}_1]} \] 3.2.8

\[ \text{Mn}_{\text{Oct}}^{4+} + \text{V}_1 \leftrightarrow \text{Mn}_{\text{Oct}}^{4+} + \text{V}_{\text{Oct}} \] 3.2.9

\[ \Rightarrow K_5 = \frac{[\text{Mn}_{\text{Oct}}^{4+}] \cdot [\text{V}_{\text{Oct}}]}{[\text{Mn}_{\text{Oct}}^{4+}] \cdot [\text{V}_1]} \] 3.2.10
cation disorder between $8a$ and $16d$ sites

\[
\text{Li}^{+}_{\text{Tet}} + V_{\text{Oct}} \leftrightarrow \text{Li}^{+}_{\text{Oct}} + V_{\text{Tet}}
\]

\[
\Rightarrow K_b = \frac{[\text{Li}^{+}_{\text{Oct}}][V_{\text{Tet}}]}{[\text{Li}^{+}_{\text{Tet}}][V_{\text{Oct}}]}
\]

\[
\text{Mn}^{3+}_{\text{Oct}} + V_{\text{Tet}} \leftrightarrow \text{Mn}^{3+}_{\text{Tet}} + V_{\text{Oct}}
\]

\[
\Rightarrow K_7 = \frac{[\text{Mn}^{3+}_{\text{Tet}}][V_{\text{Oct}}]}{[\text{Mn}^{3+}_{\text{Oct}}][V_{\text{Tet}}]}
\]

\[
\text{Mn}^{4+}_{\text{Oct}} + V_{\text{Tet}} \leftrightarrow \text{Mn}^{4+}_{\text{Tet}} + V_{\text{Oct}}
\]

\[
\Rightarrow K_8 = \frac{[\text{Mn}^{4+}_{\text{Tet}}][V_{\text{Oct}}]}{[\text{Mn}^{4+}_{\text{Oct}}][V_{\text{Tet}}]}
\]

Furthermore, it was reported\cite{16}\cite{17}\cite{54} by some research groups that manganese ions occupy the tetrahedral $8a$ or insertion into octahedral $16c$ sites probably as form of Mn$^{2+}$. Therefore, the introduction of Mn$^{2+}$ in the defect structure is also discussed in this work. Furthermore, the cation disorder will not be further involved, because the oxygen nonstoichiometry is independent of it (see equation 3.1.17). In order to determine the interstitial concentration of Mn$^{2+}$, addition reaction equations are written to describe the existence of Mn$^{2+}$ on interstitial $16c$ sites:

if Mn$^{2+}$ initially occupying on tetrahedral sites

\[
\text{Mn}^{2+}_{\text{Tet}} + V_{\text{I}} \leftrightarrow \text{Mn}^{2+}_{\text{I}} + V_{\text{Tet}}
\]

3.2.17

if Mn$^{2+}$ is formed from Mn$_{\text{Oct}}$

\[
2\text{Mn}^{3+}_{\text{Oct}} + V_{\text{I}} \leftrightarrow \text{Mn}^{2+}_{\text{I}} + \text{Mn}^{4+}_{\text{Oct}} + V_{\text{Oct}}
\]

3.2.18

where the charge variation of Mn$^{2+}$ formation from Mn$^{3+}$ is neutralized by oxidizing Mn$^{3+}$ to Mn$^{4+}$. The equilibrium constants of those reactions are defined by
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\[ K_g = \frac{[\text{Mn}^{2+}][V_{\text{Tet}}]}{[\text{Mn}^{2+}_{\text{Tet}}] \cdot [V_1]} \quad \text{(3.2.19)} \]

\[ K_{i0} = \frac{[\text{Mn}^{2+}][\text{Mn}^{4+}_{\text{Oct}}][V_{\text{Oct}}]}{[\text{Mn}^{3+}_{\text{Oct}}] \cdot [V_1]} \quad \text{(3.2.20)} \]

The reaction equilibrium constants are only functions of temperature. As a result, according to the equation 3.1.17 and the equilibrium constants defined above with the general charge neutrality condition

\[ [\text{Li}^{+}_{\text{Tet}}] + [\text{Li}^{+}_{\text{Oct}}] + [\text{Li}^{+}_1] + 3 \cdot [\text{Mn}^{3+}_{\text{Oct}}] + 4 \cdot [\text{Mn}^{4+}_{\text{Oct}}] + m \cdot [\text{Mn}^{m+}_{\text{Tet}}] + n \cdot [\text{Mn}^{n+}_1] = 2[O^{2-}_{\text{O}}] \quad \text{(3.2.21)} \]

the oxygen nonstoichiometry \( \delta \) could be written as the function of the defect concentration and the reaction equilibrium constant. Therefore, if the temperature is fixed, the dependence of oxygen nonstoichiometry \( \delta \) on the defect concentration for the samples with certain composition is actually on the oxygen partial pressure, which could be in principle experimentally determined.

### 3.3 \( \delta – \text{pO}_2 \) of Li-Mn-O spinel

#### 3.3.1 LiMn2O4 spinel

The stoichiometric spinel LiMn2O4 has equal moles of Mn\(^{3+}\) and Mn\(^{4+}\) on the octahedral sites, which can be written as \( (\text{Li}^+_1)_{\text{Tet}} [\text{Mn}^{3+}_1 \text{Mn}^{4+}_{\text{Oct}}] \text{O}_4 \), where the concentration of ions, vacancies and interstitials are

\[
\begin{aligned}
[\text{Li}^{+}_{\text{Tet}}] &= 1 \\
[V_{\text{Tet}}] &= 0 \\
[Mn^{m+}_{\text{Tet}}] &= 0 \\
[\text{Li}^{+}_{\text{Oct}}] &= 0 \\
[V_{\text{Oct}}] &= 0 \\
[Mn^{3+}_{\text{Oct}}] &= 1 \\
[Mn^{4+}_{\text{Oct}}] &= 1 \\
[O^{2-}_{\text{O}}] &= 4 \\
[V^{3-}_{\text{O}}] &= 0 \\
[\text{Li}^{+}_1] &= 0 \\
[Mn^{n+}_1] &= 0 \\
[V_1] &= 2
\end{aligned}
\]
According to the function 3.2.2 the concentration of oxygen vacancies was determined by

\[ [V_0] = 4K_1 \cdot \left( \frac{pO_2}{p_0} \right)^{-1/2} \]  \hspace{1cm} 3.3.1

Considering all defects in a nonstoichiometric spinel have quite small concentration, those could be expressed as the functions of cation vacancies:

\[ [\text{Li}^+_1] = \frac{2K_3}{[V_{\text{Tet}}]} \] \hspace{1cm} \[ [\text{Mn}^{3+}] = \frac{2K_4}{[V_{\text{Oct}}]} \] \hspace{1cm} \[ [\text{Mn}^{4+}] = \frac{2K_5}{[V_{\text{Oct}}]} \]

\[ [\text{Li}^+_{\text{Oct}}] = \frac{K_6 \cdot [V_{\text{Oct}}]}{[V_{\text{Tet}}]} \] \hspace{1cm} \[ [\text{Mn}^{3+}_{\text{Tet}}] = \frac{K_7 \cdot [V_{\text{Tet}}]}{[V_{\text{Oct}}]} \] \hspace{1cm} \[ [\text{Mn}^{4+}_{\text{Tet}}] = \frac{K_8 \cdot [V_{\text{Tet}}]}{[V_{\text{Oct}}]} \]

with \( \text{Mn}^{2+} \) according to equation 3.2.20

\[ [\text{Mn}_{\text{i}}^{3+}] = \frac{2K_{10}}{[V_{\text{Oct}}]} \]

Then together with

\[ K_2 = [V_{\text{Tet}}] \cdot [V_{\text{Oct}}]^2 \cdot [V_0]^4 \]  \hspace{1cm} 3.2.4

and

\[ \frac{[\text{Li}_{\text{Tet}}^+] + [\text{Li}_{\text{Oct}}^+] + [\text{Li}_i^+]}{[\text{Mn}^{3+}_{\text{Tet}}] + [\text{Mn}^{4+}_{\text{Oct}}] + [\text{Mn}_{\text{i}}^{n+}]} = \frac{n_{\text{Li}}}{n_{\text{Mn}}} = \frac{1}{2} \]  \hspace{1cm} 3.3.2

the concentration of all the possible defects could be principally dissolved and written as a function of oxygen partial pressure. As a result, the dependence of oxygen nonstoichiometry \( \delta \) on oxygen partial pressure for the defect spinel \( \text{LiMn}_2\text{O}_4-\delta \) could be determined by equation

\[ \delta = [V_0] - \frac{4}{3} \cdot ([V_{\text{Tet}}] + [V_{\text{Oct}}]) + \frac{4}{3} \cdot ([\text{Li}_i^+] + [\text{Mn}_{\text{i}}^{n+}]) \]  \hspace{1cm} 3.1.17
3.3.2 Lithium excess spinel

The lithium excess spinel refers to the spinel with the composition of \( 0.5 < n_{Li}/n_{Mn} < 0.8 \). Excessive lithium ions disturb the original cation distribution in a LiMn\(_2\)O\(_4\) spinel, where the concentrations of \( Mn^{3+} \) and \( Mn^{4+} \) are also drifted off the original 1/1 ratio to compensate the charge variation. Apparently, the initial cation distribution plays a very important role in the defect structure of a spinel, where the nonstoichiometric defect is also different correspondingly. Considering the excessive Li\(^+\) has a quite small concentration compared to the cations in the LiMn\(_2\)O\(_4\) spinel host, it is reasonable to believe that the excessive Li\(^+\) ions are distributed homogeneously in the spinel only as a single form, of which the lowest energy level is achieved. Three types of the possible cation distribution are put forward to describe the initial occupancy of excessive Li ions:

(i) On octahedral 16\( d \) sites
\[
\left( Li^+ \right)_{\text{Oct}} \left[ Li^+_{x} Mn^{3+}_{1-3x} Mn^{4+}_{1+2x} \right]_{\text{Oct}} O_4
\]

(ii) On interstitial 16\( c \) sites
\[
\left( Li^+ \right)_{\text{Int}} \left( Li^+ \right)_{\text{Int}} \left[ Mn^{3+}_{1+x} Mn^{4+}_{1-x} \right]_{\text{Int}} O_4
\]

(iii) On octahedral 8\( a \) sites with vacancies on 16\( d \) octahedral sites
\[
\left( Li^+ \right)_{\text{Oct}} \left[ Mn^{3+}_{1-4x} Mn^{4+}_{1+3x} V_x \right]_{\text{Oct}} O_4
\]

where \( x \) denotes the concentration of the excessive Li ions.

In a \( \left( Li^+ \right)_{\text{Oct}} \left[ Li^+_{x} Mn^{3+}_{1-3x} Mn^{4+}_{1+2x} \right]_{\text{Oct}} O_4 \) spinel all the 8\( a \) and 16\( d \) sites are occupied, where excessive Li ions substitute for Mn ions and occupy previously on octahedral 16\( d \) sites. The difference of ion concentration from LiMn\(_2\)O\(_4\) in this case is reflected on the octahedral 16\( d \) sites:
\[
\left[ Li^{+}_{\text{Oct}} \right] = x, \quad \left[ Mn^{3+}_{\text{Oct}} \right] = 1 - 3x \quad \text{and} \quad \left[ Mn^{4+}_{\text{Oct}} \right] = 1 + 2x.
\]
If assuming all defect concentrations are much smaller compared to \( x \), according to the reaction equilibrium constants defined in chapter 3.2, the concentrations of ion vacancy and cation interstitial are determined.
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\[ [V_0] = 4K_1 \left( \frac{1+2x}{1-3x} \right)^2 \left( \frac{pO_2}{p_0} \right)^{-1/2} \]  
3.3.3

\[ [Li^{iv}_i] = 2K_3 \left( \frac{(4K_1)^4 \cdot x^2 \cdot (1+2x)^8}{K_2 \cdot K_6^2 \cdot (1-3x)^8} \right)^{1/3} \left( \frac{pO_2}{p_0} \right)^{-2/3} \]  
3.3.4

\[ [Mn^{iv}_i] = 2K_4 \left( \frac{(4K_1)^4 \cdot K_6 \cdot (1+2x)^8}{K_2 \cdot x \cdot (1-3x)^8} \right)^{1/3} \left( \frac{pO_2}{p_0} \right)^{-2/3} \]  
3.3.5

\[ [Mn^{iv+}_i] = 2K_5 \left( \frac{(4K_1)^4 \cdot K_6 \cdot (1+2x)^8}{K_2 \cdot x \cdot (1-3x)^8} \right)^{1/3} \left( \frac{pO_2}{p_0} \right)^{-2/3} \]  
3.3.6

\[ [V_{Te}] = \left( \frac{K_2 \cdot K_6 \cdot (1-3x)^8}{(4K_1)^4 \cdot x^2 \cdot (1+2x)^8} \right)^{1/3} \left( \frac{pO_2}{p_0} \right)^{-2/3} \]  
3.3.7

\[ [V_{Oct}] = \left( \frac{K_2 \cdot x \cdot (1-3x)^8}{(4K_1)^4 \cdot K_6 \cdot (1+2x)^8} \right)^{1/3} \left( \frac{pO_2}{p_0} \right)^{-2/3} \]  
3.3.8

\[ [V_{Oct}] = \left( \frac{K_2 \cdot x \cdot (1-3x)^8}{(4K_1)^4 \cdot K_6 \cdot (1+2x)^8} \right)^{1/3} \left( \frac{pO_2}{p_0} \right)^{-2/3} \]  
3.3.9

It is found that all the defect concentrations are exponential functions of oxygen partial pressure with different exponents. According to equation 3.1.17 the oxygen nonstoichiometry, \( \delta \), of this model can be simplified expressed by

\[ \delta = a_1 \left( \frac{pO_2}{p_0} \right)^{-1/2} - b_1 \left( \frac{pO_2}{p_0} \right)^{2/3} + c_1 \left( \frac{pO_2}{p_0} \right)^{-2/3} \]  
3.3.10

where \( a_1 \), \( b_1 \), and \( c_1 \) refer to the pre-parameters of the pO\(_2\) items, respectively, which are dependent on the equilibrium constants defined above and the concentration of excessive lithium ions.

Due to the initial occupancy of Li ions on 16\( d \) sites, the formation of Li interstitials could also follow another mechanism, where Li ions insertion directly from 16\( d \) sites:

\[ Li^{iv}_i + V_1 \leftrightarrow Li^{iv+}_i + V_{Oct} \]  
3.3.11

with
\[ K_{11} = \frac{[Li_1^+] [V\text{oct}]}{[Li_{1\text{oct}}] \cdot [V]}, \quad 3.3.12 \]

then

\[ [Li_1^+] = 2K_{11} \cdot \left( \frac{4K_1 \cdot K_4 \cdot x^2 \cdot (1 + 2x)^8}{K_2 \cdot (1 - 3x)^8} \right)^{1/3} \cdot \left( \frac{pO_2}{p_0} \right)^{-2/3}, \quad 3.3.13 \]

Apparently, the concentration of \( Li_1^+ \) has a different pre-parameter but a same exponent of \( pO_2 \) compared to that of other interstitial defect species. As a result, the oxygen non-stoichiometry of the lithium excess spinel could be written by a general formula

\[ \delta = a'_{\text{i}} \left( \frac{pO_2}{p_0} \right)^{-1/2} - b'_{\text{i}} \left( \frac{pO_2}{p_0} \right)^{2/3} + c'_{\text{i}} \left( \frac{pO_2}{p_0} \right)^{-2/3}, \quad 3.3.14 \]

where \( c'_{\text{i}} \) represents the parameters of all the possible interstitial forms discussed above.

Comparing model (iii) \( (Li_1^{+\text{i}})_{\text{ex}} (Li_1^{+\text{o}}) \) \( \left[ Mn_{1-x}^{3\text{v}} Mn_{1-x}^{4\text{v}} \right]_{\text{oct}} O_4 \) with model (i), the differences between them lie in the previous distribution of excessive lithium ions as well as the correspondent variation of \( Mn^{3+} \) and \( Mn^{4+} \) concentration, where

\[ [Li_1^{+\text{i}}] = x \quad [Mn_{\text{oct}}^{3\text{v}}] = 1 + x \quad [Mn_{\text{oct}}^{4\text{v}}] = 1 - x \quad [V_1] = 2 - x \]

which indicates the original occupancy on interstitial 16c site by excessive lithium ions. The concentration of the possible defects is determined similarly

\[ [V_{\text{o}}] = \frac{4K_1 \cdot (1 - x)^2}{(1 + x)^2} \left( \frac{pO_2}{p_0} \right)^{-1/2}, \quad 3.3.15 \]

\[ [V_{\text{tet}}] = \frac{K_1 \cdot (2 - x)}{x}, \quad 3.3.16 \]

\[ [V_{\text{oct}}] = \frac{(1 + x)^4}{(4K_1)^2 \cdot (1 - x)^4} \left( \frac{K_2 \cdot x}{K_1 \cdot (2 - x)} \right)^{1/2} \cdot \left( \frac{pO_2}{p_0} \right)^{-1}, \quad 3.3.17 \]

\[ [Mn_{1}^{3\text{v}}] = \frac{K_4 \cdot (4K_1)^2 \cdot (1 - x)^4}{(1 + x)^4} \left( \frac{(2 - x)^3 \cdot K_3}{K_2 \cdot x} \right)^{1/2} \cdot \left( \frac{pO_2}{p_0} \right)^{-1}, \quad 3.3.18 \]
Moreover, Li ions initial occupancy on interstitial $16c$ sites results in the pre-existence of nonstoichiometry in $(\text{Li}^{+})_{0}\text{Mn}^{4+}_{3+x}\text{Mn}^{3+}_{1-x}\text{K}_{4}\text{O}_{4}$, which could be equivalently expressed by the formula $(\text{Li},\text{Mn})_{0}\text{O}_{4-\delta}$ with nominal oxygen deficiency $\delta = \frac{4}{3}x$, where the sum of Li and Mn is 3. As a result, the oxygen nonstoichiometry, in this case, is determined by using the general formula 3.1.17 with the additional deviation $\delta_0$:

$$\delta = [V_o] - \frac{4}{3}([V_{\text{Tet}}] + [V_{\text{Oct}}]) + \frac{4}{3}([\text{Li}^{+}] + [\text{Mn}^{n+}]) - \delta_0$$ 3.3.21

Therefore, if the lithium excess spinel has the ion distribution as described by model (ii), the oxygen nonstoichiometry $\delta$ could be expressed by a common formula

$$\delta = a_2 \left( \frac{\text{pO}_2}{\text{p}_0} \right)^{-1/2} - b_2 \left( \frac{\text{pO}_2}{\text{p}_0} \right)^{1/2} + c_2 \left( \frac{\text{pO}_2}{\text{p}_0} \right)^{-1} + d_2$$ 3.3.22

Apparently, although the possible oxidation states of the interstitial Mn ions are different, the concentration expressions have always the same exponent (–1) of $\text{pO}_2$. $c_2$ refers to the pre-parameter of the possible interstitial form. The constant $d_2$ refers to the items, which are independent of $\text{pO}_2$. In this case, it represents the concentration of tetrahedral vacancies, Li ion interstitials and also the initial nonstoichiometry $\delta_0$. Compared to model (i) the oxygen nonstoichiometry $\delta$ has a similar expression but different exponential dependence on $\text{pO}_2$.

The defect concentration of model (iii) $(\text{Li}^{+})_{0}\text{Mn}^{3+}_{1-4x}\text{Mn}^{4+}_{1+3x}\text{V}_{x}\text{K}_{4}\text{O}_{4}$, in which the excessive lithium ions hold the occupancy of tetrahedral $8a$ sites and the vacancies exist previously on $16d$ octahedral sites, are analogically analyzed according to the possible defect formation process discussed above. The octahedral vacancies bring about the initial non-
stoichiometric deviation: $\delta_0 = -\frac{4}{3}x$. A general function of oxygen nonstoichiometry is also obtained from equation 3.3.21

$$
\delta = a_3 \left( \frac{pO_2}{p_0} \right)^{-1/2} - b_3 \left( \frac{pO_2}{p_0} \right)^2 + c_3 \left( \frac{pO_2}{p_0} \right)^{-2} + d_3
$$

3.3.23

where the exponents of $pO_2$ are different from that of the first two models. $a_3$, $b_3$, $c_3$ and $d_3$ represent the parameters, which are dependent on the equilibrium constants of the respective reactions and the concentration of excessive Li ions in spinel.

### 3.3.3 Lithium deficit spinel

The Li-Mn-O spinels with $n_{Li}/n_{Mn} < 0.5$ are called Lithium deficit spinels, which have also three possible previous ion distributions:

(i) vacancies on $8a$ sites

$$
\left( \text{Li}^{1+}_{1-x} V_x \right)_{\text{ref}} \left[ \text{Mn}^{3+}_{1-x} \text{Mn}^{4+}_{x} \right]_{\text{ext}} \text{O}_4
$$

(ii) excessive manganese ions on the $8a$ sites with different oxidation state

$$
\left( \text{Li}^{1+}_{1-x} \text{Mn}^{2+}_x \right)_{\text{ref}} \left[ \text{Mn}^{3+}_{1-x} \text{Mn}^{4+}_{x} \right]_{\text{ext}} \text{O}_4

\left( \text{Li}^{1+}_{1-x} \text{Mn}^{3+}_x \right)_{\text{ref}} \left[ \text{Mn}^{3+}_{1-x} \text{Mn}^{4+}_{x} \right]_{\text{ext}} \text{O}_4

\left( \text{Li}^{1+}_{1-x} \text{Mn}^{4+}_x \right)_{\text{ref}} \left[ \text{Mn}^{3+}_{1-x} \text{Mn}^{4+}_{x} \right]_{\text{ext}} \text{O}_4
$$

(iii) excessive manganese ions on $16c$ sites with different oxidation state

$$
\left( \text{Li}^{1+}_{1} \right)_{\text{ref}} \left( \text{Mn}^{2+}_x \right) \left[ \text{Mn}^{3+}_{1-2x} \text{Mn}^{4+}_{1-2x} \right]_{\text{ext}} \text{O}_4

\left( \text{Li}^{1+}_{1} \right)_{\text{ref}} \left( \text{Mn}^{3+}_x \right) \left[ \text{Mn}^{3+}_{1-3x} \text{Mn}^{4+}_{1-3x} \right]_{\text{ext}} \text{O}_4

\left( \text{Li}^{1+}_{1} \right)_{\text{ref}} \left( \text{Mn}^{4+}_x \right) \left[ \text{Mn}^{3+}_{1-4x} \text{Mn}^{4+}_{1-4x} \right]_{\text{ext}} \text{O}_4
$$

where $x$ denotes the concentration of excessive Mn ions. The mole ratio of Mn$^{3+}$/Mn$^{4+}$ varies correspondingly to maintain the charge neutrality in the spinel.
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If assuming that vacancies are located on tetrahedral 8a sites in a lithium deficit spinel with the ion distribution \( \left[ Li_{\text{tet}}^{\text{i}} \right] = 1 - x \), \( \left[ V_{\text{tet}} \right] = x \), \( \left[ Mn_{\text{oct}}^{3+} \right] = 1 - x \) and \( \left[ Mn_{\text{oct}}^{4+} \right] = 1 + x \) as model (i), according to the equilibrium constant defined in chapter 3.2, the defect concentrations are determined respectively on grounds of the different formation mechanisms:

\[
\left[ V_{\text{tet}} \right] = \frac{4K_1 \cdot (1 + x)^2}{(1 - x)^2} \left( \frac{pO_2}{p_0} \right)^{-1/2}
\]

\[
\left[ V_{\text{oct}} \right] = \frac{(1 - x)^4}{(4K_1)^2 \cdot (1 + x)^4} \left( \frac{K_2}{x} \right)^{1/2} \left( \frac{pO_2}{p_0} \right)^{1}
\]

\[
\left[ Li_{\text{i}} \right] = \frac{2K_3 \cdot (1 - x)}{x}
\]

\[
\left[ Mn_{\text{i}}^{3+} \right] = \frac{(4K_1)^2 \cdot 2K_4 \cdot (1 + x)^4}{(1 - x)^3} \left( \frac{x}{K_2} \right)^{1/2} \left( \frac{pO_2}{p_0} \right)^{-1}
\]

\[
\left[ Mn_{\text{i}}^{4+} \right] = \frac{(4K_1)^2 \cdot 2K_5 \cdot (1 + x)^5}{(1 - x)^4} \left( \frac{x}{K_2} \right)^{1/2} \left( \frac{pO_2}{p_0} \right)^{-1}
\]

\[
\left[ Mn_{\text{i}}^{2+} \right] = \frac{(4K_1)^2 \cdot 2K_{10} \cdot (1 + x)^5}{(1 - x)^4} \left( \frac{x}{K_2} \right)^{1/2} \left( \frac{pO_2}{p_0} \right)^{-1}
\]

with the nominal oxygen excess \( \delta_0 = -\frac{4}{3}x \). According to equation 3.3.21 the oxygen non-stoichiometry \( \delta \) is written as a function of oxygen partial pressure with a general formula

\[
\delta = a_4 \cdot \left( \frac{pO_2}{p_0} \right)^{-1/2} - b_4 \cdot \left( \frac{pO_2}{p_0} \right)^1 + c_4 \cdot \left( \frac{pO_2}{p_0} \right)^{-1} + d_4
\]

which has the same \( pO_2 \) exponents as the lithium excess spinel with lithium on 16c sites.

If regarding that the occupancy on 8a sites by manganese ions with either of the possible oxidation state could take place, the previous ion concentration of \( Mn_{\text{oct}}^{3+} \) and \( Mn_{\text{oct}}^{4+} \) in model (ii) is different due to the various charge neutrality conditions, which are described respectively by the three formulas as given above. As a result, the defect concentrations for all...
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The possible defect formation mechanisms are determined, which are functions of oxygen partial pressure. The oxygen nonstoichiometry in this model could be generally written as

\[
\delta = a_\delta \left( \frac{p_{O_2}}{p_0} \right)^{-1/2} - b_\delta \left( \frac{p_{O_2}}{p_0} \right)^{2/3} + c_\delta \left( \frac{p_{O_2}}{p_0} \right)^{-2/3}
\]

where \(-1/2, 2/3\) and \(-2/3\) represent the \(pO_2\) exponents of oxygen vacancy, cation vacancy and cation interstitial respectively. It is found that the valence variation of manganese ion as well as the different formation processes of defect has effect on the pre-parameters \(a_\delta, b_\delta,\) and \(c_\delta\) but not exponential dependence on \(pO_2\).

In model (iii) it is assumed that the excessive manganese insertion on the 16c sites with possible oxidation state. The previous ion concentration is given in the formula with different mole ratio of \(Mn^{3+}/Mn^{4+}\) according to the charge neutrality conditions. In the same way, the similar analysis is performed in this case for the model by using different equilibrium constants defined in chapter 3.2. A common function is obtained to describe the oxygen nonstoichiometry \(\delta\):

\[
\delta = a_\delta \left( \frac{p_{O_2}}{p_0} \right)^{-1/2} - b_\delta \left( \frac{p_{O_2}}{p_0} \right)^{2} + c_\delta \left( \frac{p_{O_2}}{p_0} \right)^{-2} + d_\delta
\]

3.3.4 \(\delta\) dependence on \(pO_2\)

The different defect formation mechanisms on grounds of various ion distribution models are put forward for the lithium manganese spinel with lithium excess and deficit, respectively. The defect concentrations are determined according to the different cation distributions and defect models. It is found that the defect concentrations are all exponential functions of oxygen partial pressure, if considering that the constant has the exponent equal to 0. The defect of oxygen vacancies is always a function of \(\left( pO_2 \right)^{-1/2} \). The other two exponents of \(pO_2\) vary for different forms of defect and cation occupancy. Furthermore, according to equation 3.3.21, the oxygen nonstoichiometry \(\delta\) could be described by three general formulas for both lithium excess and deficit spinel under the respective assumptions:
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\[
\delta = a \left( \frac{pO_2}{p_0} \right)^{-1/2} - b \cdot \left( \frac{pO_2}{p_0} \right)^n + c \cdot \left( \frac{pO_2}{p_0} \right)^{-n} + d \quad (n = 2/3, 1, 2)
\]

where the pre-parameters as well as the exponent n of pO₂ item are different from different models. The relationship between ionic defect and exponents of pO₂ is summarized in table 3.3.1. The parameters a, b and c indicate respectively the factors of oxygen vacancies, cation vacancies and cation interstitials.

### Table 3.3.1. Dependence of defect concentration on pO₂ exponent

<table>
<thead>
<tr>
<th>Spinel type</th>
<th>Model</th>
<th>V₀</th>
<th>Vₜₖ</th>
<th>Vₖₜ</th>
<th>Li₁</th>
<th>Mn₁</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>a</td>
<td>b</td>
<td>c</td>
<td></td>
<td></td>
</tr>
<tr>
<td>pO₂ exponent</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lithium excess nₗᵢ/nₘₙ &gt; 0.5</td>
<td>Li⁺ᵢ</td>
<td>–1/2</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>–1</td>
</tr>
<tr>
<td></td>
<td>Li²⁺ᵦₖ</td>
<td>–1/2</td>
<td>2/3</td>
<td>2/3</td>
<td>–2/3</td>
<td>–2/3</td>
</tr>
<tr>
<td></td>
<td>Vₖₜ</td>
<td>–1/2</td>
<td>2</td>
<td>0</td>
<td>–2</td>
<td>0</td>
</tr>
<tr>
<td>Lithium deficit nₗᵢ/nₘₙ &lt; 0.5</td>
<td>Mn₁</td>
<td>–1/2</td>
<td>2</td>
<td>0</td>
<td>–2</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>Mn⁻ᵦₖₜ</td>
<td>–1/2</td>
<td>2/3</td>
<td>2/3</td>
<td>–2/3</td>
<td>–2/3</td>
</tr>
<tr>
<td></td>
<td>Vₜₖ</td>
<td>–1/2</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>–1</td>
</tr>
</tbody>
</table>

3.4 \(\delta – pO_2\) of doped Li-Me-Mn-O spinel (Me = Mg, Ni, Co)

3.4.1 Nonstoichiometry in doped Li-Me-Mn-O spinel (Me = Mg, Ni, Co)

It was generally accepted that some elements like Mg, Ni, Co could dope into the Li-Mn-O spinel crystal and the compounds maintain the spinel construction after doping, which have the general formula of LiMeₙMn₂₋ₙO₄₋δ. \(\delta\) refers to the oxygen nonstoichiometry, and \(y\) the concentration of doped elements, respectively. If considering that the dopant elements could occupy either the 8a and 16d sites or insertion on interstitial 16c sites in a spinel structure with possible oxidation state, the ion distribution is written as
Chapter 3. Defect chemistry in spinel

on tetrahedral 8\(a\) sites: \(\text{Li}^{+}_{\text{Tet}}, \text{V}_{\text{Tet}}, \text{Mn}^{m+}_{\text{Tet}}, \text{Me}^{M+}_{\text{Tet}}\)

on octahedral 16\(d\) sites: \(\text{Li}^{+}_{\text{Oct}}, \text{V}_{\text{Oct}}, \text{Mn}^{3+}_{\text{Oct}}, \text{Mn}^{4+}_{\text{Oct}}, \text{Me}^{L+}_{\text{Oct}}\)

on oxygen 32\(e\) sites: \(\text{O}^{2-}_{\text{O}}, \text{V}_{\text{O}}\)

on interstitial 16\(c\) sites: \(\text{Li}^{+}_{\text{i}}, \text{Mn}^{n+}_{\text{i}}, \text{Me}^{N+}_{\text{i}}, \text{V}_{\text{i}}\)

where \(M\), \(L\) and \(N\) denote the possible valences of the dopant elements. By using the same definition of ion concentration in an undoped spinel with additional description for dopants

\[
\frac{n_{\text{Me}^{M+}_{\text{Tet}}}}{n_{\text{Tet}\text{-sites}}} = \left[\text{Me}^{M+}_{\text{Tet}}\right] \quad 3.4.1
\]

\[
\frac{n_{\text{Me}^{L+}_{\text{Oct}}}}{n_{\text{Tet}\text{-sites}}} = \left[\text{Me}^{L+}_{\text{Oct}}\right] \quad 3.4.2
\]

\[
\frac{n_{\text{Me}^{N+}_{\text{i}}}}{n_{\text{Tet}\text{-sites}}} = \left[\text{Me}^{N+}_{\text{i}}\right] \quad 3.4.3
\]

\[
\left[\text{Me}^{M+}_{\text{Tet}}\right] + \left[\text{Mn}^{m+}_{\text{Tet}}\right] + \left[\text{Mn}^{L+}_{\text{Oct}}\right] = \frac{n_{\text{Me}}}{n_{\text{Tet}\text{-sites}}} \quad 3.4.4
\]

and \(\frac{n_{\text{Me}}}{n_{\text{O}}} = \frac{y}{4-\delta}\) \(3.4.5\)

the concentration of ions and defects is similarly described as the undoped spinel given in chapter 3.1 but with additional doped cation \(\text{Me}\):

\[
\left[\text{Li}^{+}_{\text{Tet}}\right] + \left[\text{Mn}^{m+}_{\text{Tet}}\right] + \left[\text{Me}^{M+}_{\text{Tet}}\right] + \left[\text{V}_{\text{Tet}}\right] = 1 \quad 3.4.6
\]

\[
\left[\text{Li}^{+}_{\text{Oct}}\right] + \left[\text{Mn}^{3+}_{\text{Oct}}\right] + \left[\text{Mn}^{4+}_{\text{Oct}}\right] + \left[\text{Me}^{L+}_{\text{Oct}}\right] + \left[\text{V}_{\text{Oct}}\right] = 2 \quad 3.4.7
\]

\[
\left[\text{O}^{2-}_{\text{O}}\right] + \left[\text{V}_{\text{O}}\right] = 4 \quad 3.4.8
\]

\[
\left[\text{Li}^{+}_{\text{i}}\right] + \left[\text{Mn}^{n+}_{\text{i}}\right] + \left[\text{Me}^{N+}_{\text{i}}\right] + \left[\text{V}_{\text{i}}\right] = 2 \quad 3.4.9
\]

Furthermore, the charge neutrality condition is also different:
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\[
[\text{Li}^{+}]_{\text{Tet}} + [\text{Li}^{+}]_{\text{Oct}} + [\text{Li}^{+}] + 3 \cdot [\text{Mn}^{3+}]_{\text{Oct}} + 4 \cdot [\text{Mn}^{4+}]_{\text{Oct}} + m \cdot [\text{Mn}^{m+}]_{\text{Tet}} + n [\text{Mn}^{n+}]_{\text{Tet}} + M \cdot [\text{Me}^{M+}]_{\text{Tet}} + L \cdot [\text{Me}^{L+}]_{\text{Oct}} + N \cdot [\text{Me}^{N+}]_{\text{Tet}} = 2 \cdot [O^{2-}]_{\text{Tet}}
\]

3.4.10

As a result, the oxygen nonstoichiometry \( \delta \) of a doped spinel is expressed by

\[
\delta = [V_{\text{o}}] - \frac{4}{3} \cdot (V_{\text{Tet}} + V_{\text{Oct}}) + \frac{4}{3} \cdot (L_{\text{Tet}} + [\text{Mn}^{n+}] + [\text{Me}^{N+}]) + \delta_0
\]

3.4.11

where \( \text{Mn}^{n+} \) and \( \text{Me}^{N+} \) refer to the possible oxidation state of Mn ion and the doped elements, respectively. Apparently, if the defect concentration of the oxygen vacancy, cation vacancy and cation interstitial are determined, the oxygen nonstoichiometry is thereafter obtained, which has a similar expression as the undoped spinel.

### 3.4.2 Magnesium doped Li-Mn-O spinel

In principle, Magnesium could occupy initially either on 8\( a \), 16\( d \) cation sites or 16\( c \) interstitial sites when doping into the Li-Mn-O spinel. Compared to the undoped spinel additional reactions and equilibrium constants are needed to describe the formation mechanism of new defect species. In this work, the case of that Mg ions occupy initially only on 16\( d \) sites in the Mg-doped spinel is discussed, which is generally accepted according to the reports before.\(^{[57][58][85][86]}\)

The ion distribution for a Mg-doped spinel of \( n_{\text{Li}}/n_{(\text{Mg}+\text{Mn})} < 0.5 \) with vacancies on 8\( a \) sites could be written as \( \left( \text{Li}^{+} \right)_{\text{Tet}} \left[ \text{Mg}^{2+} y \cdot \text{Mn}^{3+} l-x-y \cdot \text{Mn}^{4+} l+x,y \right]_{\text{Tet}} \) \( \text{O}_4 \) with

\[
\begin{align*}
[\text{Li}^{+}]_{\text{Tet}} &= 1 - x & [V_{\text{Tet}}]_{\text{Tet}} &= x & [\text{Mn}^{m+}]_{\text{Tet}} &= 0 & [\text{Mg}^{2+}]_{\text{Tet}} &= 0 \\
[\text{Li}^{+}]_{\text{Oct}} &= 0 & [V_{\text{Oct}}]_{\text{Oct}} &= 0 & [\text{Mg}^{2+}]_{\text{Oct}} &= y \\
[\text{Mn}^{3+}]_{\text{Oct}} &= (1 - x) - 2y & [\text{Mn}^{4+}]_{\text{Oct}} &= (1 + x) + y \\
[\text{O}^{2-}]_{\text{Tet}} &= 4 & [V_{\text{o}}]_{\text{Tet}} &= 0 \\
[\text{Li}^{+}]_{\text{Tet}} &= 0 & [\text{Mn}^{n+}]_{\text{Tet}} &= 0 & [\text{Mg}^{2+}]_{\text{Tet}} &= 0 & [V_{\text{i}}]_{\text{Tet}} &= 2
\end{align*}
\]
It is shown that the ion distribution is similar with that of undoped spinel under the same assumption. Apparently, the equilibrium constants of Li and Mn defined in chapter 3.2 are also suitable in this case only with the different original ion concentration. In other words, the defect concentration of Li, Mn interstitial and vacancies maintains the same dependences on pO$_2$ exponents with different pre-parameters. Therefore, only the relationship between dopant interstitial and oxygen partial pressure is discussed further, which is necessary to determine the oxygen nonstoichiometry. The defect formation of Mg interstitial is described by

\[
\text{Mg}^{2+}_{\text{Oct}} + V_i \leftrightarrow \text{Mg}^{2+}_i + V_{\text{Oct}}
\]

\[
\Rightarrow K_{12} = \frac{\left[ \text{Mg}^{2+}_i \right]}{\left[ \text{Mg}^{2+}_{\text{Oct}} \right] \cdot \left[ V_i \right]}
\]

then we have

\[
\left[ \text{Mg}^{2+}_i \right] = \frac{2K_{12} \cdot (4K_i)^2 \cdot y \cdot (1-x-2y)^4 \cdot \left( \frac{x}{K_2} \right)^{1/2} \cdot \left( \frac{pO_2}{p_0} \right)^{-1}}{(1+x+y)^4}
\]

where the concentration of Mg interstitials is the same exponential function of pO$_2$ as that of Mn interstitials. Therefore, the oxygen nonstoichiometry in this case could be written by a general formula for the Mg-doped Li-Mn-O spinel according to equation 3.4.11:

\[
\delta = a_2 \cdot \left( \frac{pO_2}{p_0} \right)^{-1/2} - b_2 \cdot \left( \frac{pO_2}{p_0} \right)^{-1} + c_2 \cdot \left( \frac{pO_2}{p_0} \right)^{-1} + d_2
\]

where $c_2$ is the factor including the pre-parameters of Mn and Mg interstitials.

When Mn$^{2+}$ ions replace partial of Li ions on 8$a$ sites and Mg$^{2+}$ occupy the 16$d$ sites as an example, another kind of spinel with formula $\left( \text{Li}_{1-x}^{1+} \text{Mn}_x^{2+} \right)_{\text{oct}} \left[ \text{Mg}^{2+}_i \text{Mn}^{3+}_{(1-x)-2y} \text{Mn}^{4+}_{(1-x)-y} \right]_{\text{Tet}} \text{O}_4$ is produced, in which the cation distribution and concentration are different from the first one. Using the equation 3.4.13 the concentration of Mg$_i^{2+}$ is determined by

\[
\left[ \text{Mg}^{2+}_i \right] = \frac{2K_{12} \cdot y \cdot (1-x+y)^3 \cdot (4K_i)^2 \cdot K_{15} \cdot x \cdot \left( \left( \frac{4K_i}{K_2 \cdot (1+x-2y)} \right)^{1/3} \cdot \left( \frac{pO_2}{p_0} \right)^{-2/3} \right)}{(1+x-2y)^3}
\]
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with

\[ \text{Mn}^{2+}_\text{Tet} + V_{\text{Oct}} + \text{Mn}^{4+}_{\text{Oct}} \leftrightarrow 2\text{Mn}^{3+}_\text{Tet} + V_{\text{Tet}} \]  

\[ \Rightarrow K_{13} = \frac{[\text{Mn}^{3+}_\text{Tet}]^2 \cdot [V_{\text{Tet}}]}{[\text{Mn}^{2+}_\text{Tet}] \cdot [V_{\text{Oct}}] \cdot [\text{Mn}^{4+}_{\text{Oct}}]} \]  

where the concentration of Mg interstitial has the same pO\(_2\) exponent dependence as that of Li and Mn interstitials. Similar analysis is performed in case of Mn\(^{3+}\) or Mn\(^{4+}\) occupying on 8a sites, the same exponential dependence on pO\(_2\) is obtained. Finally, the oxygen non-stoichiometry in this case has the common expression according to equation 3.4.11

\[ \delta = a_8 \cdot \left( \frac{\text{pO}_2}{p_0} \right)^{-1/2} - b_8 \cdot \left( \frac{\text{pO}_2}{p_0} \right)^{2/3} + c_8 \cdot \left( \frac{\text{pO}_2}{p_0} \right)^{-2/3} \]  

which is independent of the oxidation state of Mn ions previously on 8a sites in the Mg-doped spinel.

Furthermore, if partial of the interstitial 16c sites are occupied, for example, by Mn\(^{2+}\) ions, the lithium deficit spinel of a formula \( (\text{Li}^{+})_{\text{Tet}}(\text{Mn}^{2+}_x)_{\text{Tet}}(\text{Mg}^{2+}_{y}\text{Mn}^{3+}_{1+2x-y}\text{Mn}^{4+}_{1-2x+y})_{\text{Oct}} \text{O}_4 \) is formed. The concentration of Mg interstitials is determined according to equations 3.2.20 and 3.4.13:

\[ [\text{Mg}^{2+}_\text{Tet}] = \frac{K_{12} \cdot y \cdot x \cdot (1-2x+y)}{K_{10} \cdot (1+2x-2y)^2} \]  

It indicates that the defect of Mg interstitial is not affected by oxygen partial pressure when the 16c sites are occupied previously by Mn ions. The oxygen nonstoichiometry has thereafter the original expression

\[ \delta = a_9 \cdot \left( \frac{\text{pO}_2}{p_0} \right)^{-1/2} - b_9 \cdot \left( \frac{\text{pO}_2}{p_0} \right)^2 + c_9 \cdot \left( \frac{\text{pO}_2}{p_0} \right)^{-2} + d_9 \]  

where the influence of Mg doping on \( \delta \) is included in parameter \( d_9 \).
Three different models of Mn ion distribution in Mg-doped spinel are discussed above. It is found that Mg doping on $16d$ sites in spinel plays no roles on the relationships between oxygen nonstoichiometry and $pO_2$ exponents, which have the same simplified expression as undoped spinel with lithium deficit for the same Mn distribution. The difference between them is that the pre-parameter of each item is dependent on the equilibrium constant as well as the concentration of dopant Mg and excessive Mn ions. The rule could be analogically applied for the Mg-doped spinel with lithium excess, $n_{Li}/n_{(Mg+Mn)} > 0.5$, where the defect concentrations have always the same $pO_2$ exponents and different pre-parameters for the same cation distribution compared to the undoped spinel with excess lithium. As a result, the expressions of $\delta$ is obtained for the Mg-doped spinel, which dependence on $pO_2$ exponents is different from various models of cation distribution and same as the undoped spinel as given in table 3.3.1.

### 3.4.3 Ni/Co doped Li-Mn-O spinel

The defect aspect of nickel or cobalt doped Li-Mn-O spinels are more complicated because both Ni and Co can exhibit different oxidation states of $+2$, $+3$ and $+4$ in the spinel. It was reported that the doped nickel or cobalt ions occupy previously on octahedral $16d$ sites as form of Ni$^{2+}$ or Co$^{3+}$ by substitution for Mn ions.$^{[60][63][64][65]}$ Under this condition, the formation of dopant interstitials as well as correspondent equilibrium constants in view of different oxidation states of the dopants is given in table 3.4.1.

When comparing the equilibrium constants listed in the table, it is found that the concentration of the dopant interstitials is only proportional to the reciprocal of $[V_{Oct}]$, because the other ion concentration could be approximately regarded as constant, no matter which kind of oxidation state the dopant elements exhibit on $16c$ sites. The different dependence of $[V_{Oct}]$ on oxygen partial pressure in ground of different defect models indicates just that of interstitial defect of dopant. The valence change of the doped elements is neutralized by oxidation and reduction of Mn$^{3+}$/Mn$^{4+}$ pair, where only the ion concentration of Mn$^{3+}$/Mn$^{4+}$ varies correspondingly, but the mechanism of defect formation is not changed. Thus, it could be concluded, if the ion distribution model is determined, the oxygen nonstoichiometry of the spinel has always the same dependence on $pO_2$ exponents, which is described by the common formula 3.3.33. The parameters a, b, c and d of the $pO_2$ item are functions of equilibrium constants defined in respective cases and the concentration of cations determined experimentally.
### Table 3.4.1. Interstitial defect of dopant Co/Ni

<table>
<thead>
<tr>
<th></th>
<th>Ni(^{2+}) doping</th>
<th>Co(^{3+}) doping</th>
</tr>
</thead>
</table>
| \(K_{14}\)       | \[
\frac{[\text{Ni}_{\text{Oct}}^{2+}] \cdot [V_{\text{Oct}}]}{[\text{Ni}_{\text{Oct}}^{2+}] \cdot [V_{\text{Oct}}]} \]
|                  |                     | \[
\frac{[\text{Co}_{\text{Oct}}^{3+}] \cdot [V_{\text{Oct}}]}{[\text{Co}_{\text{Oct}}^{3+}] \cdot [V_{\text{Oct}}]} \]
| \(K_{16}\)       | \[
\frac{[\text{Ni}_{\text{Oct}}^{3+}] \cdot [V_{\text{Oct}}] \cdot [\text{Mn}_{\text{Oct}}^{3+}]}{[\text{Ni}_{\text{Oct}}^{2+}] \cdot [V_{\text{Oct}}] \cdot [\text{Mn}_{\text{Oct}}^{4+}]} \]
|                  | \[
\frac{[\text{Co}_{\text{Oct}}^{4+}] \cdot [V_{\text{Oct}}] \cdot [\text{Mn}_{\text{Oct}}^{3+}]}{[\text{Co}_{\text{Oct}}^{3+}] \cdot [V_{\text{Oct}}] \cdot [\text{Mn}_{\text{Oct}}^{4+}]} \]
| \(K_{17}\)       | \[
\frac{[\text{Ni}_{\text{Oct}}^{3+}] \cdot [V_{\text{Oct}}] \cdot [\text{Mn}_{\text{Oct}}^{3+}]}{[\text{Ni}_{\text{Oct}}^{2+}] \cdot [V_{\text{Oct}}] \cdot [\text{Mn}_{\text{Oct}}^{4+}]} \]
|                  | \[
\frac{[\text{Co}_{\text{Oct}}^{2+}] \cdot [V_{\text{Oct}}] \cdot [\text{Mn}_{\text{Oct}}^{4+}]}{[\text{Co}_{\text{Oct}}^{3+}] \cdot [V_{\text{Oct}}] \cdot [\text{Mn}_{\text{Oct}}^{3+}]} \]

### 3.5 Defect with squeeze effect

Except for the defect formation mechanisms discussed above, more complicated defect cluster could be formed. If the 8\(\alpha\) sites are already filled with ions, the bigger ions inserting on 16\(c\) sites could squeeze the ions on 8\(\alpha\) into the next 16\(c\) to keep the enough distance between them, thereafter, to maintain a lower energy level. When observing the ionic radius of the different ions (Appendix: table A–2), three possible ionic combinations could result is the “squeeze effect”, which are schematically illustrated in figure 3.5.1. In all of the three
Chapter 3. Defect chemistry in spinel

a. Mn$^{2+}$ ion from 16$d$ squeeze two next 8$a$ Li$^+$ ions

b. Mn$^{2+}$ ion from 8$a$ site squeeze one next 8$a$ Li$^+$ ion

c. Mn$^{2+}$ ion from 16$d$ site squeeze the next 8$a$ Li$^+$ and Mn$^{2+}$ ions

The squeezed Mn$^{2+}$ ion squeeze further the next Li$^+$ ion from 8$a$ to 16$c$

Fig. 3.5.1. Schematic illustration of “squeeze effect”
cases, the force between two large ions with a short distance is relaxed by means of the ion movement, where the distance between the large ions is increased.

In case a, when the Mn ion on 16d insertion into 16c as form of +2 valence, the distance between the 16c and next 8a site (177 pm) is bigger than that of the minimum distance between Mn$^{2+}$ and Li$_{\text{Tet}}^+$ ions (170 pm), however, because the minimum distance between Li$_{\text{Tet}}^+$ and Li$_{\text{Tet}}^+$ is even smaller (163 pm), in order to keep the lowest energy level, the next two Li$_{\text{Tet}}^+$ ions could move from the original 8a sites into the interstitial 16c sites. Thereafter, the defect cluster $V_{\text{Tet}} - \text{Mn}^{2+} - V_{\text{Tet}}$ is formed, which is described by

$$2\text{Mn}_{\text{Oct}}^{3+} + 3V_1 + 2\text{Li}_{\text{Tet}}^+ \leftrightarrow (V_{\text{Tet}} - \text{Mn}^{2+} - V_{\text{Tet}}) + 2\text{Li}_{\text{Tet}}^+ + V_{\text{Oct}} + \text{Mn}_{\text{Oct}}^{4+}$$ 3.5.1

$$\Rightarrow K_{20} = \frac{[V_{\text{Tet}} - \text{Mn}^{2+} - V_{\text{Tet}}][\text{Li}_{\text{Tet}}^+][V_{\text{Oct}}][\text{Mn}_{\text{Oct}}^{4+}]}{[\text{Mn}_{\text{Oct}}^{3+}]^2[V_1][\text{Li}_{\text{Tet}}^+]^2}$$ 3.5.2

It is shown that the formation of the defect cluster has a quite different mechanism from that of the point defect. The concentration of the defect cluster could be determined according to the equilibrium constant as defined above.

If the Mn ion occupy initially on the tetrahedral 8a site, it moves into the neighbor interstitial 16c site as form of Mn$^{2+}$ could push the next Li$_{\text{Tet}}^+$ into interstitial, which is described in figure 3.5.1 b, where the same defect cluster as case a is built. The reaction and equilibrium constants of different Mn oxidation state on 8a sites are written as following:

$$\text{Mn}_{\text{Tet}}^{3+} + 2V_1 + \text{Li}_{\text{Tet}}^+ + \text{Mn}_{\text{Oct}}^{3+} \leftrightarrow (V_{\text{Tet}} - \text{Mn}^{2+} - V_{\text{Tet}}) + \text{Li}_{\text{Tet}}^+ + \text{Mn}_{\text{Oct}}^{4+}$$ 3.5.3

$$\Rightarrow K_{21} = \frac{[V_{\text{Tet}} - \text{Mn}^{2+} - V_{\text{Tet}}][\text{Li}_{\text{Tet}}^+][\text{Mn}_{\text{Oct}}^{4+}]}{[\text{Mn}_{\text{Tet}}^{3+}]^2[V_1][\text{Li}_{\text{Tet}}^+]\text{Mn}_{\text{Oct}}^{3+]}$$ 3.5.4

$$\text{Mn}_{\text{Tet}}^{4+} + 2V_1 + \text{Li}_{\text{Tet}}^+ + 2\text{Mn}_{\text{Oct}}^{3+} \leftrightarrow (V_{\text{Tet}} - \text{Mn}^{2+} - V_{\text{Tet}}) + \text{Li}_{\text{Tet}}^+ + 2\text{Mn}_{\text{Oct}}^{4+}$$ 3.5.5

$$\Rightarrow K_{22} = \frac{[V_{\text{Tet}} - \text{Mn}^{2+} - V_{\text{Tet}}][\text{Li}_{\text{Tet}}^+][\text{Mn}_{\text{Oct}}^{3+}]}{[\text{Mn}_{\text{Tet}}^{4+}]^2[V_1][\text{Li}_{\text{Tet}}^+][\text{Mn}_{\text{Oct}}^{3+}]}$$ 3.5.6
Chapter 3. Defect chemistry in spinel

\[
\begin{align*}
\text{Mn}_{\text{Tet}}^{2+} + 2V_1 + Li_{\text{Tet}}^{+} & \leftrightarrow (V_{\text{Tet}} - \text{Mn}_{\text{Tet}}^{2+} - V_{\text{Tet}}) + Li_{1}^{+} \\
& \Rightarrow K_{21} = \frac{(V_{\text{Tet}} - \text{Mn}_{\text{Tet}}^{2+} - V_{\text{Tet}}) \cdot [Li_{1}^{+}]}{[\text{Mn}_{\text{Tet}}^{2+}] \cdot [V_{1}] \cdot [Li_{\text{Tet}}^{+}]} 
\end{align*}
\]

3.5.7

3.5.8

Furthermore, when two Mn\textsuperscript{2+} ions are located on the neighbor 8\textit{a} and 16\textit{c} sites, the minimum distance between them is 177 pm, which is not only bigger than that between Mn\textsubscript{i}\textsuperscript{2+} and Li\textsubscript{Tet}\textsuperscript{+}, but also Li\textsubscript{i}\textsuperscript{+} and Li\textsubscript{Tet}\textsuperscript{+}. Thus, at the same time of building the Li\textsubscript{i}\textsuperscript{+} by squeeze effect, the Mn\textsubscript{2+} ion could also be push away by the Mn\textsubscript{i}\textsuperscript{2+} ion from the initial tetrahedral site to form another Mn\textsubscript{i}\textsuperscript{2+} ion, which could further squeeze the next Li\textsubscript{Tet}\textsuperscript{+} into interstitial 16\textit{c} site. The formation mechanism is schematically described in figure 3.5.1 and is expressed by

\[
\begin{align*}
2\text{Mn}_{\text{Oct}}^{2+} + \text{Mn}_{\text{Tet}}^{2+} + 4V_1 + 2Li_{\text{Tet}}^{+} & \leftrightarrow (V_{\text{Tet}} - \text{Mn}_{\text{Tet}}^{2+} - V_{\text{Tet}} - \text{Mn}_{\text{Tet}}^{2+} - V_{\text{Tet}}) + 2Li_{1}^{+} + V_{\text{Oct}} + \text{Mn}_{\text{Oct}}^{4+} \\
& \Rightarrow K_{24} = \frac{(V_{\text{Tet}} - \text{Mn}_{\text{Tet}}^{2+} - V_{\text{Tet}} - \text{Mn}_{\text{Tet}}^{2+} - V_{\text{Tet})} \cdot [Li_{1}^{+}] \cdot [V_{\text{Oct}}] \cdot [\text{Mn}_{\text{Oct}}^{4+}]}{[\text{Mn}_{\text{Oct}}^{3+}] \cdot [\text{Mn}_{\text{Tet}}^{2+}] \cdot [V_{1}] \cdot [Li_{\text{Tet}}^{+}]} 
\end{align*}
\]

3.5.9

3.5.10

where a large defect cluster is formed.

When applying the squeeze effect for the lithium excess and deficit as well as the various doped spinels, in the same way, on the basis of different cation distribution and the equilibrium constants defined above for different formation mechanisms, the concentration of the defect clusters is determined, of which the dependence on oxygen partial pressure is summarized in table 3.5.1.

It is shown that the oxidation state of Mn and dopant elements as well as the formation mechanism has no effect on the pO\textsubscript{2} exponential relationship. The exponents vary only with the different cation distribution models. According to the definition discussed in chapter 3.1, the oxygen nonstoichiometry \( \delta \) with either of the squeeze clusters could be expressed by a general formula

\[
\delta = [V_{\text{o}}] - \frac{4}{3} \cdot ([V_{\text{Tet}}] + [V_{\text{Oct}}] + \text{Clu.}) + \frac{4}{3} \cdot ([Li_{1}^{+}] + [\text{Mn}_{\text{i}}^{n+}])
\]

3.5.11
where \([\text{Clu.}]\) denotes the concentration of the defect clusters. When comparing the \(pO_2\) exponents of the cluster with that of point defects (see table 3.3.1), it is found that the formation of defect clusters does not introduce any new exponents of \(pO_2\). However, the contributions of the defect clusters to \(\delta\) are different from various cation distribution models. According to equation 3.5.11, the oxygen nonstoichiometry with squeeze effect could also be written as

\[
\delta = a \left( \frac{pO_2}{p_0} \right)^{-1/2} - b \left( \frac{pO_2}{p_0} \right)^n + c \left( \frac{pO_2}{p_0} \right)^{-n} + d \quad (n = 2/3, 1, 2) \tag{3.3.33}
\]

where the pre-parameter of the item with exponent \(-1\) is included in \(c\), while that with \(2/3\) and 2 are in \(b\), respectively.

**Table 3.5.1. Dependence of defect cluster concentration on \(pO_2\) exponent**

<table>
<thead>
<tr>
<th>Spinel type</th>
<th>Model</th>
<th>(pO_2) exponent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lithium excess</td>
<td>(\text{Li}_i^+)</td>
<td>(-1)</td>
</tr>
<tr>
<td>(n_{Li}/n_{Mn} &gt; 0.5)</td>
<td>(\text{Li}_{\text{Oct}})</td>
<td>(2/3)</td>
</tr>
<tr>
<td>(n_{Li}/n_{Me+Mn} &gt; 0.5)</td>
<td>(\text{V}_{\text{Oct}})</td>
<td>(2)</td>
</tr>
<tr>
<td>Lithium deficit</td>
<td>(\text{Mn}_i)</td>
<td>(2)</td>
</tr>
<tr>
<td>(n_{Li}/n_{Mn} &lt; 0.5)</td>
<td>(\text{Mn}_{\text{Tet}})</td>
<td>(2/3)</td>
</tr>
<tr>
<td>(n_{Li}/n_{Me+Mn} &lt; 0.5)</td>
<td>(\text{V}_{\text{Tet}})</td>
<td>(-1)</td>
</tr>
</tbody>
</table>
4 Experimental results and discussion

4.1 As-prepared samples

The samples used in this work were prepared by a modified Pechini procedure.\cite{76} The composition was analyzed by ICP-OES at Forschungszentrum Jülich, where the relative weight of each element in a sample was determined as given in table 4.1.1 and 4.1.2. The composition of the samples is described by the ratio of the molar amount of the cations, which were calculated and also listed in the tables.

<table>
<thead>
<tr>
<th>Li-Mn-O Sample</th>
<th>Weight % Li</th>
<th>Weight % Mn</th>
<th>(n_{Li}/n_{Mn})</th>
</tr>
</thead>
<tbody>
<tr>
<td>LMO-1</td>
<td>3.12 ± 0.06</td>
<td>60.2 ± 0.4</td>
<td>0.410</td>
</tr>
<tr>
<td>LMO-2</td>
<td>3.36 ± 0.08</td>
<td>58.4 ± 0.5</td>
<td>0.455</td>
</tr>
<tr>
<td>LMO-3</td>
<td>3.57 ± 0.07</td>
<td>59.2 ± 0.4</td>
<td>0.477</td>
</tr>
<tr>
<td>LMO-4</td>
<td>3.64 ± 0.05</td>
<td>59.4 ± 0.5</td>
<td>0.485</td>
</tr>
<tr>
<td>LMO-5</td>
<td>3.8 ± 0.05</td>
<td>61.0 ± 0.4</td>
<td>0.493</td>
</tr>
<tr>
<td>LMO-6</td>
<td>3.9 ± 0.08</td>
<td>60.5 ± 0.7</td>
<td>0.510</td>
</tr>
<tr>
<td>LMO-7</td>
<td>4.16 ± 0.05</td>
<td>58.9 ± 0.7</td>
<td>0.559</td>
</tr>
<tr>
<td>LMO-8</td>
<td>4.18 ± 0.06</td>
<td>58.7 ± 0.3</td>
<td>0.564</td>
</tr>
<tr>
<td>LMO-9</td>
<td>4.2 ± 0.2</td>
<td>56.4 ± 0.4</td>
<td>0.589</td>
</tr>
<tr>
<td>LMO-10</td>
<td>4.58 ± 0.07</td>
<td>58.1 ± 0.6</td>
<td>0.624</td>
</tr>
<tr>
<td>LMO-11</td>
<td>4.8 ± 0.2</td>
<td>55.4 ± 0.5</td>
<td>0.686</td>
</tr>
<tr>
<td>LMO-12</td>
<td>5.33 ± 0.08</td>
<td>55.9 ± 0.9</td>
<td>0.755</td>
</tr>
</tbody>
</table>
The experimental results in table 4.1.1 show that the Li-Mn-O samples LMO-1 to LMO-5 are lithium deficient, the Li/Mn molar ratio of which is smaller than 0.5, while the other samples LMO-6 to LMO-12 are lithium excess with \( n_{\text{Li}}/n_{\text{Mn}} > 0.5 \). The content of lithium and dopant cations in a Li-Me-Mn-O sample are described by the molar ratios \( n_{\text{Li}}/(n_{\text{Mn}}+n_{\text{Me}}) \) and \( n_{\text{Me}}/(n_{\text{Mn}}+n_{\text{Me}}) \), respectively. As given in table 4.1.2 all the doped samples show \( n_{\text{Li}}/(n_{\text{Mn}}+n_{\text{Me}}) \leq 0.5 \) after they were prepared by using the nitrates with \( n_{\text{Li}}/(n_{\text{Mn}}+n_{\text{Me}}) = 0.5 \). The content of the dopants is distributed approximately between \( n_{\text{Me}}/(n_{\text{Mn}}+n_{\text{Me}}) = 0.025 \) and 0.1. It was found that nearly all the samples have less lithium content than that calculated according to the nitrates applied. The same lithium loss was reported also in literature, which was explained as the lithium evaporating during the synthesis due to the high temperature brought by self ignition.\[^{[76]}\]

### Table 4.1.2. The composition of Li-Me-Mn-O samples (Me = Mg, Ni, Co)

<table>
<thead>
<tr>
<th>Li-Me-Mn-O sample</th>
<th>Weight % Li</th>
<th>Weight % Mn</th>
<th>Weight % Me</th>
<th>( n_{\text{Li}}/n_{\text{Mn}}+n_{\text{Me}} )</th>
<th>( n_{\text{Me}}/n_{\text{Mn}}+n_{\text{Me}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg-1</td>
<td>3.71 ± 0.07</td>
<td>0.66 ± 0.02</td>
<td>58.6 ± 0.5</td>
<td>0.489</td>
<td>0.025</td>
</tr>
<tr>
<td>Mg-2</td>
<td>3.74 ± 0.06</td>
<td>1.31 ± 0.02</td>
<td>57.0 ± 0.3</td>
<td>0.494</td>
<td>0.049</td>
</tr>
<tr>
<td>Mg-3</td>
<td>3.67 ± 0.06</td>
<td>1.98 ± 0.03</td>
<td>55.6 ± 0.4</td>
<td>0.484</td>
<td>0.074</td>
</tr>
<tr>
<td>Mg-4</td>
<td>3.74 ± 0.08</td>
<td>2.70 ± 0.03</td>
<td>55.8 ± 0.2</td>
<td>0.478</td>
<td>0.099</td>
</tr>
<tr>
<td>Ni-1</td>
<td>3.6 ± 0.07</td>
<td>1.6 ± 0.09</td>
<td>58.1 ± 0.3</td>
<td>0.478</td>
<td>0.025</td>
</tr>
<tr>
<td>Ni-2</td>
<td>3.6 ± 0.06</td>
<td>3.1 ± 0.05</td>
<td>56.0 ± 0.5</td>
<td>0.484</td>
<td>0.049</td>
</tr>
<tr>
<td>Ni-3</td>
<td>3.6 ± 0.06</td>
<td>4.8 ± 0.07</td>
<td>55.4 ± 0.4</td>
<td>0.476</td>
<td>0.075</td>
</tr>
<tr>
<td>Ni-4</td>
<td>3.7 ± 0.06</td>
<td>6.6 ± 0.2</td>
<td>53.3 ± 0.4</td>
<td>0.492</td>
<td>0.104</td>
</tr>
<tr>
<td>Co-1</td>
<td>3.7 ± 0.1</td>
<td>1.7 ± 0.02</td>
<td>57.0 ± 0.5</td>
<td>0.500</td>
<td>0.027</td>
</tr>
<tr>
<td>Co-2</td>
<td>3.6 ± 0.08</td>
<td>3.4 ± 0.07</td>
<td>56.9 ± 0.5</td>
<td>0.474</td>
<td>0.053</td>
</tr>
<tr>
<td>Co-3</td>
<td>3.7 ± 0.08</td>
<td>5.1 ± 0.09</td>
<td>55.6 ± 0.9</td>
<td>0.485</td>
<td>0.079</td>
</tr>
<tr>
<td>Co-4</td>
<td>3.7 ± 0.07</td>
<td>6.8 ± 0.1</td>
<td>54.9 ± 0.9</td>
<td>0.478</td>
<td>0.103</td>
</tr>
</tbody>
</table>

### 4.2 Phase stability of Li-Mn-O spinel

#### 4.2.1 Lithium excess spinel
The Li-Mn-O samples with lithium excess maintain the single phase cubic spinel crystal structure under certain conditions, which was investigated by several research groups as discussed in chapter 1. Both the composition of the spinel and the oxygen partial pressure have the key effects on the thermal stability of the spinel phase. The stability region of the single phase spinel was defined by two critical limits: upper critical temperature, $T_{c1}$, and lower critical temperature, $T_{cL}$.

### 4.2.1.1 In situ X-ray diffraction (XRD)

When heated above the upper critical temperature $T_{c1}$, the single phase spinel sample changes into a two-phase mixture, the spinel phase together with monoclinic Li$_2$MnO$_3$. It was confirmed that $T_{c1}$ is dependent on the sample composition and the oxygen partial pressure. $T_{c1}$ given in literature $^{19,34,35,37}$ was mostly obtained from the XRD analysis of the quenched samples. Apparently, if the phase transformation occurs very quickly at higher temperature, the XRD patterns of the quenched samples are not able to reflect the actual phase condition in time. To avoid the disadvantage, the in situ XRD measurements were performed in this work.

A series of in situ powder XRD patterns of the Li-Mn-O sample (LMO-8) with lithium excess ($n_{Li}/n_{Mn} = 0.564$) collected at room temperature (RT) to 1000°C as a function of temperature (50°C intervals) under 0.2 bar pO$_2$ is shown in figure 4.2.1. Only single phase spinel peaks were detected up to 650°C. The lattice parameter calculated from the XRD at room temperature is 821.8 pm, which is smaller than that of stoichiometric LiMn$_2$O$_4$ ($a = 824.762$ pm). It agrees to the reports before$^{31,87}$ that the lattice constant decreases with increasing lithium content in the spinel phase, which indicates that the content of smaller Mn$^{4+}$ (ionic radius on octahedral site: 67.0 pm$^{88}$) increases, while that of bigger Mn$^{3+}$ (ionic radius on octahedral site: 78.5 pm$^{88}$) decreases. The charge variation resulted from lithium excess is compensated by the correspondent change of Mn$^{3+}$ and Mn$^{4+}$ content. The peaks of Li$_2$MnO$_3$ begin to exist at 700°C, which is pointed out by red asterisks on the graph. It is the direct evidence of the decomposition of the spinel phase at higher temperature. In the same way, the in situ XRD patterns of lithium excess samples (LMO-6, 9, 11 in table 4.1.1) were also collected, which exhibit the second phase Li$_2$MnO$_3$ at higher temperature and single phase spinel at lower temperature similarly. Furthermore, with temperature increasing the relative intensity of Li$_2$MnO$_3$ peaks increases, while that of the spinel peaks decreases, which refers to the in-
crease of the amount of Li$_2$MnO$_3$ phase in the two-phase mixture. According to the \textit{in situ} XRD patterns the upper limit of the single phase region, $T_{c1}$, was determined in the region between 650 and 700°C for the sample with $n_{Li}/n_{Mn} = 0.564$.

It is generally agreed that at lower temperature the air-prepared Li-Mn-O spinel coexists with the M$_2$O$_3$ or MnO$_2$.[19][40][41][45] It indicates that the spinel phase is not stable when cooled down to lower temperature, where the spinel decomposes into a two-phase mixture. The temperature, at which the phase transition takes place, was defined as the lower critical temperature, $T_{cL}$, in this work. It is the lower temperature limit of the stability region for single phase Li-Mn-O spinel. However, the Mn$_2$O$_3$ or MnO$_2$ phase was not found in the \textit{in situ} XRD patterns in this work, where the sample shows the single phase spinel at room temperature up to 650°C as given in figure 4.2.1 for the sample investigated. The reason will be discussed further in the next part.

\textbf{Fig. 4.2.1. In situ powder XRD patterns}

(Li$_2$MnO$_3$ --- red asterisks, LiMn$_2$O$_4$ --- not marked peaks)
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4.2.1.2 Thermogravimetry analysis (TGA)

According to the *in situ* XRD patterns given above $T_{c1}$ could not be determined accurately because of the 50°C intervals between two measurements. In order to find the exact temperature, at which the phase transition occurs, the TG measurements were carried out by heating up the samples in the thermal balance from room temperature to 1000°C with a slope 1°C/min under the same atmosphere ($p_{O_2} = 0.2$ bar). The TG plot for the sample with $n_{Li}/n_{Mn} = 0.564$ during heating is shown in figure 4.2.2. During heating the weight loss of the Li-Mn oxide could result mainly from the sample giving out oxygen or Li$_2$O evaporation, where the latter is absolutely not reversible. In our measurements, no evident irreversible weight loss was found after heating and cooling cycles at the temperature region involved, which was also mentioned by Thackeray and Paulsen,\cite{17,19} who indicated that the Li$_2$O evaporates only at higher temperature (above 1200°C). Thus, the effect of the Li$_2$O evaporation on the TG measurements will not be discussed further in this work.

One discontinuous mass change takes place at 695 °C, which is pointed by the red arrow as shown in figure 4.2.2, where the mass begins to decrease intensively along with heating. For the sample investigated the temperature at the turn point, corresponds very well to the phase transition temperature determined *in situ* XRD measurement (between 650 and 700°C), at which Li$_2$MnO$_3$ was found. Generally, the discontinuous mass change on TG plots refers to the onset of the phase transition when heating or cooling, as the atmosphere around the sample is fixed. The temperature is considered as the upper critical temperature, $T_{c1}$, where the single phase spinel begins to decompose into a two-phase mixture. If assuming that the oxygen nonstoichiometry is negligible compared to the oxygen release resulted from the decomposition, the reaction above $T_{c1}$ could be described by

$$
dfrac{a_1 \cdot Li - Mn - O \text{ spinel} (n_{Li}/n_{Mn} = n_1)}{a_2 \cdot Li - Mn - O \text{ spinel} (n_{Li}/n_{Mn} = n_2)} + b_1 \cdot Li_2MnO_3 \xrightarrow{\text{Heating}} b_2 \cdot Li_2MnO_3 + c_2 / 2 \cdot O_2 \text{(g)}
$$

During heating more monoclinic Li$_2$MnO$_3$ are produced ($b_2 > b_1$) and the ratio $n_{Li}/n_{Mn}$ in the spinel phase decreases to compensate the disproportional loss of Li and Mn ($n_2 < n_1$), accompanied with a large amount of oxygen release ($c_2 > 0$) compared to the mass change when $T < T_{c1}$. 

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Fig. 4.2.2. TG curve recorded when heating from RT to 1000°C

Li-Mn-O sample: \( n_{Li}/n_{Mn} = 0.564 \)

Another discontinuous mass change takes place at about 451°C as pointed by the blue arrow on the TG plot (figure 4.2.2.), which indicates another phase transformation at that temperature. Since the existence of Mn\(_2\)O\(_3\) phase at lower temperature was confirmed in many works as discussed in chapter 1, it is reasonable to believe that this temperature is the lower critical temperature, \( T_{cL} \), as defined above, which refers to the boundary between the pure spinel phase and a two-phase mixture region. Under the same assumption given in equation 4.2.1, the following equation is proposed to describe the reaction occurs when \( T < T_{cL} \):

\[
\begin{align*}
  a_3 \cdot \text{Li} - \text{Mn} - \text{O spinel} & (n_{Li}/n_{Mn} = n_3) + b_3 \cdot \text{Mn}_2\text{O}_3 \xrightarrow{\text{Heating}} \\
  a_4 \cdot \text{Li} - \text{Mn} - \text{O spinel} & (n_{Li}/n_{Mn} = n_4) + b_4 \cdot \text{Mn}_2\text{O}_3 + c_4 / 2 \cdot \text{O}_2(g)
\end{align*}
\]

where during heating Mn\(_2\)O\(_3\) is consumed \( (b_3 > b_4) \) to produce spinel with smaller \( n_{Li}/n_{Mn} \) \( (n_3 > n_4) \) accompanied with release of oxygen \( (c_4 > 0) \). At \( T_{cL} \) Mn\(_2\)O\(_3\) disappears \( (b_4 = 0) \) and only single phase spinel exists. It is shown that at lower temperature \( (T < T_{cL}) \) the total mass change of the investigated sample is very small (less than 0.025%), which corresponds to the oxygen consumption of a quite small amount of Mn\(_2\)O\(_3\) impurity resolving into spinel host to produce a single phase compound. Such a small amount of Mn\(_2\)O\(_3\) content is difficult to be
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detected by XRD analysis in our measurements, even though at room temperature the XRD has a better resolution. It could be the reason that no peaks of the second phase \( \text{Mn}_2\text{O}_3 \) were found in XRD patterns (figure 4.2.1).

Between \( T_{cL} \) and \( T_{c1} \) a small mass increase was observed for all the lithium excess samples investigated in this work, which was also mentioned in literature.\[^89\] The exact explanation was not given for the mass ascent during heating. The weight change results naturally from the oxygen exchange between the sample and the atmosphere around. This region is considered as the single phase spinel region, where the mass change is only due to the change of oxygen nonstoichiometry:

\[
\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_{4-\delta} \leftrightarrow \text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_{4-\delta} + (\delta^-\delta)/2\text{O}_2(g)
\]

4.2.2 Lithium deficit spinel

Until now, the thermal stability of lithium deficient spinel has not been investigated in detail. It was reported that the spinel with lithium deficiency is possible to perform a local tetragonal distortion replacing the normal cubic construction.\[^19\] The spinel stability limit at higher temperature has not been discussed before. Furthermore, it was found that at lower temperature the air-prepared Li-Mn-O samples are not single phase spinel but accompanied with \( \text{Mn}_2\text{O}_3 \) as the spinel with lithium excess.\[^19,40,41,46-49\] However, as we known, the phase transformation temperature has not been determined accurately.

4.2.2.1 In situ X-ray diffraction (XRD)

As for Li-excess spinel, the same in situ X-ray Diffraction (XRD) measurement was carried out for the lithium deficit sample, \( n_{\text{L}}/n_{\text{Mn}} = 0.455 \). The diffraction patterns was collected at room temperature to 1000°C every 50°C interval as shown in figure 4.2.3. The oxygen partial pressure was controlled under 0.2 bar during the whole measurement. At 900°C the second phase monoclinic \( \text{Li}_2\text{MnO}_3 \) was shown up, and the intensity of that increases rapidly with temperature increasing, which is similar to the behavior of lithium excess sample discussed above, but the onset temperature of \( \text{Li}_2\text{MnO}_3 \) formation for lithium deficient sample is higher. It is an indication that at higher temperature the lithium deficit spinel has a better stability. At lower temperature between 300 and 850°C only the peaks of the single phase
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spinel were collected. However, at room temperature the Mn$_2$O$_3$ phase was found, which is the evidence of the phase transition at lower temperature. The exact temperature of the phase change could not be determined according to the \textit{in situ} XRD patterns. When compared to the XRD plot for the sample with $n_{Li}/n_{Mn} = 0.564$ at room temperature, it was concluded that increasing the lithium content improve the stability of the spinel phase at lower temperature.

The \textit{in situ} XRD measurements were performed for other lithium deficit samples (LMO-1, 3 in table 4.1.1). Similarly, the peaks of Li$_2$MnO$_3$ were found at higher temperature and disappeared at lower temperature for the samples investigated. The upper critical temperature, $T_{c1}$, exists also for the spinel with lithium deficit. The peaks of Mn$_2$O$_3$ phase were detected only for the sample with strong lithium deficit at room temperature, which was explained as a relative longer period for the reaction to reach equilibrium at lower temperature and a very small amount of Mn$_2$O$_3$ phase coexistence with spinel. The exact critical temperature, $T_{c1}$, at which Mn$_2$O$_3$ was disappeared during heating, was difficult to be confirmed by XRD measurements, which was also mentioned in Paulsen’s work.$^{[19]}$ The [220] peak at $2\theta = 30.7^\circ$, which indicates Mn ions on the tetragonal sites of the lithium deficient spinel.$^{[10][19]$

![Fig. 4.2.3. \textit{In situ} powder XRD patterns](image)

(Li$_2$MnO$_3$ — red asterisks, Mn$_2$O$_3$ — red arrows, LiMn$_2$O$_4$ — not marked peaks)
was not detected for the sample with lithium deficit in our measurements. The single phase spinel without Mn\(^{2+}\) on the tetragonal sites for even lower \(n_{Li}/n_{Mn}\) sample was also confirmed by Xia.\(^{[68]}\) It seems that the air-prepared spinel with \(n_{Li}/n_{Mn}<0.5\) in our work, even at higher temperature, has another kind of manganese ion distribution, which is different from the description by Björk\(^{[16]}\) and Paulsen.\(^{[19]}\) Furthermore, the split of the [311] peak of the cubic LiMn\(_2\)O\(_4\) phase into the [311] and [113] peaks of the tetragonal phase, which is the indication of Jahn-Teller distortion, was not found in the in situ XRD patterns. The single phase tetragonal spinel, which was found by Yamada and Tarascon,\(^{[18][45]}\) actually, exists only at certain temperature (about 900–950°C), where the Li\(_2\)MnO\(_3\) has disappeared and LiMnO\(_2\) was still not formed during heating according to their in situ XRD patterns. But at this temperature region the spinel phase coexists always with Li\(_2\)MnO\(_3\) in our work, which was also indicated by Thackeray.\(^{[17]}\) Taking into account the resolution of the in situ XRD measurements in our work, the lower intensity of the split peaks was probably covered by the high background in the XRD patterns. However the peaks of Li\(_2\)MnO\(_3\) phase indicate that the Li-Mn-O sample investigated in our work at this temperature region is not single phase spinel any more.

### 4.2.2.2 Thermogravimetry analysis (TGA)

The TGA measurements were carried out for the sample with lithium deficit. Similarly, the sample was heated from room temperature to 1000°C with 1°C/min heating rate under constant pO\(_2\) = 0.2 bar. The mass change was recorded as the function of temperature variation. The TG plot of the lithium deficit sample (\(n_{Li}/n_{Mn} = 0.455\)) is given in figure 4.2.4. Two distinct discontinuous mass changes are shown on the curve. The temperature region 850 to 900°C determined in XRD measurement, where the monoclinic phase Li\(_2\)MnO\(_3\) formed, is correspondent to the turn point at 880°C very well. Above this temperature, the sample begins to lose weight rapidly due to oxygen release. The reaction could be described similarly by equation 4.2.1, where the only difference is the mole fraction of Li/Mn < 0.5. The discontinuous mass change at 610°C indicates also a phase transition, which was defined as the lower critical temperature, \(T_{cL}\). The XRD pattern at room temperature shown above in figure 4.2.3 gives the evidence that the lithium deficit sample decomposes into two phases at lower temperature. The impurity Mn\(_2\)O\(_3\) phase is dissolved back into the spinel phase during heating, where the mole fraction of Li/Mn decreases and mass increases due to oxygen consumption, which could be describe by equation 4.2.2 with \(n_{Li}/n_{Mn} < 0.5\).
Fig. 4.2.4. TG curve recorded when heating from RT to 1000°C  
Li-Mn-O sample: $n_{Li}/n_{Mn} = 0.455$

Fig. 4.2.5. TG plots with different heating rate
The region between 610 and 880°C was considered as the single phase spinel region for the sample $n_{Li}/n_{Mn} = 0.455$, where the mass change results only from the oxygen non-stoichiometry change in the spinel structure. Compared to the single phase region of lithium excess spinel determined above (see figure 4.2.2), the spinel with deficient lithium has higher critical temperature $T_{c1}$ and $T_{cL}$ and a broader stability region. It indicates that the spinel with lithium deficit has a better stability at higher temperature, while increasing the lithium content improve the stability of the spinel phase at lower temperature.

Because of the smaller driving force of the reaction at lower temperature, generally, a longer reaction time is required to reach the equilibrium. Therefore, in order to confirm the accuracy of $T_{cL}$ determined by TG with 1°C/min heating rate in this work, two TG measurements were carried out for the lithium deficit sample $n_{Li}/n_{Mn} = 0.485$ with a heating slope of 1°C/min and 0.5°C/min, respectively. The TG plot recorded is shown in figure 4.2.5, where the $T_{cL}$s determined by two different heating procedures are pointed out. Only 1°C difference between two lower critical temperatures indicates that the reaction at this temperature region has a nearly equilibrated state with 1°C/min heating rate.

### 4.2.3 Differential thermal analysis (DTA)

In order to identify the existence of the phase transformation at the temperature determined by TG, the DTA-TG measurements were carried out by heating the sample from room temperature to 1000°C with 1°C/min heating rate under $pO_2 = 0.2$ bar. The DTA-TG plot for the lithium deficit sample ($n_{Li}/n_{Mn} = 0.485$) is shown in figure 4.2.6. The discontinuous mass decrease was found on the TG curve, which refers to the upper critical temperature, $T_{c1}$. On the DTA curve a downward peak was obtained at the same temperature region, which corresponds to the upper critical temperature determined by TG very well. It is another evidence of the phase transition occurrence at $T_{c1}$. According to the characteristics of DTA measurements, the DTA-peak results from the temperature descent at the sample side. Thus, it was concluded that the phase transition at $T_{c1}$ is an endothermic process (see equation 4.2.1 with $b_1 = 0$).

Furthermore, the enthalpy change during the phase transition was also obtained from the DTA curve. The area of the DTA peak is associated with the enthalpy change, which can
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Fig. 4.2.6. DTA-TG curves recorded when heating from RT to 1000°C
Li-Mn-O sample: \( \frac{n_{Li}}{n_{Mn}} = 0.485 \)

Fig. 4.2.7. DTA calibration curve
be determined by DTA calibration. The calibration was carried out by observing the peak area of several metals, of which the fusion energy and melting point are known (Appendix: table A–1). Then the dependence of the energy change on the peak area was obtained. The conversion parameter determined in this work is a function of temperature as given in figure 4.2.7. According to the calibration data and the area A shown in figure 4.2.6, the enthalpy change for the phase transition at $T_{c1}$ is $\Delta H = 8.6$ J/g of the sample investigated. At lower temperature, where the discontinuous mass change occurred, no DTA peak was found. It seems that at $T_{cL}$ the enthalpy change is difficult to be detected due to the slow reaction process and the low level energy variation.

4.2.4 Thermal stability of Li-Mn-O spinel

4.2.4.1 Dependence of the critical temperatures on $n_{Li}/n_{Mn}$

A series of in situ powder XRD and TG measurements was performed for samples with different molar ratios of Li/Mn ($0.455 \leq n_{Li}/n_{Mn} \leq 0.755$) under $pO_2 = 0.2$ bar. The samples with lithium excess and deficit exhibit the similar XRD patterns and TG plots as discussed above. The upper and lower critical temperatures were determined accurately, which are functions of the composition of the samples as shown in figure 4.2.8. The single phase spinel is stable only with certain $n_{Li}/n_{Mn}$ at certain temperature. Both of the upper and lower critical temperature decrease with $n_{Li}/n_{Mn}$ increasing. The descend rate of the critical temperature curves in the region of lithium deficit is more sharp than that of lithium excess. Compared to the phase diagram presented by Paulsen\cite{19} as shown in figure 4.2.9, the single phase spinel region determined in our work is broader. Both limits of the single phase spinel region are not straight lines. No breaks on the critical temperature lines were found between the regions of lithium excess and deficit, which corresponds well to the arguments mentioned above. At lower temperature the spinel with higher $n_{Li}/n_{Mn}$ keeps a single phase, while at higher temperature the spinel with lower $n_{Li}/n_{Mn}$ is more stable.

If considering that a single phase spinel with lithium deficit ($n_{Li}/n_{Mn}=0.455$) is composed with a spinel ($n_{Li}/n_{Mn}=0.5$) and relevant $Mn_2O_3$ by heating up from the two-phase region into the single phase spinel region, the sample will lose 0.27% total weight due to release of oxygen (see equation 4.2.2). However, the weight loss below $T_{cL}$ determined by TG as shown in figure 4.2.4 is about 0.4%, which is more than that needed to produce a single phase spinel with $n_{Li}/n_{Mn}=0.455$. It indicates that at relative lower temperature a great amount of
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Fig. 4.2.8. Dependence of upper and lower critical temperature, $T_{c1}$ and $T_{cL}$, on $n_{Li}/n_{Mn}$

Fig. 4.2.9. Comparison of the single phase spinel region

Single phase spinel region determined in this work
oxygen is absorbed to produce more Mn$_2$O$_3$, which results in the increase of $n_{Li}/n_{Mn}$ in the spinel over 0.5, where a spinel with lithium excess is formed. Similarly, above $T_{c1}$ if the spinel with lithium excess ($n_{Li}/n_{Mn}$=0.564) loses 0.74% sample weight due to oxygen release during heating, it will change into a two-phase mixture of a spinel with $n_{Li}/n_{Mn}$=0.5 and relevant Li$_2$MnO$_3$ (see equation 4.2.1). When heating, before another new phase, LiMnO$_2$, is formed at $T_{c2}$, the weight loss determined by TG in our work is about 2%, which is apparently more than that to form the spinel with $n_{Li}/n_{Mn}$=0.5. It shows that in order to compensate the formation of more Li$_2$MnO$_3$, the $n_{Li}/n_{Mn}$ in the spinel decreases deeply, where the spinel with lithium excess changes into that with lithium deficit. The continuous release of oxygen during heating in the two temperature regions, below $T_{cL}$ and above $T_{c1}$, implies that both $n_{Li}/n_{Mn}$ in the spinel phase and the concentration of the second phase are continuous functions of temperature change. No sudden weight change was found in the two-phase mixture regions on TG curves, even though the ratio of lithium and manganese varied across the $n_{Li}/n_{Mn}$=0.5 critical point.

Furthermore, if considering the reaction (see equation 4.2.1) between $T_{c1}$ and $T_{c2}$ reaches the equilibration when the sample is heated with a constant slope of 1°C/min, the ratio of $n_{Li}/n_{Mn}$ in the spinel phase as well as the concentration of Li$_2$MnO$_3$ at certain temperature

![Diagram showing temperature and Li/Mn ratio relationship](image)

**Fig. 4.2.10.** $T_{c1}$ determined by using the law of the lever
could be determined by using the law of the lever according to the amount of oxygen release. The variation of $n_{Li}/n_{Mn}$ in spinel with temperature change indicates exactly the composition of the spinel that is stable at corresponding temperature. In other words, the upper critical temperature, $T_{c1}$, could be determined by calculating the change of $n_{Li}/n_{Mn}$ in spinel phase during heating. Four exemplar curves of different original composition are given in figure 4.2.10, which are obtained according to the respective TG curves. It is shown that the calculated curves agree to the results determined above very well. No sudden change exists between the regions of lithium deficit and excess, which is another evidence of the argument discussed above. Moreover, the spinel phase and $Li_2MnO_3$ could keep the two-phase equilibration even when the spinel phase has a quite small $n_{Li}/n_{Mn}$ ($\approx 0.37$), which is also different from the spinel region reported in literature.[19]

4.2.4.2 Dependence of the critical temperature on oxygen partial pressure

The upper and lower critical temperature, $T_{c1}$ and $T_{cL}$, were also investigated for different samples ($0.455 \leq n_{Li}/n_{Mn} \leq 0.755$) by the same TG procedure but under different $pO_2$. The similar mass change process was recorded on the TG plots as described above in the $pO_2$ variation region investigated in this work, where two discontinuous weight losses during heating were collected.

It was reported in literature that the upper critical temperature, $T_{c1}$, is a linear function of $\log(pO_2)$ for the lithium excess spinel. Above the lines the spinel decomposed partially into $Li_2MnO_3$ phase. The same dependence was obtained in this work as shown in figure 4.2.11. New results were given for the sample with strong lithium excess. Furthermore, $T_{c1}$ for the sample with lithium deficit ($n_{Li}/n_{Mn} = 0.485$) determined in this work was also shown on the graph, which has a similar linear correlation as lithium excess spinel that $T_{c1}$ increases with $pO_2$ increasing. It indicates that the spinel phase is more stable under higher oxygen partial pressure at higher temperature. In another word, at certain temperature increasing $pO_2$ will prevent the occurrence of the spinel decomposition into $Li_2MnO_3$. 


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The dependence of $T_{cL}$ on oxygen partial pressure was determined as shown in figure 4.2.12. The lower critical temperature is a linear function of $\log(pO_2)$ not only for the lithium excess spinel but also lithium deficit one. Below the limit lines the Li-Mn-O compound is composed by the spinel phase and the impurity Mn$_2$O$_3$, while above that only single phase spinel exists. $T_{cL}$ increases with $pO_2$ increasing, which indicates that increasing the oxygen content in the atmosphere around the sample could promote the spinel decomposition process at lower temperature. Moreover, the limit of the stability region moves to lower temperature when increasing $n_{Li}/n_{Mn}$.

As a result, the stability region of the spinel phase could be described by oxygen partial pressure as given in figure 4.2.13. Both the upper and lower critical temperature lines increase with $pO_2$ increasing. It indicates that the spinel decomposes partially to Mn$_2$O$_3$ when oxidation and Li$_2$MnO$_3$ when reduction, respectively. The single phase region of this sample was constricted within the two straight lines.

**Fig. 4.2.11.** Dependence of upper critical temperature, $T_{c1}$, on oxygen partial pressure, $pO_2$

![Graph showing the dependence of $T_{c1}$ on $pO_2$](image)
Fig. 4.2.12. Dependence of lower critical temperature, $T_{cl}$, on oxygen partial pressure, $pO_2$

Fig. 4.2.13. Single phase spinel region of another kind
4.2.4.3 Three-dimensional phase diagram

Moreover, since the stability region is functions of both $n_{Li}/n_{Mn}$ and $pO_2$, a three-dimensional diagram is put forward to describe the single phase spinel region as shown in figure 4.2.14. Two areas are given in the figure to represent the boundary of the spinel phase. It indicates that the Li-Mn-O samples located between the two areas are single phase spinel.

![3-D phase diagram of Li-Mn-O spinel](image)

**Fig. 4.2.14.** 3-D phase diagram of Li-Mn-O spinel

(Upper and lower critical temperatures are indicated by red and blue area respectively.)

4.3 Phase stability of doped Li-Mn-O spinel

4.3.1 XRD measurements

It is generally accepted that the doped element $Mg^{2+}, Ni^{2+}$ or $Co^{3+}$ replaces the Mn ions on the octahedral $16d$ sites in the Li-Mn-O spinel phase, where the compounds maintain the single phase spinel construction. The doped Li-Me-Mn-O (Me = Mg, Ni, Co) samples prepared in this work were analyzed by X-ray diffraction at room temperature. The XRD patterns are shown in figure 4.3.1. All the samples investigated exhibit single phase spinel composi-
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Fig. 4.3.1. XRD patterns of doped Li-Mn-O samples

Fig. 4.3.2. Lattice constant of doped Li-Mn-O spinel
Chapter 4. Experimental results and discussion

tion, where the concentration of the dopants is distributed in the region $0.025 < n_{\text{Me}}/n_{(\text{Me+Mn})} < 0.1$, which is apparently coincident of the results reported before. According to the Bragg equation, the lattice constants of the Li-Me-Mn-O samples was determined, which was given as the function of dopant concentration in figure 4.3.2, when regarding all the samples have approximately same lithium content. If considering the lattice constant of the undoped spinel pointed by arrows in figure 4.3.2, the lattice constant of Li-Me-Mn-O increases at the beginning when the spinel is doped by Mg, Co or Ni, until reaches the maximum value, and then decreases rapidly with the increasing of the dopant concentration. Co-doped spinel has the most descent rate.

Two factors affect the change of lattice parameter. On one hand, all the doped elements as well as Li and Mn have different ion radius (Appendix: table A–2). If the dopants replace the bigger Mn ions in spinel phase, the lattice constant decreases with increasing of dopant concentration. However, the lattice constant increases if the substituted ions are the smaller ions. On the other hand, to keep the charge neutrality the amount of Mn$^{2+}$, Mn$^{3+}$ and Mn$^{4+}$ varies with the content of the dopant elements with different valence, where the lattice parameter decreases correspondingly with the concentration ascent of Mn ion with higher valence but smaller radius. The increase of the lattice constant at lower dopants concentration indicates that the substituted Mn ions should be the smaller Mn$^{3+}$ or Mn$^{4+}$ but not the bigger Mn$^{2+}$. The lattice constants begin to decrease with increasing of dopant concentration after reaching a maximum point. The descend tendency of the different dopants as shown in figure 4.3.2 is proportional to the ionic radius, where the decreasing rates are Co > Ni > Mg, and the radius Co < Ni < Mg. It seems that the dopants could substitute for the bigger Mn ions when the dopant concentration is high. At the same time the second effect discussed above could also accelerate the decreasing rate. Taking into account that the spinel sample investigated in this work is lithium deficient, the doped elements as well as Li and Mn in the host could have quite different ion distribution as well as Mn oxidation state from that of Li$_{11}$(Me$_3$Mn$_{2-y}$)O$_4$ reported before, where the lattice parameter is always smaller than that of undoped LiMn$_2$O$_4$ spinel.[58][60][63]

4.3.2 DTA-TG analysis

In order to investigate the thermal stability of the doped samples, the DTA-TG plots were recorded when heating to 1000°C under 0.2 bar oxygen partial pressure. It was found
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Fig. 4.3.3. TG plot of Li-Mg-Mn-O sample

Fig. 4.3.4. Dependence of upper critical temperature, $T_{c1}$, on dopant concentration
that all the samples prepared in this work as given in table 4.1.2 exhibit the similar TG characteristics as the undoped samples. A exemplar TG curve of the sample Li-Mg-Mn-O \((n_{Li}/n_{(Mg+Mn)} = 0.489, n_{Mg}/n_{(Mg+Mn)} = 0.025)\) is shown in figure 4.3.3. The compounds lose mass discontinuously at two temperatures, 539 and 806°C, which correspond to the lower and upper critical temperature defined for the undoped spinel very well. Therefore, it could be concluded that the doped spinel is a high temperature stable phase. The upper critical temperature, \(T_{c1}\), determined by TG for the doped samples are summarized in figure 4.3.4, which is always lower than that of undoped Li-Mn-O sample indicated by star, and decreases when increasing the concentration of dopants. Mg doped sample has the worst stability of the three. Apparently, the spinels doped by Mg, Ni or Co show the similar stability characteristics as the spinel with lithium excess, which could be interpreted as the spinel doped by Li ions, where the doping always worsens the stability of the spinel phase at higher temperature. The decomposition reaction of the doped spinel phase above the upper limit could be principally confirmed \textit{in situ} by XRD measurements. The lower critical temperatures for the doped spinel, especially the spinel with higher concentration dopant, are very difficult to be determined by using DTA-TG measurement head, because only few amount of the sample could be applied in DTA crucible, and the small mass variation is not detectable. Furthermore, no DTA peaks were found at both critical temperatures determined by TG. As a result, in order to observe the lower limit of the spinel stability region accurately, the pure TG process is proposed, which has a better sensitivity for the mass change.

4.4 Oxygen nonstoichiometry of Li-Mn-O spinel

4.4.1 Determination of \(\Delta\delta-pO_2\)

The defect models of Li-Mn-O spinel have been discussed in chapter 3 in detail. According to the possible ion and vacancy distribution in the spinel structure, several defect models are put forward, where the oxygen nonstoichiometry of \((\text{LiMn})_2\text{O}_{4.5}\) is expressed by a general formula

\[
\delta = a \left(\frac{pO_2}{p_0}\right)^{1/2} - b \left(\frac{pO_2}{p_0}\right)^n + c \left(\frac{pO_2}{p_0}\right) - d \quad (n = 2/3, 1, 2)
\]

3.3.33
where the oxygen nonstoichiometry $\delta$ is a function of oxygen partial pressure with different exponents corresponding to various defect models. Therefore, the information of the defect structure in spinel crystal could be obtained by observing the relationship between $\delta$ and $pO_2$.

Taking the stability region of the single phase spinel into account, the measurements were performed at 600, 650 and 700°C respectively. The samples were oxidized and reduced several times by changing oxygen partial pressure, $pO_2$, in the region allowed. The exemplar original measured curve of the Li-Mn-O sample with $n_{Li}/n_{Mn} = 0.477$ at 700°C was shown in figure 4.4.1. After each $pO_2$ jump the atmosphere was maintained for a few hours to guarantee an equilibrated reaction, and the mass changes were recorded. It was found that both oxidation and reduction processes were almost finished in the first a few minutes, which implies a rapid ions and vacancies transportation in the sample. Furthermore, when the sample is oxidized or reduced of the same $pO_2$ step, the approximately same mass change is exhibited on the TG curve, which refers to a well reversible reaction process. Therefore, the average mass change of the oxidation and reduction procedures was taken to calculate the nonstoichiometry change of the correspondent $pO_2$ change.

![Fig. 4.4.1. TG raw data when $pO_2$ jumping at 700°C](image-url)
The reaction during oxidation and reduction is described by equation

\[
\text{Li}_{x}\text{Mn}_{y}\text{O}_{4-\delta} \leftrightarrow \text{Li}_{x}\text{Mn}_{y}\text{O}_{4-\delta} + (\delta^{-\delta})/2 \text{O}_2(\text{g}) \tag{4.4.1}
\]

Apparently, when increasing or decreasing the oxygen content in the atmosphere around the Li-Mn-O sample, the previous equilibration is broken, and the reaction proceeds to the left or right side, respectively. The oxygen nonstoichiometry change, \(\Delta\delta\), could be determined correspondingly according to equation 4.4.1 by

\[
\frac{M_{\text{Li},\text{Mn},\text{O}_{4-\delta}}}{m_1} = \frac{M_{\text{Li},\text{Mn},\text{O}_{4-\delta}}}{m_2} = \frac{(\delta^{-\delta})/2 \cdot M_\text{O}}{\Delta m} \tag{4.4.2}
\]

where \(M\) refers to the molar mass, and \(m\) to mass, if considering

\[
M_{\text{Li},\text{Mn},\text{O}_{4-\delta}} \approx M_{\text{Li},\text{Mn},\text{O}_{4-\delta}} \approx M_{\text{Li},\text{Mn},\text{O}_{4}} \tag{4.4.3}
\]

\[
\Delta\delta = \delta^{-\delta} \tag{4.4.4}
\]

\[
m_1 \approx m_2 \approx m_0 \tag{4.4.5}
\]

\[
\Delta m = m_1 - m_2 \tag{4.4.6}
\]

\(m_0\) is the sample weight obtained before the TG measurement. \(\Delta m\) refers to the mass change between two equilibrated state before and after \(p\text{O}_2\) jumping, which is determined by TG. Since the mole fraction of Li/Mn was given by ICP-OES analysis, the molar mass of Li-Mn-O spinel could be thereafter determined according to the different designated models. Practically, because of the little different of the molar mass among the models, the formulas \(\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4\) and \(\text{Li}_{1-x}\text{Mn}_{2+x}\text{O}_4\) are applied to calculate \(\delta\) for lithium excess and deficit spinel respectively, where the influence of \(\delta\) on molar mass is also neglected. As a result, the change of oxygen nonstoichiometry, \(\Delta\delta\), is informed. If considering that \(\Delta\delta = 0\) under certain referential oxygen partial pressure, \(p(\text{O}_2)_{\text{ref}}\), and \(p_0\) corresponds to the standard air pressure, 1 bar, the dependence of oxygen nonstoichiometry change, \(\Delta\delta\), on \(p\text{O}_2\) is obtained according to equation 3.3.33:

\[
\Delta\delta = a \left[ (p\text{O}_2)^{-1/2} - (p\text{O}_2)_{\text{ref}}^{-1/2} \right] - b \left[ (p\text{O}_2)^n - (p\text{O}_2)_{\text{ref}}^n \right] + c \left[ (p\text{O}_2)^n - (p\text{O}_2)_{\text{ref}}^n \right]
\]

\(\Delta\delta\) is the change of oxygen nonstoichiometry. The exponent \(n\) varies with different spinel structures, and for lithium excess and deficit spinel, \(n = 2/3, 1, 2\).
4.4.2 Oxygen nonstoichiometry of Li excess spinel

4.4.2.1 $\Delta\delta$–$pO_2$ dependence

The relationship between oxygen nonstoichiometry change, $\Delta\delta$, and oxygen partial pressure of sample $n_{Li}/n_{Mn} = 0.510$ is shown in figure 4.4.2. The experimental results were collected at 650°C, where $pO_2$ was varied in the spinel stability region between 0.5 and 0.01 bar. The point when $pO_2 = 0.5$ bar is regarded as the referential state, $\Delta\delta = 0$. Under lower $pO_2$ the spinel sample loses oxygen and the oxygen nonstoichiometry $\delta$ in $(Li,Mn)_3O_{4-\delta}$ increases. In order to determine the defect structure in the spinel phase the results for $\Delta\delta$ are respectively fitted by using three models in view of the ion distribution for lithium excess spinel under different assumptions.

The fitted curves shown in figure 4.4.2 are corresponding to the assumptions that only one of the point defect types is dominant in the nonstoichiometric spinel, which are denoted by different colors. Apparently, all fitted curves do not agree with the experimental results. Furthermore, no matched curves are found by performing the similar fitting processes for other two models of cation distribution, which have the different $pO_2$ exponents of $\pm1$ and $\pm2$. It indicates that in the region of $pO_2$ change investigated in this work the nonstoichiometric structure in the spinel could not been explained by single defect specie.

When applying possible combined point defect models on the fitting process, three series of fitted curves are obtained. In figure 4.4.3, the experimental results are fitted by using the combination of oxygen vacancies and cation interstitials for different ion distributions, which are represented by different colors: red — $Li_{Oct}$, green — $Li_{I}$ and blue — $V_{Oct}$. It is shown that all the three fitted curves are not in agreement with the measurements. When decreasing the oxygen partial pressure the nonstoichiometry $\delta$ of the given defect model increases more rapidly than its actual change, where both oxygen vacancies and cation interstitials give the positive contribution to $\Delta\delta$. Apparently, this combined model in this case is not the appropriate one.

The curves shown in figure 4.4.4 are based on the assumption that the cation interstitials are independent of the oxygen partial pressure, which is described by the formula 4.4.7 with $c = 0$. The blue curve is not fit well for the experimental results, especially under higher
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Fig. 4.4.2. Fitted curves of $\Delta \delta$ – $pO_2$ by single defect model

Ion distribution: $[Li]_{tet}[Li^{1+}Mn^{3+}_{i-1}Mn^{4+}_{i+2}]_{oct}O_{4-\delta}$

Fig. 4.4.3. Fitted curves of $\Delta \delta$ – $pO_2$ for different ion distributions

Defect model: $\delta = K_o \cdot [V_0] + K_i \cdot ([Li] + [Mn]) + K$
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\[ pO_2, \text{ which implies the ion distribution as form of } (Li^{+}_{tet})_{tet}[Mn^{3+}_{1-4x}Mn^{4+}_{1+3x}V_x]_{x=1} O_{4-x} \text{ is not a favorable one comparing to the others. Both red and green fitted curves are located in the region of error tolerance, where the red one has a better fit similarity. In another case, if presuming } a = 0, \text{ namely the oxygen vacancies play no roles in the nonstoichiometric defect, the fitted curves are plotted in figure 4.4.5. It is shown that only the red curve is coincident well with the experimental data. It is found that both of the best fitted curves under the different defect assumptions correspond to the same cation distribution, where Li ions substitute Mn ions on 16\textit{d} sites in a lithium excess spinel. This kind of cation distribution was also determined by some research groups, where the neutron diffraction measurements were performed.}^{[33][90]}

However, it is difficult to distinguish the two combined point defect models in the pO2 region investigated in this work due to the limited measurement range, where the change of oxygen partial pressure is constricted by the conditions of the spinel phase stability. Ammundsen\textsuperscript{[53]} and Koyama\textsuperscript{[54]} have respectively calculated the formation energy of different defect types by simulating the formation of ionic defect in LiMn\textsubscript{2}O\textsubscript{4}. It was shown that the formation of the Li ion interstitial (Li\textsuperscript{+}_{tet} \rightarrow Li\textsuperscript{+}) consumes the lowest energy (see table 4.4.1), which gives the additional information that the Li ion interstitial is the preferable defect specie in spinel compared to the oxygen vacancies. Moreover, in the lithium excess spinel, the formation of lithium interstitial could also follow another mechanism: Li\textsuperscript{+}_{oct} \rightarrow Li\textsuperscript{+}, due to excessive Li ions initial occupancy on 16\textit{d} sites. Both lithium interstitial models exhibit the same pO2 exponents (–2/3) as discussed in chapter 3. Therefore, it is difficult to distinguish them according to the results obtained in this work.

<table>
<thead>
<tr>
<th>Table 4.4.1. Defect formation energies</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Defect</strong></td>
</tr>
<tr>
<td>---------------</td>
</tr>
<tr>
<td>Li Frenkel</td>
</tr>
<tr>
<td>Mn Frenkel</td>
</tr>
<tr>
<td>O Vacancy</td>
</tr>
<tr>
<td>Schottky</td>
</tr>
</tbody>
</table>
$\delta = a (\text{pO}_2)^{1/2} - b (\text{pO}_2)^{2/3} + d$
$\delta = a (\text{pO}_2)^{1/2} - b (\text{pO}_2)^{1} + d$
$\delta = a (\text{pO}_2)^{1/2} - b (\text{pO}_2)^{2} + d$

Fig. 4.4.4. Fitted curves of $\Delta \delta$ – $\text{pO}_2$ for different ion distributions
Defect model: $\delta = K_{\text{O}} \cdot [V_{\text{o}}] - K_{\text{V}} \cdot ([V_{\text{tet}}] + [V_{\text{oct}}]) + K$

Fig. 4.4.5. Fitted curves of $\Delta \delta$ – $\text{pO}_2$ for different ion distributions
Defect model: $\delta = -K_{\text{V}} \cdot ([V_{\text{tet}}] + [V_{\text{oct}}]) + K_{\text{V}} \cdot ([\text{Li}_1] + [\text{Mn}_1]) + K$
Furthermore, the item with exponent 2/3 includes two possible defect forms: cation vacancies and defect clusters. Among the three formation mechanisms of defect clusters shown in figure 3.5.1, only case a is considered to be the possible one in a lithium excess spinel, because Mn ions previous occupancy on 8a sites in spinel as described in model b and c is actually the minor defect form when Li ions are excessive. However, the formation of the defect cluster results from the simultaneous creation of one Mn octahedral interstitial and two tetrahedral vacancies, which needs apparently more energy than that of single cation vacancy. It indicates that the cation vacancies are the dominant defect species in the lithium excess spinel when comparing to the defect clusters.

As a result, it is concluded that the lithium excess spinel has excessive Li ions on the octahedral 16d sites and the nonstoichiometric defect is consists of the combination of cation vacancies and Li ion interstitials.

In the same way, the dependence of $\Delta\delta$ on pO$_2$ for the lithium excess spinel at 600 and 700°C is investigated by fitting the experimental data with the possible defect models. Similar fitted results are obtained as given in figure 4.4.6, where the defect structure could be well explained by the combination of Li ion interstitials and cation vacancies with excess Li ions substitution for Mn ions on 16d sites. According to the fitted curves, the parameters b and c of the Li-Mn-O sample with $n_{Li}/n_{Mn} = 0.510$ at different temperature are determined as listed in

![Graph of $\Delta\delta$ vs pO$_2$](image)

**Fig. 4.4.6.** Fitted curves of $\Delta\delta$–pO$_2$ at different temperature

Defect model: $\delta = -K_V \cdot [V_{16d}^\cdot] + K_I \cdot [Li_i^\dagger]$

Cation distribution: $[Li_i^\dagger]_{16d} \cdot [Li_i^\dagger + Mn_{1-3x}^{3+}Mn_{1+2x}^{4+}]_{16c} \cdot O_{4-\delta}$
table 4.4.2, where \( b \) represents the pre-parameters for possible Li ion interstitial mechanisms (see equation 3.3.4 and 3.3.13), and \( c \) for possible cation vacancies (see equation 3.3.8 and 3.3.9). It is shown that both parameters are dependent on temperature. \( b \) decreases with temperature increasing, while \( \log c \) is a linear function of \( T \) (see figure 4.4.7).

### Table 4.4.2. Parameter \( b \) and \( c \) at different temperatures (lithium excess)

<table>
<thead>
<tr>
<th>Parameters</th>
<th>600°C</th>
<th>650°C</th>
<th>700°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>( b )</td>
<td>((12.0 \pm 0.5) \times 10^{-4})</td>
<td>((9.7 \pm 0.4) \times 10^{-4})</td>
<td>((9.0 \pm 0.4) \times 10^{-4})</td>
</tr>
<tr>
<td>( c )</td>
<td>((2 \pm 0.12) \times 10^{-5})</td>
<td>((4 \pm 0.22) \times 10^{-5})</td>
<td>((8 \pm 0.35) \times 10^{-5})</td>
</tr>
</tbody>
</table>

![Parameter b and c vs. Temperature](image)

**Fig. 4.4.7**. Dependence of parameter \( b \) and \( c \) on temperature

#### 4.4.2.2 \( \delta-pO_2 \) dependence

According to the values of \( b \) and \( c \) determined by fitting, the oxygen nonstoichiometry is written as the exponential functions of \( pO_2 \) at different temperature, which are plotted in figure 4.4.8. It is shown that the spinel exhibits the biggest nonstoichiometry at 650°C in the \( pO_2 \) region investigated. The stoichiometric points are also indicated respectively. Oxygen partial pressure of the stoichiometric point increases with temperature increasing. Under
higher $pO_2$ below $\delta = 0$ the defect is dominated by cation vacancies. With $pO_2$ decreasing, the cation vacancies are eliminated gradually and the cation interstitials become the main defect type in the spinel structure. It is also found that with temperature increasing under same $pO_2$ the nonstoichiometry $\delta$ varies from negative to positive, which indicates the transformation of the defect form from that dominated by cation vacancies to cation interstitials. Furthermore, the maximum nonstoichiometry change, $\Delta\delta_{\text{max}}$, is about 0.0015 in the $pO_2$ region investigated in this work, which is much smaller than that reported before ($\delta \leq 0.2^{[50]}$ and $0.018^{[52]}$). When observing the region of $pO_2$ change in literature, it seems that the measurements performed in their works left the stability region of the single phase spinel due to the strong reduction, where the second phase $\text{Li}_2\text{MnO}_3$ was produced.

![Graph](image)

**Fig. 4.4.8.** $\delta - pO_2$ of $\left(\text{Li}_{1.5}^{\text{Li}}\right)_{\text{Tet}}\left[\text{Li}^{\text{Li}^+}_{x}\text{Mn}^{\text{Mn}^2_{3x}}_{1-3x}\text{Mn}^{\text{Mn}^4_{2x}}_{1+2x}\right]_{\text{Oct}}\text{O}_{4-\delta}$

Model: $\delta = -K_v \cdot (\left[V_{\text{Tet}}^+\right] + \left[V_{\text{Oct}}^-\right]) + K_1 \cdot (\left[\text{Li}_i\right] + \left[\text{Mn}_i\right]) + K$

### 4.4.3 Oxygen nonstoichiometry of Li deficit spinel

The oxygen nonstoichiometry of lithium deficit spinels is investigated in the same methods. Since the defect structure of the spinel could not be explained by the single defect
model, it will not be discussed further. The $\Delta \delta$–$pO_2$ graph of Li-Mn-O sample with $n_{Li}/n_{Mn} = 0.477$ at 650°C is shown in figure 4.4.9 (a and b), where the experimental results are fitted respectively by using different combined defect models. Apparently, the stability of lithium deficit spinel is better than that of lithium excess under lower oxygen partial pressure at the same temperature, which is coincident with the results determined in chapter 4.2. Furthermore, compared to the lithium excess spinel, the spinel with deficient lithium has not only a bigger oxygen nonstoichiometric change in the same region of $pO_2$ variation, but also a bigger $\Delta \delta_{\text{max}}$. However, none of the fitted curves agree well to the experimental data as shown in the figures, which are located outside of the error limits.

\[ \delta = a (pO_2)^{\frac{3}{2}} - b (pO_2)^{\frac{1}{2}} + d \]

\[ \delta = a (pO_2)^{\frac{3}{2}} - b (pO_2)^{\frac{2}{3}} + d \]

\[ \delta = a (pO_2)^{\frac{3}{2}} - b (pO_2)^{\frac{2}{3}} + d \]

\[ \delta = a (pO_2)^{\frac{3}{2}} - b (pO_2)^{\frac{2}{3}} + d \]

In the same way, the oxygen nonstoichiometry of the sample with $n_{Li}/n_{Mn} = 0.477$ is also investigated at 600 and 700°C. The experimental results as well as the fitted curves by using various combined defect models are shown in figure 4.4.10–11. It is found that the maximum nonstoichiometry change in the $pO_2$ region investigated exhibits relative small difference when comparing the experimental data collected at different temperature. No appropriate fitted curves are obtained as the results shown at 650°C. It seems that the defect structure in the lithium deficit spinel could not been well explained by the cation distribution and corresponding defect models proposed in this work. When observing the cation concentration supposed for the reference states in chapter 3, the concentration of deficient lithium, $x$, is applied always as a constant, which is independent of the nonstoichiometry change. The effect of nonstoichiometry change on $x$ could be neglected under the condition $x \gg \Delta \delta_{\text{max}}$. However,
the maximum nonstoichiometry change in the lithium deficit spinel measured in this work is approximate 0.005, which is about 1/6 of the concentration of deficient lithium, x (about 0.031). Therefore, the concentration of deficient lithium could not be treated as a constant any more. It could be the reason that the defect models do not fit well for the experimental data. The influence of $\Delta \delta$ on x should be taken into account to describe the cation distribution of the reference states.
4.5 Oxygen nonstoichiometry of Li-Me-Mn-O spinel (Me=Mg, Ni, Co)

The oxygen nonstoichiometry of doped spinel is similarly investigated in this work. The relationship between oxygen partial pressure and nonstoichiometry change at same temperature are determined by TG measurements. The experimental results are shown in figure 4.4.12 (Mg dopant), 4.4.13 (Ni dopant) and 4.4.14 (Co dopant). All the doped samples have an approximately similar content of Li and dopant as given in the figures. It is shown that the stability of Mg- or Co-doped spinel under lower pO$_2$ is worse than that of the Ni-doped spinels, which agree to the results determined in chapter 4.3. Furthermore, the maximum stoichiometry change of all the doped spinels exhibits nearly the same value (Δδ$_{\text{max}}$ ≈ 0.0061). It indicates that the Δδ$_{\text{max}}$ is independent of the sort of the dopant elements if the spinel has the same concentration of Li, Mn and dopants. However, the change tendency of Δδ with pO$_2$ variation is quite different, which shows that the dependence of δ on pO$_2$ is related with dopant elements. Δδ$_{\text{max}}$ in the pO$_2$ region investigated in this work is much bigger than that of lithium excess spinel and similar with that of the spinel with deficient lithium.

The experimental results are fitted by the defect models discussed in chapter 3. As the case of the lithium deficient spinel, all fitted curves do not agree well to the experiments. If comparing the concentration of deficient lithium (x ≈ 0.015) and dopant element (y ≈ 0.05)
Chapter 4. Experimental results and discussion

\[ \delta = a (pO_2)^{1/2} - b (pO_2)^{1/3} + d \]

\[ \delta = a (pO_2)^{1/2} - b (pO_2)^{1} + d \]

\[ \delta = a (pO_2)^{1/2} - b (pO_2)^{2} + d \]

\[ \delta = -b (pO_2)^{1/3} + c (pO_2)^{2/3} + d \]

\[ \delta = -b (pO_2)^{1} + c (pO_2)^{2} + d \]

\[ \delta = -b (pO_2)^{2} + c (pO_2)^{2} + d \]

\[ \delta = -b (pO_2)^{1/3} + c (pO_2)^{-2/3} + d \]

\[ \delta = -b (pO_2)^{1} + c (pO_2)^{-1} + d \]

\[ \delta = -b (pO_2)^{2} + c (pO_2)^{-2} + d \]

**Fig. 4.4.13.** Fitted curves of $\Delta \delta - pO_2$ for different ion distributions

$\left( n_{Li}/n_{Ni+Mn} = 0.478, n_{Ni}/n_{Ni+Mn} = 0.025, 650^\circ C \right)$

**Fig. 4.4.14.** Fitted curves of $\Delta \delta - pO_2$ for different ion distributions

$\left( n_{Li}/n_{Co+Mn} = 0.500, n_{Co}/n_{Co+Mn} = 0.027, 650^\circ C \right)$

with $\Delta \delta_{\text{max}}$ of doped spinel determined in this work, it is found that the influence of the nonstoichiometry change on the concentration of the initial cation distribution is not negligible. In other words, the reference state of the doped spinels discussed in chapter 3 is not suitable for the case that the spinel has a bigger nonstoichiometry change. In order to understand the defect structure of the nonstoichiometric doped spinels new equations are needed, in which the variation of cation concentration with $\Delta \delta$ should be involved.
This thesis has been an effort to interpret the defect structure of the nonstoichiometric spinel. The Li-Mn-O spinel and doped Li-Me-Mn-O (Me = Mg, Co, Ni) spinel are synthesized in modified Pechini method. The stability of the Li-Mn-O spinel phase is investigated by \textit{in situ} X-ray diffraction (XRD), thermogravimetry (TG) and differential thermal analysis (DTA). The single phase spinel exists only under certain conditions, which are described by upper and lower critical temperature, $T_{c1}$ and $T_{cL}$. Above $T_{c1}$ the spinel coexists with the second phase Li$_2$MnO$_3$, while below $T_{cL}$ with impurity Mn$_2$O$_3$. The phase transformation at $T_{c1}$ during heating is an endothermic process. Both $T_{c1}$ and $T_{cL}$ are continuous functions of the molar ratio of lithium to manganese, $n_{Li}/n_{Mn}$, and decrease with $n_{Li}/n_{Mn}$ increasing. The descent rate for the lithium deficit spinel is much faster. $T_{c1}$ and $T_{cL}$ are also dependent on the oxygen partial pressure, $pO_2$. Over oxidation results in the appearance of Mn$_2$O$_3$, while when deep reduction Li$_2$MnO$_3$ arises. Both upper and lower critical temperature lines increase linearly with log($pO_2$) increasing. The ascent rate of $T_{c1}$ is faster than that of $T_{cL}$. A three-dimensional phase diagram is put forward to describe the stability region of the single phase Li-Mn-O spinel, where the single phase spinel boundary is described by $n_{Li}/n_{Mn}$, $pO_2$ and temperature.

The phase stability of doped Li-Me-Mn-O spinel (Me = Mg, Ni, Co) at higher temperature is also investigate by TG under 0.2 bar $pO_2$. The upper critical temperature of the doped spinel is lower than that of undoped spinel with the same lithium content. In other words, doping worsens the phase stability at higher temperature. $T_{c1}$ decreases with increase of the dopant concentration, $n_{Me}/n_{Me+Mn}$, where the descent rate follows Ni < Co < Mg.

The nonstoichiometry structure of the un- and doped spinels is discussed in view of the defect chemistry. Three types of cation distribution are proposed to describe the referential state of the lithium excess or lithium deficit spinel, which are

1. Excess Li substitute for Mn on octahedral 16$d$ sites or excess Mn substitute for Li on tetrahedral 8$a$ sites;
2. Excess Li or Mn insertion into interstitial 16$c$ site;
3. Excess Li occupy on 8\(a\) sites while 16\(d\) vacancies are built, or excess Mn occupy on 16\(d\) site while 8\(a\) vacancies are built.

On the basis of referential state of cation distribution the oxygen nonstoichiometry in \(\text{(Li, Mn)}_3\text{O}_{4-\delta}\) and \(\text{(Li, Me, Mn)}_3\text{O}_{4-\delta}\) is determined, which is expressed by a general formula:

\[
\delta = a \cdot \left( \frac{p_{O_2}}{p_0} \right)^{1/2} - b \cdot \left( \frac{p_{O_2}}{p_0} \right)^n + c \cdot \left( \frac{p_{O_2}}{p_0} \right)^{-n} + d \quad (n = 2/3, 1, 2)
\]

where parameters \(a, b, c\) and \(d\) are dependent on the equilibrium constants defined on the ground of the different defect formation mechanisms and the concentration of Li, Mn and dopants.

The nonstoichiometry change is measured as function of \(p_{O_2}\) variation, and \(\Delta\delta–p_{O_2}\) diagram is fitted by using different defect models. It is concluded that in a lithium excess spinel, the excess Li ions substitute for Mn ions on octahedral 16\(d\) sites, of which the defect structure is explained by the combined defect model of lithium interstitials and cation vacancies with \(\delta–p_{O_2}\) dependence:

\[
\delta = -b \cdot \left( \frac{p_{O_2}}{p_0} \right)^{2/3} + c \cdot \left( \frac{p_{O_2}}{p_0} \right)^{-2/3}
\]

Under higher \(p_{O_2}\) the cation vacancies are dominant defect form, while under lower \(p_{O_2}\) the Li ion interstitials play more important role. Furthermore, under same \(p_{O_2}\) the oxygen nonstoichiometry, \(\delta\), decreases with temperature increasing. The parameters \(b\) and \(c\) are determined for the sample with \(n_{\text{Li}}/n_{\text{Mn}} = 0.510\) at 600, 650 and 700°C. \(b\) decreases with temperature increasing, while \(\log c\) is a linear function of \(T\). The maximum nonstoichiometry change, \(\Delta\delta_{\text{max}}\), is about 0.0015, which are much smaller than that reported in literature.

Compared to the lithium excess spinel, the un- and doped spinel with deficient lithium has better phase stability, and bigger maximum nonstoichiometry change. The nonstoichiometric defect structure of Li deficit spinel and doped Li deficit spinel could not be well explained by the cation distribution and defect models proposed in this work. It seems that large nonstoichiometry change results in the big deviation of the concentration pre-specified for the deficient lithium, which is considered to be constant in the models. In order to obtain the information of the lithium deficit spinels, new models are needed to be put forward, in which the dependence of deficient lithium concentration on \(\delta\) change should be taken into account.
Appendix

Figures

Fig. A–1. Comparison of the original XRD patterns at RT and 300°C

Tables

<table>
<thead>
<tr>
<th>Metal</th>
<th>Melting point (°C)</th>
<th>Fusion energy (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Indium (In)</td>
<td>156.2</td>
<td>3.26</td>
</tr>
<tr>
<td>Tin (Sn)</td>
<td>232</td>
<td>7.2</td>
</tr>
<tr>
<td>Lead (Pb)</td>
<td>327.5</td>
<td>4.77</td>
</tr>
<tr>
<td>Zinc (Zn)</td>
<td>419.6</td>
<td>7.38</td>
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<tr>
<td>Aluminum (Al)</td>
<td>660.5</td>
<td>10.7</td>
</tr>
<tr>
<td>Silver (Ag)</td>
<td>961.9</td>
<td>11.30</td>
</tr>
<tr>
<td>Element</td>
<td>Coordination type</td>
<td>Radius (pm)</td>
</tr>
<tr>
<td>---------</td>
<td>------------------</td>
<td>-------------</td>
</tr>
<tr>
<td>Li⁺</td>
<td>tetrahedral</td>
<td>73.0</td>
</tr>
<tr>
<td>Li⁻</td>
<td>octahedral</td>
<td>90</td>
</tr>
<tr>
<td>Mn²⁺</td>
<td>tetrahedral</td>
<td>80</td>
</tr>
<tr>
<td>Mn⁴⁺</td>
<td></td>
<td>53</td>
</tr>
<tr>
<td>Mn²⁺</td>
<td></td>
<td>97.0</td>
</tr>
<tr>
<td>Mn³⁺</td>
<td>octahedral</td>
<td>78.5</td>
</tr>
<tr>
<td>Mn⁴⁺</td>
<td></td>
<td>67.0</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>tetrahedral</td>
<td>71</td>
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<tr>
<td>Mg²⁺</td>
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<tr>
<td>Co²⁺</td>
<td>tetrahedral</td>
<td>72</td>
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<tr>
<td>Co⁴⁺</td>
<td></td>
<td>54</td>
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<tr>
<td>Co²⁺</td>
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<td>88.5</td>
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<td>Co³⁺</td>
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<td>75</td>
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<tr>
<td>Co⁴⁺</td>
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<td>67</td>
</tr>
<tr>
<td>Ni²⁺</td>
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<td>69</td>
</tr>
<tr>
<td>Ni²⁺</td>
<td></td>
<td>83.0</td>
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<tr>
<td>Ni³⁺</td>
<td>octahedral</td>
<td>74</td>
</tr>
<tr>
<td>Ni⁴⁺</td>
<td></td>
<td>62</td>
</tr>
</tbody>
</table>
Symbols

\( n_{\text{Li}}, n_{\text{Mn}}, n_{\text{Me}} \) molar amount of Li, Mn and dopant elements
\( pO_2 \) Partial pressure of oxygen
\( x \) Concentration of excessive Li/Mn
\( y \) Concentration of dopants Mg/Ni/Co
\( T \) Temperature (°C)
\( T_{c1} \) Upper critical temperature (°C)
\( T_{cL} \) Lower critical temperature (°C)
\( K_1 - K_{24} \) Equilibrium constants of the defect formation
\( \delta \) Oxygen nonstoichiometry
\( \Delta \delta \) Change of the oxygen nonstoichiometry
\( a, b, c, d \) Pre-exponential parameters of \( pO_2 \)

Abbreviations

TGA Thermogravimetry Analysis
DTA Differential Thermal Analysis
XRD X-ray Diffraction
ICP-OES Inductively Coupled Plasma-Optical Emission Spectroscopy
CA Citric Acid
EG Ethylene Glycol
SPCS Self-Propagating Combustion Synthesis
CID Charge Injection Device
RT Room Temperature

Molar mass

\( M_{\text{Li}} \) 6.941 g/mol
\( M_{\text{Mn}} \) 54.938 g/mol
\( M_{\text{O}} \) 15.999 g/mol
\( M_{\text{Mg}} \) 24.305 g/mol
\( M_{\text{Ni}} \) 58.693 g/mol
\( M_{\text{Co}} \) 58.933 g/mol
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Lebenslauf

Persönliche Daten

Name Chunhui Luo
Anschrift Republikplatz 17, D-52072 Aachen
Geburtsdatum/-ort 22 Dez. 1972 in Gansu, V. R. China
Staatsangehörigkeit chinesisch

Schulbildung:


Studium:

Sept. 1990 – Juli 1994 Universität für Wissenschaft und Technologie Chengdu
Abschluss: Bachelor of Engineering in Fach Anlage und Mechanik des chemischen Ingenieurwesens
Sept. 1994 – Juli 1997 Union Universität Sichuan
Abschluss: Master of Engineering in Fach Prozessmechanik des chemischen Ingenieurwesens
April 2002 – Sept. 2005 Institut für Physikalisch Chemie, RWTH Aachen
Graduiertenstipendiat der Friedrich-Ebert-Stiftung
Abschluss: Doktor der Naturwissenschaften in Fach Mathematik, Informatik und Naturwissenschaften

Berufstätigkeit:

Juli 1997 – Juli 1999 Assistent der Universität Sichuan
Seit Juli 1999 Dozent der Universität Sichuan
Fortbildung:
Okt. 1999 – Juli 2000 Deutschkurs am Deutsch-Kolleg der Tongji-Universität Shanghai
Nov. 2000 – März 2001 Deutschkurs am Goethe Institut Mannheim
April 2001 – März 2002 Institut für Physikalisch Chemie, RWTH Aachen
Austauschstipendiat der Friedrich-Ebert-Stiftung

Publikationen:

Beiträge auf internationalen Konferenzen:
- Engineering Conferences International: Nonstoichiometric Compounds, Kauai (USA), April 3 - 8, 2005. Poster.
- 104. Bunsentagung: Detektion und Dynamik einzelner Moleküle, Frankfurt am Main (Deutschland), Mai 5 - 7, 2005. Poster.