Doctoral Thesis

Synthesis, optimisation and characterisation of layered electroactive materials for lithium-ion batteries

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Synthesis, optimisation and characterisation of layered electroactive materials for lithium-ion batteries

A dissertation submitted to the

SWISS FEDERAL INSTITUTE OF TECHNOLOGY ZURICH

For the degree of

DOCTOR OF NATURAL SCIENCES

Presented by

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Zurich, 2000
Ai miei genitori
Ma le vere scienze so quelle che la speranza ha fatto penetrare per i sensi, e posto silenzio alla lingua de’ litiganti, e che non pasce di sogni i suoi investigatori, ma sempre sopra i primi veri e noti principi procede successivamente e con vere seguenze insino al fine [...].

Leonardo da Vinci
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my girlfriend Miura, for correcting my Italian-English, for her continuous moral support, and especially for her love.
As civilisation has become more sophisticated and reliant on readily available sources of energy, so battery research and development has been stimulated. Nowadays, there is no doubt that the lithium-ion battery concept is projected to be the dominant chemical system for portable electronics applications. The principle of this system is based on the reversible insertion and de-insertion of lithium ions in or from suitable host materials. Most of these lithium-ion batteries use the lithium carbon/lithium cobalt oxide chemistry. Due to the elevated toxicity and the high cost of cobalt, the present work focused on the synthesis and the electrochemical characterisation of new, cobalt-free, layered electroactive materials suitable for lithium-ion batteries.

The synthesised materials were tested in electrochemical cells using electrochemical techniques such as cyclovoltammetry, chronopotentiometry and differential electrochemical mass spectrometry. In order to investigate structural changes, such as phase transformations or lattice expansion as a result of an electrochemical process, a special in-situ X-ray cell was developed and tested during this work.

Commercially available oxides, which are normally not used as electrode materials, were characterised electrochemically since their composition was similar to that of one of the insertion compounds for the negative electrode. In one case, a material gave a specific charge of more than 390 Ah/kg, but only for a limited number of cycles.

Electroactive doped layered lithium manganese oxides LiMn$_{1-x}$Al$_x$O$_2$ with the $\alpha$-NaFeO$_2$ structure-type were synthesised at a low temperature by oxidising the intermetallic phase LiAl with lithiumpermanganate. After the first cycle all the materials tended to transform into the more stable spinel phase. A specific charge of 90 Ah/kg for 50 cycles was obtained for a sample containing 25% aluminium calcined at 250 °C.
The synthesis of layered LiMnO\textsubscript{2} and LiMn\textsubscript{0.9}Al\textsubscript{0.1}O\textsubscript{2} by ion-exchange reactions from NaMnO\textsubscript{2} and NaMn\textsubscript{0.9}Al\textsubscript{0.1}O\textsubscript{2} was performed. It was shown that lithium extraction from and re-insertion into the undoped layered manganese oxide is not a reversible intercalation reaction. On the other hand, in the doped LiMn\textsubscript{0.9}Al\textsubscript{0.1}O\textsubscript{2} oxide the lithium ions were inserted and removed in a single process. This result was a first hint at the positive effect of the aluminium doping.

Homogeneous samples of aluminium containing mixed Mn/Ni oxides with the layered \(\alpha\)-NaFeO\textsubscript{2} structure-type were prepared. Electrochemical experiments performed on the doped oxides revealed the enormous positive effect of aluminium on the cycling stability. An oxide with the composition LiMn\textsubscript{0.5}Ni\textsubscript{0.3}Al\textsubscript{0.2}O\textsubscript{2} presented a specific charge of 115 Ah/kg for more than 200 cycles, with a specific charge loss of 4% every 100 cycles. To our best knowledge such an excellent performance was never achieved before for mixed manganese nickel oxides. By reducing the amount of the redox inactive aluminium in the compound while preserving the layered structure, it was possible to obtain a material with the composition LiMn\textsubscript{0.5}Ni\textsubscript{0.4}Al\textsubscript{0.1}O\textsubscript{2} which maintained a specific charge of 140 Ah/kg for more than 60 cycles. This specific charge of about 140 Ah/kg seems to be high enough to make this electrode material a real candidate for substituting LiCoO\textsubscript{2} in Li-ion batteries. The electrochemical performance of these materials at 55 °C was also very good. Specific charges of 120 Ah/kg for LiMn\textsubscript{0.5}Ni\textsubscript{0.3}Al\textsubscript{0.2}O\textsubscript{2} and 155 Ah/kg for LiMn\textsubscript{0.5}Ni\textsubscript{0.4}Al\textsubscript{0.1}O\textsubscript{2} were demonstrated for more than 50 cycles.

The influence of four different electrolytes with different compositions and with different salts on the electrochemical intercalation of lithium into graphite during the first charge process was studied with the in-situ X-ray cell. The results showed that all four electrolytes used, form the same graphite intercalation compound at a same potential. These results suggest that the size of the anion of the lithium salt plays only a minor role in the intercalation of lithium ions in graphite. The composition of the electrolyte solution also seemed to have a small, or no influence on the intercalation process.
La ricerca e lo sviluppo nel campo delle batterie, sono stimolati dal sempre più crescente fabbisogno di sorgenti energetiche da parte di una civiltà sempre più sofisticata. Al giorno d’oggi non c’è dubbio che la batteria al litio è destinata ad assumere un ruolo determinante per quanto riguarda gli apparecchi elettronici portatili.

Il principio di questo sistema è basato sulla inserzione e rimozione reversibile di ioni litio da un substrato appropriato. La maggior parte di queste batterie sono basate sulla chimica del ossido di litio e cobalto (polo positivo) e del litio-carbonio (polo negativo). Data l’elevata tossicità e l’alto costo del cobalto la ricerca è orientata alla ricerca di materiali privi di cobalto.

Il presente lavoro è focalizzato sulla sintesi e la caratterizzazione elettrochimica di nuovi ossidi, con struttura stratiforme, da usarsi quali materiali elettroattivi per le batterie agli ioni litio.

I materiali sintetizzati sono stati testati in celle elettrochimiche usando tecniche quali la ciclovoltammetria, cronopotenziofotometria e la spettrometria di massa differenziale elettrochimica. All’ scopo di investigare cambiamenti strutturali, quali cambiamenti di fase risultanti da un processo elettrochimico, nell’ambito di questo lavoro, è stata sviluppata e testata una speciale cella in-situ per raggi X.

In virtù della loro somiglianza con materiali normalmente usati per l’elettrodo negativo, sono stati caratterizzati elettrochimicamente ossidi disponibili sul mercato, anche se normalmente non usati come materiali elettroattivi. Uno di questi materiale ha fornito una carica specifica di addirittura 390 Ah/kg, anche se per un numero limitato di cicli.

È stata sintetizzata a bassa temperatura una classe di ossidi di litio, manganese e alluminio (LiMn$_{1-x}$Al$_x$O$_2$) con struttura del tipo $\alpha$-NaFeO$_2$ tramite una ossidazione della
fase intermetallica LiAl con permanganato di litio. Dopo il primo ciclo la struttura di tutti i materiali si riarrangiava in una fase termodinamicamente più stabile, tipo spinello. Per un ossido preparato a 250 °C contenente il 25% di alluminio, è stata ottenuta una carica specifica di 90 Ah/kg mantenuta per 50 cicli.

Sono stati preparati, per mezzo di scambio ionico, ossidi con struttura stratiforme (LiMnO\textsubscript{2} e LiMn\textsubscript{0.9}Al\textsubscript{0.1}O\textsubscript{2}). È stato dimostrato che la rimozione e reinserimento degli ioni litio da LiMnO\textsubscript{2} procede in maniera irreversibile. Per quanto riguarda LiMn\textsubscript{0.9}Al\textsubscript{0.1}O\textsubscript{2} la reazione avviene in un singolo stadio. Questo risultato rappresenta un primo indizio sull’effetto stabilizzatore dell’alluminio.

Sono stati sintetizzati ossidi misti Mn/Ni contenenti alluminio, con la struttura stratiforme del tipo α-NaFeO\textsubscript{2}. Ed è stato così confermato l’effetto stabilizzante dell’alluminio sui cicli di carica e scarica. Un ossido con la composizione LiMn\textsubscript{0.5}Ni\textsubscript{0.3}Al\textsubscript{0.2}O\textsubscript{2} ha fornito una carica specifica di 115 Ah/kg per più di 200 cicli, con una perdita massima del 4 % ogni 100 cicli. Una tale prestazione non è mai stata raggiunta fino ad ora per un ossido misto manganese/nichel. Riducendo la quantità di alluminio (inattivo elettrochimicamente), ma preservando la struttura stratiforme, è stato possibile ottenere un ossido con la composizione LiMn\textsubscript{0.5}Ni\textsubscript{0.4}Al\textsubscript{0.1}O\textsubscript{2}. Questo materiale ha fornito una carica specifica di 140 Ah/kg per più di 60 cicli. Questi 140 Ah/kg sembrano poter essere sufficienti per fare di questo materiale un serio candidato per la sostituzione dell’ossido di litio e cobalto nelle batterie agli ioni litio. Sono state riguardevoli anche le prestazioni di questi due materiali alla temperatura di 55 °C, in quanto sono state ottenute per più di 50 cicli cariche specifiche di 120 Ah/kg per LiMn\textsubscript{0.5}Ni\textsubscript{0.3}Al\textsubscript{0.2}O\textsubscript{2} e di 155 Ah/kg per LiMn\textsubscript{0.5}Ni\textsubscript{0.4}Al\textsubscript{0.1}O\textsubscript{2}.

È stato investigato, usando la speciale cella in-situ, il ruolo svolto sulla intercalazione elettrochimica di ioni litio nella grafite durante la prima carica, da quattro diversi elettroliti (con differenti composizioni e con diversi sali). L’esperimento ha dato come risultato che, con ogni elettrolita, lo stesso composto litio-carbonio si è formato allo stesso potenziale. Questo suggerisce che la grandezza dell’anione del sale svolge un ruolo secondario nella reazione di intercalazione, come pure sembra essere secondario il ruolo svolto dalla differente composizione dell’elettrolita.
## Symbols and abbreviations

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Name</th>
<th>Unit</th>
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<tr>
<td>ΔG</td>
<td>Gibbs free energy</td>
<td>[J/mol]</td>
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<tr>
<td>E°</td>
<td>Standard potential</td>
<td>[V]</td>
</tr>
<tr>
<td>ΔE°, U°</td>
<td>Theoretical cell voltage</td>
<td>[V]</td>
</tr>
<tr>
<td>F</td>
<td>Faraday constant</td>
<td>[C/mol]</td>
</tr>
<tr>
<td>z</td>
<td>Number of electrons exchanged</td>
<td>[-]</td>
</tr>
<tr>
<td>A</td>
<td>Electrode area</td>
<td>[cm²]</td>
</tr>
<tr>
<td>I</td>
<td>Electric current</td>
<td>[A]</td>
</tr>
<tr>
<td>j</td>
<td>Current density</td>
<td>[A/cm²]</td>
</tr>
<tr>
<td>Q</td>
<td>Charge capacity</td>
<td>[Ah]</td>
</tr>
<tr>
<td>qth</td>
<td>Theoretical specific charge</td>
<td>[Ah/kg]</td>
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<tr>
<td>Qv,th</td>
<td>Theoretical charge density</td>
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<tr>
<td>Wv</td>
<td>Practical energy density</td>
<td>[Wh/l]</td>
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<tr>
<td>p</td>
<td>Specific power</td>
<td>[W/kg]</td>
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<tr>
<td>PV</td>
<td>Power density</td>
<td>[W/l]</td>
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<tr>
<td>νi</td>
<td>Stoichiometric coefficient</td>
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<tr>
<td>R</td>
<td>Gas constant</td>
<td>[J/(mol K)]</td>
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<td>a_i</td>
<td>Activity coefficient</td>
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<td>[kg]</td>
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<tr>
<td>V, V_i</td>
<td>Volume</td>
<td>[l]</td>
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<tr>
<td>χ_mol</td>
<td>Molar susceptibility</td>
<td>[cm³/mol]</td>
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<tr>
<td>H</td>
<td>Magnetic field</td>
<td>[G]</td>
</tr>
<tr>
<td>M_r</td>
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<td>[g/mol]</td>
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<tr>
<td>M</td>
<td>Magnetic moment</td>
<td>[emu]</td>
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<tr>
<td>C</td>
<td>Curie constant</td>
<td>[K]</td>
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<tr>
<td>k</td>
<td>Boltzmann constant</td>
<td>[J/K]</td>
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<tr>
<td>T</td>
<td>Temperature</td>
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<tr>
<td>N</td>
<td>Avogadro’s number</td>
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<tr>
<td>μ</td>
<td>Magnetic moment</td>
<td>[emu]</td>
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<tr>
<td>Θ</td>
<td>Weiss constant</td>
<td>[K]</td>
</tr>
<tr>
<td>κ₀</td>
<td>Specific electrical conductivity</td>
<td>[S/cm]</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
<td></td>
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<tr>
<td>--------------</td>
<td>--------------------------------------------------</td>
<td></td>
</tr>
<tr>
<td>SHE</td>
<td>Standard hydrogen electrode</td>
<td></td>
</tr>
<tr>
<td>SEI</td>
<td>Solid electrolyte interphase</td>
<td></td>
</tr>
<tr>
<td>DEMS</td>
<td>Differential electrochemical mass spectrometry</td>
<td></td>
</tr>
<tr>
<td>DTA</td>
<td>Differential thermal analysis</td>
<td></td>
</tr>
<tr>
<td>PTFE</td>
<td>Polytetrafluoroethylene</td>
<td></td>
</tr>
<tr>
<td>PVDF</td>
<td>Polyvinylidenfluoride</td>
<td></td>
</tr>
<tr>
<td>PC</td>
<td>Propylene carbonate</td>
<td></td>
</tr>
<tr>
<td>EC</td>
<td>Ethylene carbonate</td>
<td></td>
</tr>
<tr>
<td>DMC</td>
<td>Dimethyl carbonate</td>
<td></td>
</tr>
<tr>
<td>EMC</td>
<td>Ethyl methyl carbonate</td>
<td></td>
</tr>
<tr>
<td>DEC</td>
<td>Diethyl carbonate</td>
<td></td>
</tr>
<tr>
<td>GIC</td>
<td>Graphite intercalation compound</td>
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Chapter 1

Introduction

*The synthesis of novel solids is as much an art as a science.*


1.1 Motivation

The synthesis of new compounds is a cornerstone of solid state chemistry. Two major stimuli drive us to the synthesis of new solids. The first is our curiosity to prepare solids with new compositions, new or unusual structures as well as novel properties. The second is the great need for new materials with new levels of performance in the marketplace.

Amongst many critical steps in the “tailor-making” of solid state materials there are two central goals [1]: the first is to identify the ideal crystal structure and probable chemical composition that would give rise to the desired material property; the second is to develop and implement appropriate procedures for the synthesis and characterisation of the advanced material.

Inorganic materials with layered structures, or containing tunnels or channels, have quite a rich chemistry and topochemistry. Thus, they have been widely investigated, especially as concerns their possible use in many host-guest applications and not only.
for their chemical or physical characteristics [2]. When synthesising layered materials, two basic questions should be asked [3]: (1) To what extent can we design and synthesise a new material with a particular desired property? (2) What are the knowledge bases in chemistry and materials science that would guide the scientist in attempting to synthesise a new material with particular properties?

1.2 Aim of this work

As civilisation has become more sophisticated and reliant on readily available sources of energy, so battery research and development has been stimulated. One hitherto unsolved problem is the energy storage for traction purposes, e.g. high energy batteries for cars. Another is the demand of the global market for a small, lightweight, ultra-thin, longer operating time rechargeable battery for mobile computing and communication applications. This market is growing at a phenomenal rate as the trends of increased wireless usage and miniaturisation of electronics continue unabated.

This demand also originates from a series of crucial problems, ranging from the need to better utilise our energy resources to the obligation to respect our environment.

In consumer electronics there is a kind of paradox: whereas electronics circuitry has progressed dramatically, the batteries that power such devices are based on concepts dating from a century ago.

Until 1997 the nickel-cadmium was the dominant chemistry in all applications except mobile computers, called laptops. Nowadays, however, there is no doubt that the lithium-ion battery concept is projected to be the dominant chemical system for portable electronics applications. Currently, 90% of all laptops use lithium-ion batteries. A similar evolution is expected in the cellular phones market. Most of these lithium-ion batteries use the lithium carbon/lithium cobalt oxide chemistry. Although this system works well, there is still ongoing research to develop improved chemical systems. It is clear that in order to develop high-energy-density batteries we need high-specific charge electrode materials. Most of the efforts are concentrated on new cathode materials, since cobalt is expensive and somewhat toxic. Yet, before lithium-ion batteries can penetrate new markets, especially that of electric vehicles, a cheaper base material is needed. Due
to the large potential offered by solid state chemistry in building mixed materials, promising results and new discoveries are expected [4-7].

The present work focuses on the search for and the electrochemical characterisation of new electrode materials suitable for lithium-ion batteries.
Chapter 2

Basic concepts

Electrochemistry covers all phenomena in which a chemical change is the result of electric forces and, vice versa, where an electric force is generated by chemical processes.

2.1 Galvanic cells

A galvanic or voltaic cell consists of two dissimilar electrodes immersed in an electrolyte solution* [8-10]. The electrodes are electronic conductors and the electrolyte solution is a ionic conductor. At the interface between electronic and ionic conductors a passage of electrical charge is connected with a chemical reaction, a so-called redox reaction. These reactions are half-reactions and are, by convention, expressed as reductions. Each of these reactions has associated with it a standard electrode potential, $E^0$, which can be calculated from the thermodynamic data of the reaction. For equilibrium conditions we have:

$$E^0 = -\frac{\Delta G^o}{zF} \quad [V] \tag{2.1}$$

* exception: concentration cells
As it is impossible to measure individual electrode potentials in an absolute sense, they are each measured with reference to another electrode which is used as standard. The electrode normally used for this purpose is the standard hydrogen electrode (SHE) \((T = 25 \, ^{\circ}\text{C}, \, p = 1 \, \text{bar}, \, \text{all species at unity activity})\). For non-standard conditions we can use the Nernst equation to calculate the potential of the half-reactions at equilibrium:

\[
E = E^0 - \frac{RT}{zF} \sum \ln a_i^n \quad \text{[V]} 
\]

\(R: \text{gas constant} \quad T: \text{absolute temperature} \quad n_i: \text{stoichiometric coefficient} \quad a_i: \text{activity}\)

The cell voltage of an electrochemical cell is calculated from the electrode potentials (reduction potentials) of the half-reactions. The overall theoretical cell voltage, \(\Delta E^0\) or \(U^0\), is obtained by subtracting the negative electrode potential, \(E^{0,(-)}\), from the positive electrode potential, \(E^{0,(+)}\):

\[
U^0 = \Delta E^0 = E^{0,(+)} - E^{0,(-)} \quad \text{[V]} 
\]

Batteries, which are formed by two or more cells connected either in parallel or in series, can be divided into several groups:

- **Primary batteries**

Primary batteries are not designed to be recharged, since the electrochemical reactions are usually not reversible (e.g. zinc-carbon, zinc-manganese dioxide).

- **Secondary batteries**

Secondary batteries, or accumulators, are designed to be electrically recharged. The electrochemical reactions are reversible, and electric energy can be converted into chemical energy during the charging process (e.g. lead-acid, lithium-ion batteries). An important criterion to consider is the number of possible recharge cycles.
Mechanically rechargeable batteries

In this kind of batteries the charging process consists of renewing one of the electrodes of the cell once it is consumed during discharge (e.g. the zinc electrode in zinc-air cells).

The terms cathode and anode cannot be defined in an absolute way in a rechargeable cell. In fact the anode is defined as the electrode which gives the electrons to the external circuit, and the cathode as the electrode which gets the electrons from the external circuit. Thus, depending on whether the cell is charged or discharged the two terms are mixed, which leads to confusion. On the contrary, the positive and the negative electrodes remain the same, since they only depend on their respective electrode potential.

Values of potentials for various half-cell reactions are tabled [8], and these enable theoretical cell voltages to be calculated if the two half-cell reactions are known. Some important standard potential values in the battery technology are shown in Fig. 2.1. A high cell voltage is obtained by combining two electrode systems with potentials far from each other.

Figure 2.1: Some standard electrode potentials.
The Nernst equation (2.2) is valid at equilibrium conditions. If this situation is disturbed by the application of a load which causes current drain, the voltage between the electrodes will begin to fall from its equilibrium value. This process is termed polarisation or overvoltage. The overvoltage can simply be considered to be a measurable value for the losses appearing as a result of the current flow.

2.2 Characterisation of electrochemical cells

For several of the performance criteria of electrochemical power sources a distinction must be made between the theoretical values and the practical values. Theoretical values are calculated from the thermodynamics of the electrochemical cell reaction. Practical values are related to the total mass of the complete battery, including the mass of the electrolyte, the separators, the current collectors, the terminals and the cell housing [11]. In this work the specific charge always refers to the weight of the active component only.

- **Cell voltage**

The cell voltage can be calculated from the Gibbs free energy of the corresponding chemical reaction:

\[
U^0 = \Delta E^0 = \frac{-\Delta G^0}{zF} \quad [V]
\]  

(2.4)

- **Current density**

The current density \( j \) is calculated by dividing the total current \( I \) flowing through an electrode by the electrode area \( A \). The normal case is that the geometrical area is used:

\[
j = \frac{I}{A} \quad [\text{A/cm}^2]
\]

(2.5)

- **Charge capacity**

The charge capacity \( Q \) is the total amount of charge obtainable from a cell:
\( Q = \frac{1}{L} \int_{t_i}^{t_f} I(t) \, dt \quad [\text{Ah}] \quad (2.6) \)

- **Theoretical specific charge and theoretical charge density**

The theoretical specific charge \( q_{\text{th}} \) is the amount of charge per kg of reactants \( m_i \), and it can be calculated from the stoichiometry of the overall cell reaction:

\[
q_{\text{th}} = \frac{zF}{\sum_i m_i} \quad [\text{Ah/kg}] \quad (2.7)
\]

The charge divided by the volume of reactants \( V_i \) leads to the theoretical charge density \( Q_{V,\text{th}} \):

\[
Q_{V,\text{th}} = \frac{zF}{\sum_i V_i} \quad [\text{Ah/l}] \quad (2.8)
\]

- **Practical specific charge and practical charge density**

The practical specific charge \( q \), or the practical charge density \( Q_v \), is the total charge obtainable from a practical cell divided by the total mass or the volume of the cell, respectively:

\[
q = \frac{1}{L} \int_{t_i}^{t_f} \frac{I(t)}{m} \, dt \quad [\text{Ah/kg}] \quad (2.9)
\]

\[
Q_v = \frac{1}{V} \int_{t_i}^{t_f} \frac{I(t)}{V} \, dt \quad [\text{Ah/l}] \quad (2.10)
\]

Another quantity which is often used is the so-called *irreversible specific charge*. It is defined as the difference between the specific charge spent on charging and the one obtained on discharging a cell. To obtain a normalised value this difference is then divided by the specific charge spent on charging.
• **Theoretical specific energy and theoretical energy density**

The theoretical specific energy $w_{th}$, or the theoretical energy density $W_{V,th}$, can be calculated from the Gibbs energy change of the electrochemical cell reaction divided by the sum of the stoichiometric masses of the reactants or by their volumes, respectively:

$$w_{th} = \frac{zF\Delta E^0}{\sum_i m_i} \quad [\text{Wh/kg}] \quad (2.11)$$

$$W_{V,th} = \frac{zF\Delta E^0}{\sum_i V_i} \quad [\text{Wh/l}] \quad (2.12)$$

• **Practical specific energy and practical energy density**

The practical specific energy $w$, or the practical energy density $W_V$, is the total electrical energy obtainable from a practical cell divided by the mass or the volume of the cell, respectively:

$$w = \frac{\int_{\tau_1}^{\tau_2} I \Delta E \, dt}{m} \quad [\text{Wh/kg}] \quad (2.13)$$

$$W_V = \frac{\int_{\tau_1}^{\tau_2} I \Delta E \, dt}{V} \quad [\text{Wh/l}] \quad (2.14)$$

• **Specific power and power density**

The specific power $p$ is the capability to deliver power per mass. The specific power of a cell depends on the discharge current and decreases during discharge. The power density $P_V$ is the power divided by the volume of the cell. Again, one distinguishes between theoretical and practical values:

$$p = \frac{I \Delta E}{\sum_i m_i} \quad [\text{W/kg}] \quad (2.15)$$

$$P_V = \frac{I \Delta E}{\sum_i V_i} \quad [\text{W/l}] \quad (2.16)$$
In the battery technology the term *charge* resp. *discharge rate* (C/Δt) is often used. C means a nominal or, sometimes, a theoretical charge capacity of a cell or battery in [Ah]. Therefore, C/2, for example, means a current theoretically allowing a full discharge in two hours.
Lithium metal-free rechargeable batteries

3.1 Introduction

The goal of the rechargeable lithium battery research program at the Paul Scherrer Institute (PSI) and at the Swiss Federal Institute of Technology (ETHZ) is to develop a battery with high energy density, high power density, and both good cycle life and charge retention. This high performance must be delivered in a safe and reliable way. In this context the choice of the cell components is mostly a compromise in order to achieve the best result.

At the beginning the search for high energy density batteries led to the use of metallic lithium for the negative electrode [12] because of its unique characteristics ($E^0 = -3.04$ V vs. SHE, $q_{th} = 3860$ Ah/kg). The first commercial versions of a rechargeable lithium battery were produced in the eighties by Exxon and, later on, by Moli Energy [13]. Unfortunately, some fires and even explosions of the batteries were experienced. Thus, it was recognised that rechargeable lithium cells which use lithium metal as the negative electrode exhibit problems which hinder their wide utilisation (the production of the Moli battery was discontinued two years after start). One problem is the thermodynamic instability of lithium in non-aqueous electrolytes due to its strong reducing power. As a matter of fact, after immersion into the electrolyte, the lithium surface is immediately covered by a film of electrolyte decomposition products, called *solid electrolyte interphase* (SEI). Although this film, which is obviously permeable only to lithium ions, prevents lithium from further corrosion, a three- to fivefold excess of lithium is needed in order to reach a reasonable cycle life. This is because during each recharge a fresh lithium surface is formed. The new surface of the lithium reacts...
immediately to SEI. Therefore, in each cycle the practical reversibility of the lithium cycling is typically ≤ 99 % because of lithium consumption in the SEI-forming reactions. Even worse, the lithium is typically deposited on the metallic surface in dendritic forms [14]. These dendrites may form some filaments leading to local short-circuit and, taking into account the low melting point of lithium (ca. 180 °C), to a lower thermal stability of the system [15,16].

In order to avoid these problems, a new system was proposed and commercialised by Sony in 1991 which suggested the use of an intercalation compound (a carbon material) in the negative electrode. Such a replacement resulted both in a significantly enhanced reliability and safety of batteries. This new generation of rechargeable lithium cells is called in different ways: rocking-chair, shuttlecock, or Li-ion.

### 3.2 Materials for the rechargeable lithium battery

#### 3.2.1 Electrolyte

First of all, it should be pointed out that in this work, the term electrolyte refers to the solution of both the solvent and the salt, contrary to the nomenclature in physical chemistry, which defines the electrolyte as the salt alone.

The choice of the electrolyte for the lithium-ion battery can be critical. For example, the utilisation of high potential (more than 4 V vs. Li/Li+) cathode materials requires a high stability of the electrolyte in a wide potential range. Some characteristics that have to be fulfilled are listed below [15,17]:

(a) a good ionic conductivity (> 1 mS/cm) so as to minimise the internal resistance (to achieve this, the viscosity should be small);

(b) a wide electrochemical voltage window, ideally from 0 to 5 V vs. Li/Li⁺;

(c) a good thermal (up to 90 °C) and chemical stability;

(d) compatibility with other components of the cell;

(e) low cost, reliable safety, and a small environmental impact.
The two classes of electrolytes used in lithium-ion batteries are given below:

- **Liquid organic and inorganic electrolytes**

  Liquid organic electrolytes consist of pure or mixtures of aprotic organic solvents with a lithium salt dissolved in it. In particular, organic carbonates such as propylene carbonate (PC), ethylene carbonate (EC), dimethyl carbonate (DMC), and diethyl carbonate (DEC) have been in centre of interest [17].

  Liquid inorganic electrolytes are mainly SO₂-based. Their attraction originates from their high ionic conductivity [18]. However, they are hazardous and may generate some safety problems.

- **Polymer electrolytes**

  The polymer electrolyte, where the lithium ions are incorporated into a polymer matrix, is a valid alternative to the liquid electrolyte. The advantage is that the polymer is solid but flexible, so that the design and the assembling of the battery are kept simplified. On the other hand, polymer electrolytes have lower ionic conductivity compared to the liquid electrolytes. A typical example of the polymer is polyethylene oxide (PEO) [19].

  The lithium salt also has to fulfil some criteria, such as low price, high performance, and reliable safety. As far as the performance is concerned, important factors are conductivity, thermal as well as electrochemical stability, and cycling efficiency. The lithium salts most frequently used are: LiClO₄, LiPF₆, and LiN(SO₂CF₃)₂. Each of these salts has its own advantages and disadvantages [17].

3.2.2 **Negative electrode**

At present carbon materials are the most often used negative electrodes employed in Li-ion batteries, even if other materials have also been investigated in the past. In Tab. 3-1 some possible materials for the negative electrode are listed [15].
Table 3-1: Negative electrode materials.

<table>
<thead>
<tr>
<th>Material</th>
<th>Potential range vs. lithium [V]</th>
<th>Theoretical specific capacity [Ah/kg]</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiAl</td>
<td>ca. 0.3</td>
<td>790</td>
</tr>
<tr>
<td>LiC₆</td>
<td>0.0-0.5</td>
<td>372</td>
</tr>
<tr>
<td>LiWO₂</td>
<td>0.3-1.4</td>
<td>120</td>
</tr>
<tr>
<td>LiMoO₂</td>
<td>0.8-1.4</td>
<td>199</td>
</tr>
<tr>
<td>LiTiS₂</td>
<td>1.5-2.7</td>
<td>226</td>
</tr>
</tbody>
</table>

• Non carbon-based materials

One of the most investigated classes of non carbon-based materials are alloys. An advantage of using alloys as negative electrode is that the reactivity of lithium towards the electrolyte can be decreased, leading to a reduction of the dendrite formation. The main problems of lithium alloy electrodes arise from the huge difference in volume between the pure basic material and the lithium alloy. As a result, mechanical stress and cracks are induced during cycling. In the case of LiAl a volume change of about 97% was observed [20]. Other suitable alloying substrates are Sn, Pb, Bi, Sb, and As [16].

Other possible candidates for the negative electrode are transition metal compounds with a layered structure. The lithium ions can intercalate and deintercalate such structures during charge and discharge. An important feature to be fulfilled is that their electrochemical potential should be comparable with that of lithium metal or of lithiated carbon in order to achieve a high cell voltage.

• Carbon-based materials

Several reasons have made carbons to be the most attractive and investigated negative electrodes for the Li-ion cell. First of all, carbon is a low cost material. Another advantage for the battery industry is that the redox potential of lithiated carbon materials is almost identical to that of metallic lithium. Moreover, a good cycling stability is expected due to the high mechanical electrode stability (compared to alloys). In addition, the specific charge is higher compared to transition metal oxides or sulphides (see Tab. 3-1). The insertion of lithium into carbon, often called intercalation, can be written as follows:
期间，锂离子插层到碳中并在随后的放电过程中释放。许多类型的碳质材料已被提出。在这些材料中，我们可以区分石墨碳和非石墨碳。在石墨碳中，可以达到最大锂含量对应于 $x < 1 \text{Li}_x\text{C}_6$，理论比容量值为 372 Ah/kg。在插层过程中， graphite 层的堆叠顺序发生改变，从 ABA 转变为 AAA。根据方程式 (3.1)，锂插层是可逆的。在实践中，消耗的电量超过理论值，对应于 $\text{LiC}_6$，在第一次充电过程中。这部分额外的电量不能在随后的放电过程中恢复。这种不可逆的比容量，取决于所使用的电解质，在 Li-ion 电池中，只有一个锂源，因此必须保持在低值。所使用的电解质类型强烈影响 SEI 膜的形成。例如，丙烯碳酸（PC）在约 800 mV（相对于 Li/Li⁺）处被还原。在稍微更正的电位下，PC 溶剂化的锂离子被插层到 graphite（但不进入焦炭）中，导致 graphene 层的显著膨胀，进而导致 graphite 母体的破坏。结果，SEI 膜不能作为可靠的屏障。另一方面，乙烯碳酸 (EC) 比 PC 更快被还原。因此，SEI 膜迅速形成并阻止进一步溶剂化的锂插层。由于乙烯碳酸的粘度相当高，通常会与例如 dimethyl carbonate 或 diethyl carbonate 混合。几种添加剂如 CO₂ [21]，SO₂ [22]，和 polysulphides [23] 被建议用于改善 SEI 膜的质量。

非石墨碳中存在所谓的高比容量碳。此类碳 [24-27] 可以显示比容量约 400 至 2000 Ah/kg，并且主要是通过热解某些聚合物或甚至普通糖获得的。这些
disordered structures contain isolated graphene layers on either side of which intercalated lithium may undergo adsorption. Such a mechanism can double the specific charge. The main problems of these high specific charge carbons are the very high irreversible specific charge and the poor cycling stability, hinting at the formation of stable LiCₓ compounds.

Nitrogen- or boron-doped carbons [28,29] were also used as negative electrode. However, the specific charge of these materials rapidly diminished upon cycling.

### 3.2.3 Positive electrode

There is a wide choice of materials that can be used for the positive electrode. The best ones are those where no or little structural modification occurs during cycling. The insertion or intercalation compounds are therefore the best candidates. In such materials the removal and the subsequent insertion of the lithium ions in the host lattice proceeds topotactically. The reaction at the positive electrode can be described as follows:

\[
yLi^+ + ye^- + Li_x(HOST) \leftrightarrow Li_{x+y}(HOST)
\]  

(3.2)

where (HOST) is an insertion cathode. There are a lot of factors which have to be considered when choosing an insertion compound. A list is given in Tab. 3-2.

| High free energy of reaction with lithium |
| Wide range of x (amount of insertion)    |
| Little structural change on reaction   |
| Highly reversible reaction             |
| Rapid diffusion of lithium in solid   |
| Good electronic conductivity           |
| Non-solubility in electrolyte          |
| Availability or facility of synthesis  |

Table 3-2: Key requirements for the positive electrode used in rechargeable lithium cells.
Transition metal oxides, sulphides, and selenides are possible candidates. In Tab. 3-3 some electrode materials used in rechargeable lithium cells are presented with their characteristics.

<table>
<thead>
<tr>
<th>Material</th>
<th>Average potential vs. lithium [V]</th>
<th>Reversible range, Δx</th>
<th>Specific charge [Ah/kg] (charge density [Ah/l])</th>
<th>Specific power [Wh/kg] (power density [Wh/l])</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li_xTiS_2</td>
<td>2.1</td>
<td>1.0</td>
<td>239 (782)</td>
<td>502 (1642)</td>
</tr>
<tr>
<td>Li_xMoS_2</td>
<td>1.7</td>
<td>0.8</td>
<td>134 (678)</td>
<td>228 (1152)</td>
</tr>
<tr>
<td>Li_xV_2O_5</td>
<td>2.8</td>
<td>1.0</td>
<td>147 (495)</td>
<td>412 (1386)</td>
</tr>
<tr>
<td>Li_xV_6O_13</td>
<td>2.3</td>
<td>3.6</td>
<td>188 (734)</td>
<td>432 (1688)</td>
</tr>
<tr>
<td>Li_xMnO_2</td>
<td>3.0</td>
<td>0.5</td>
<td>154 (775)</td>
<td>462 (2325)</td>
</tr>
<tr>
<td>Li_xNbSe_3</td>
<td>1.9</td>
<td>3.0</td>
<td>244 (2121)</td>
<td>464 (4030)</td>
</tr>
<tr>
<td>Li_xCoO_2</td>
<td>3.7</td>
<td>0.5</td>
<td>137 (706)</td>
<td>507 (2612)</td>
</tr>
<tr>
<td>Li_xNiO_2</td>
<td>3.5</td>
<td>0.7</td>
<td>192 (919)</td>
<td>672 (3216)</td>
</tr>
<tr>
<td>Li_xMn_2O_4</td>
<td>3.8</td>
<td>1.0</td>
<td>148 (634)</td>
<td>562 (2409)</td>
</tr>
</tbody>
</table>

3.3 Classification of insertion compounds

The insertion compounds can be classified according to Fig. 3.1.
• **One-dimensional hosts**

These hosts consist of chains or rods which are only weakly interacting. An example of this rare series of compounds is NbSe$_3$.

• **Two-dimensional systems: layered hosts**

Many layered compounds are made of close-packed anions (X) with transition metals (M) in octahedral or trigonal prismatic sites. In these systems the guest ions can intercalate between the X-M-X sandwiches. The two most important compounds of this family for the Li-ion battery are LiNiO$_2$ [31-33] and LiCoO$_2$ [34,35], as well as graphite for the negative electrode.

• **Three-dimensional systems**

In these systems the guest ions are inserted into a three-dimensional network consisting of cross-linked channels. Examples of compounds of this class are zeolites or spinels (e.g. LiMn$_2$O$_4$) with a cubic framework. In the latter, the sites available both for the transition metal and guests are either octahedrally or tetrahedrally co-ordinated by oxygen. A more detailed description of electroactive materials is given in chapter 6.

### 3.4 Principle of the Li-ion cell

The Li-ion cell (Fig. 3.2) is typically composed of two insertion compounds. The lithium ions move back and forth between the positive and negative electrode. The electrochemical process is the uptake of lithium ions at the negative electrode during charge and their release during discharge. Thus, the net current-forming reaction is reduced to a continuous pumping of lithium ions between two host materials. A strength of this system is, that contrary to the lead acid, no electrolyte is consumed, so that a very little amount of electrolyte is needed. In this way, a more compact cell construction is possible.

The procedure for fabricating a lithium ion cell consists of using a lithium-rich compound as the positive electrode. The cell is thus assembled by coupling this lithium-source electrode with a lithium-sink as negative electrode. The cell is activated by
charging, by which the Li\textsuperscript{+} ions are assembled in the sink. Positive electrodes which do not contain lithium after their synthesis have to be chemical lithiated before using.

![Diagram of the electrochemical process of a Li-ion cell.](image)

**Figure 3.2:** Scheme of the electrochemical process of a Li-ion cell.

### 3.5 Advantages of the Li-ion battery

If one wants to use conventional batteries as power source for consumer electronics or electric vehicles, the principal problem is their comparatively low specific energy. This low specific energy is usually due to their low voltage. Figure 3.3 illustrates the relationship between specific energy and energy density of common batteries. It can be seen that lead-acid and nickel-cadmium batteries can deliver only 30-70 Wh/kg and 50-150 Wh/l. A major increase could be achieved through the development of advanced systems (e.g. rechargeable lithium batteries). Compared to other systems lithium batteries offer several advantages, such as higher voltages, higher energy density, and longer shelf life. It can be clearly seen that, for the same energy content, lithium batteries are lighter in weight and smaller in size than other systems. Moreover, the use of non-aqueous electrolytes in lithium batteries permits the operation over a wide range of temperatures.
Figure 3.3: Comparison of the specific energy and energy densities of rechargeable lithium batteries with those of other systems (redrawn from [36]).

Mostly thanks to the high operating voltage, the energy density of the Li-ion cell is two to three times higher than the Ni/MH or the lead-acid system, respectively, making this system very competitive. For large batteries, for example electric vehicles, this higher voltage is also an advantage as it reduces the number of cells required to achieve the necessary voltage. This would make the battery management system less complex [5,37,38]. Moreover, as can be seen from Fig. 3.4, the specific power of the lithium-ion cell is high.

Figure 3.4: Ragone plot [39].
Experimental part

4.1 Synthesis

4.1.1 Air- and moisture-sensitive compounds

The manipulation of air- and moisture sensitive compounds was performed in dry boxes (MBrann) under an argon atmosphere. The atmosphere was controlled regularly showing that O\textsubscript{2}, H\textsubscript{2}O, and N\textsubscript{2} impurities were below 2 ppm.

The synthesis of air- and moisture-sensitive compounds was performed in welded niobium or tantalum tubes (external diameter: 12 mm; wall width: 0.5 mm) which were between 30 and 50 mm long. The tubes were pressed together at one end using a vice and sealed by arc melting under argon (ca. 400 mbar). They were then filled with the components in the dry box. The open side was closed using a pair of pliers and then sealed under argon. The tubes were subsequently heated in an evacuated quartz tube and at the end of the reaction always opened in the dry box to prevent reactions of the products with air and moisture.

4.1.2 Oxides

The oxides were synthesised using different routes, namely solid state, wet chemistry, and chimie douce.

For solid state syntheses the starting compounds were mixed together in an agate mortar and then transferred to a crucible. When synthesising the oxides only corundum
(α-Al₂O₃) crucibles were used. The reactions were performed in a tube furnace (Heraeus) under different atmospheres. The crucible was put in the middle of a quartz tube and then the latter was put in the oven. At one end of the tube the desired gas could be introduced. The flux was controlled by a bubble counter. For reactions under inert atmosphere, nitrogen (5N) or argon (4.8N) were used. Before use, the gases were let pass through a column filled with phosphorus pentoxide to remove traces of water. Oxygen (4.6N) was used directly from the bomb.

For the oxides synthesised via a wet chemistry or via a chimie douce route, glass equipment was used and the manipulations were made under argon.

The majority of the syntheses were performed according to the temperature program shown in Fig. 4.1. The normal heating and cooling rate \( r_{1,2} \) was 100 °C/h, whereas the reaction time \( t_i \) and the reaction temperature \( T_i \) were different for each synthesis and will be discussed in the experimental part of each chapter.

\[
\begin{align*}
&T_{\text{start}} = 25 ^\circ \text{C} \\
&T_{1} \\
&t_i \\
&T_{1} \\
&T_{\text{end}} = 25 ^\circ \text{C}
\end{align*}
\]

Figure 4.1: Typical temperature program for the syntheses.

The starting materials used in the syntheses are summarised in Tab. 4-1.

<table>
<thead>
<tr>
<th>Starting Materials</th>
<th>Purity</th>
<th>( M_r ) [g/mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiOH·H₂O</td>
<td>Fluka</td>
<td>≥ 99%</td>
</tr>
<tr>
<td>Ni(NO₃)₂·6H₂O</td>
<td>Fluka</td>
<td>≥ 99%</td>
</tr>
<tr>
<td>Mn(NO₃)₂·4H₂O</td>
<td>Fluka</td>
<td>≥ 97%</td>
</tr>
<tr>
<td>Al(NO₃)₃·9H₂O</td>
<td>Fluka</td>
<td>≥ 99%</td>
</tr>
<tr>
<td>Br₂</td>
<td>Fluka</td>
<td>≥ 99.5%</td>
</tr>
</tbody>
</table>
4.2 Characterisation

4.2.1 Powder diffraction

The powder diagrams were collected on a STOE powder diffractometer (STADI P, CuKα1 = 1.54056 Å) applying Debye-Scherrer geometry. The samples were ground in an agate mortar, then transferred to a glass capillary (Mark-Röhrchen; length = 80 mm; diameter = 0.3 mm). For air sensitive compounds the capillaries were sealed in a dry box by melting the ends by means of a red-hot platinum wire. Calculations of theoretical powder diagrams, as well as data processing of the experimental powder diagrams, were performed with a STOE program package.

A Scintag Θ-Θ PAD-X powder diffractometer with Bragg-Brentano geometry and equipped with a solid state detector was used for samples containing manganese. The solid state detector allowed us to filter the strong fluorescence caused by manganese. The sample was mounted in a rotating flat plate holder and no monochromator was
used. CuKα radiation (45 mA, 45 kV) was selected using the solid-state detector. A silicon sample (NBS Standard Reference Material 640a) was used as an external standard.

4.2.2 Magnetic measurements

The magnetic measurements were performed on a SQUID magnetometer (MPMS 5S, Quantum Design) between 2 and 300 K in a constant magnetic field. The samples were finely ground and transferred into a small glass tube, which was mounted in the magnetometer in a small quartz tube. The diamagnetic contribution of the sample container was always subtracted.

The molar susceptibility $\chi_{mol}$ is calculated as follows [40,41]:

$$\chi_{mol} = \frac{M \cdot M_r}{H \cdot m} \text{ [cm}^3\text{/mol]}$$

(M: magnetic moment \quad m: weight of the sample \quad H: magnetic field \quad M_r: molar weight of the sample)

generally, the susceptibility is the sum of different contributions:

$$\chi_{mol} = \chi_{\text{para}}(T) + \chi_{\text{TUP}} + \chi_{\text{dia}}$$

where $\chi_{\text{TUP}}$ is a T-independent paramagnetic contribution, and $\chi_{\text{dia}}$ a T-independent diamagnetic contribution.

The total susceptibility is positive for paramagnetic substances and negative for diamagnetic substances. The susceptibilities of the different kinds of magnetic materials are distinguished by their different temperature dependence. Many paramagnetic substances obey the simple Curie law, especially at high temperatures. According to this law the magnetic susceptibility is inversely proportional to the temperature:

$$\chi_{\text{para}}(T) = \frac{C}{T}$$

(C: Curie constant)
The magnetic properties of materials are often conveniently expressed in terms of the magnetic moment, $\mu$, since this is a parameter that may be directly related to the number of unpaired electrons present. The relationship between $\chi$ and $\mu$ is:

$$\chi_{\text{mol}}^\text{para} (T) = \frac{N\mu^2}{3kT} \quad (4.4)$$

$N$: Avogadro's number $k$: Boltzmann constant

By comparing the last two equations we obtain:

$$C = \frac{N\mu^2}{3k} \quad (4.5)$$

and at any given temperature:

$$\mu = \sqrt{3k / N} \cdot \sqrt{\chi_{\text{mol}}^\text{para} (T) \cdot T} = 2.83 \sqrt{\chi_{\text{mol}}^\text{para} (T) \cdot T} \quad (4.6)$$

Often, however, a better fit to the experimental data is provided by the Curie-Weiss law:

$$\chi_{\text{mol}}^\text{para} (T) = \frac{C}{T - \Theta} \quad (4.7)$$

$\Theta$: Weiss constant

The Weiss constant is characteristic for each particular substance under consideration. By plotting the inverse of the molar susceptibility against the temperature, the constant $C$ can be calculated from the slope of the linear function. This constant and the intercept with the y-axis are then used to calculate the Weiss constant $\Theta$. The magnetic moment is then calculated as follows:

$$\mu = 2.84 \sqrt{\chi_{\text{mol}}^\text{para} (T) \cdot (T - \Theta)} \quad (4.8)$$

A positive $\Theta$ indicates a net ferromagnetic coupling, and a negative one an antiferromagnetic interaction characteristic.
4.2.3 Chemical analysis

The chemical analysis for the determination of trace metals was performed with ICP-AES (Induced Coupled Plasma-Atomic Emission Spectroscopy). The sample was dissolved in concentrated hydrochloric acid or in concentrated hydrochloric acid/nitric acid.

4.2.4 Electrical conductivity

The electrical conductivities were measured using tempered powder pellets (diameter: 6 mm, thickness ca. 1 mm). A four-point contact method [42] (with rhodium/iridium electrodes) was used: a constant current $I$ was applied across two electrodes, while the potential across the two other electrodes was measured. The electrical resistance $R$ can be calculated according to the Ohm’s law $R = U/I$. According to this method the specific resistance $\rho$ of the sample is only a function of the resistance $R$ and the thickness $d$ of the pellet. The specific electronic conductivity is the reciprocal value of the specific resistance. The measurements were performed in a dry box. The samples were cooled to 11 K under vacuum using a helium cryostat, and heated to about 700 K under argon. For semiconductors the band gap can be calculated from the temperature dependence of the electrical resistance:

$$R = \frac{L}{A \cdot \kappa_0} \cdot e^{-\frac{AE}{kT}}$$  \hspace{1cm} (4.9)

$L$: length of the conductor [m]  \hspace{1cm} $A$: section of the conductor [m$^2$]

$\kappa_0$: specific electrical conductivity [S/m]  \hspace{1cm} $AE$: band gap [eV]

The band gap $\Delta E$ can be derived from a plot of $\ln(R)$ or $\ln(1/R)$ vs. $1/T$, if a linear dependence is found. The values obtained must however be interpreted very carefully because of potential problems arising from the contacts, grain boundary effects, or electrochemical corrosion processes.
5.1 Instrumentation

If an electrochemical system is subjected to a passage of current between the two electrodes, it is out of equilibrium. Usually we are interested in investigating the electrode process on one electrode, the working electrode. Such investigations are done by controlling the cell potential (potentiostatic control) or the current that passes (galvanostatic control). The other electrode, the counter electrode, is used to complete the external circuit. In this study, potentiostatic and galvanostatic measurements were performed using an AMEL potentiostat/galvanostat which was modified in our laboratory [43]. The generation of the potential or current function as well as the data collection were computer controlled using the program WORKBENCH (Strawberry Tree, Inc.) [44]. From the middle of 1999 onwards a new, user-friendlier instrumentation (Astrol) was available.

5.2 The cell

For the electrochemical investigations a cell has to be assembled. During this work two types of electrochemical cells were used, both of which simulated the behaviour of a button cell. The schematic picture of the first cell, which was used at the beginning of this work, can be found in [45]. From the beginning of 1999, a new cell was developed and used [46]. This new cell (Fig. 5.1) was mainly made of titanium. The counter electrode was brought onto a titanium-made cylinder (8) and pressed with a spring (5)
against the working electrode coated onto a titanium current collector (10). A separator soaked with the electrolyte was put between the two electrodes. The cell assembling was set up in the dry box under an argon atmosphere.

5.3 Electrode preparation

5.3.1 The working electrode

Since the electronic conductivity of the oxide is not high enough, a component that enhances the conductivity of the complete electrode has to be added. Carbons are employed as additives for this purpose. To keep the active material and the conductivity enhancer together, a binder was used. The carbons and the binders used are listed in Tab. 5-1. The carbon black XC72 was thermally treated under nitrogen at 2700 °C for
2 hours in order to enhance its electronic conductivity. In order to obtain a good mixing, the three components were suspended in an organic solvent.

<table>
<thead>
<tr>
<th>Material</th>
<th>Delivered by</th>
<th>Solvent for suspension (Fluka)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphite SFG6</td>
<td>TIMCAL</td>
<td></td>
</tr>
<tr>
<td>Ensaco 250E</td>
<td>M.M.M.</td>
<td></td>
</tr>
<tr>
<td>Carbon Black XC72</td>
<td>Cabot Corporation</td>
<td></td>
</tr>
<tr>
<td>Oppanol (polyisobutene)</td>
<td>BASF</td>
<td>Hexane or Petroleumther</td>
</tr>
<tr>
<td>Teflon (PTFE)</td>
<td>Du Pont</td>
<td>Hexane</td>
</tr>
<tr>
<td>PVDF</td>
<td>Aldrich</td>
<td>NMP (N-methylpyrrolidone) or Acetone</td>
</tr>
</tbody>
</table>

Since the method for the preparation of the electrode and its composition (active material, carbon and binder) is an ongoing process aiming at finding an optimum, the synthesised active materials were not all treated in the same way. As a matter of fact, while this work was in process, several methods for the electrode preparation were developed [45] and will now be presented.

- **Ball milling**

At the beginning of this work a ball mill was used to prepare the electrode mass. The active material, carbon black and oppanol (or PTFE) were put into a vessel made of zirconium oxide and suspended in hexane (active material: XC72 = 1:1 (w/w), with 2 wt % binder). After two hours of milling the suspension was put in a vacuum oven at 80 °C overnight, allowing the solvent to evaporate. After discovering that after two hours the suspension was contaminated with ZrO₂ and that the specific surface area of some oxides was increased by a factor of four, the mixing time was reduced to 5 minutes [45]. This method was employed for a short period only because in the meantime a better technique had been developed.
• **High-speed mixer**

When using this process, some graphite SFG6 was added to the carbon black in order to improve the electronic conductivity. The suspension was prepared as follows. The active material, the carbons and the binder (oppanol or PVDF) were suspended in acetone or petroleumether and mixed for a few minutes using a high-speed mixer (active material:XC72:SFG6 = 12:3:1 wt %, with 2 wt % binder). Oppanol was used as "solution" (5 wt % in Ligroin:Petroleum special 3:1 (v/v), FLUKA). The suspension was then put in the oven at 80 °C overnight allowing the solvents to evaporate.

Once obtained, the electrode mass (active material, carbon, and binder) had to be put on the current collector, for which three methods were used:

• **Pill**

After the suspension was obtained, the solvent was allowed to evaporate. The resulting mixture was then ground in a mill. By using a pill-maker, 10 to 40 mg of active material were brought onto the current collector. The pressure was generated with a finger and was estimated to about 100 N/cm². Using this method, the best mechanical stability was obtained with oppanol as binder.

• **Spraying**

In this case a slurry of the three components dissolved in NMP was sprayed with an air brush onto the current collector. After reaching the desired amount of active mass, the current collector was put in an oven, allowing NMP to evaporate until the mass remained constant.

• **Doctor blade**

With the doctor blade method large-scale electrodes can be produced. The electrode is formed by casting the slurry on a substrate using a moving adjustable blade gap.

The spraying and the doctor blade processes need a large amount of material (> 5 g) in order to yield reproducible electrodes. Since the quantities of material that were synthesised in the laboratory in the corundum crucible were in the order of 1-2 grams, the pill method was used, with the awareness that this method did not represent the
optimal one. However, measurements were done to compare electrodes made with the pill and with the spraying method and no significant difference in the electrochemical behaviour was observed.

Whatever method was used, the prepared electrodes were dried in a vacuum oven at 120 °C for at least 16 hours in order to remove water traces from the surface of the electrodes. The applied current collector is displayed schematically in Fig. 5.2.

![Schematic picture of the current collector filled with active mass.](image)

Figure 5.2: Schematic picture of the current collector filled with active mass. Geometric surface area: 1.3 cm².

5.3.2 The counter electrode

If not otherwise specified, all measurements were performed using metallic lithium (ribbon 0.75 mm thick, Aldrich) as the counter electrode. Because the potential of metallic lithium is nearly constant at moderate or low current densities, the counter electrode was also used as the reference electrode.

5.3.3 The electrolyte

The electrolyte was used as received. In this work, all measurements were performed with a mixture of ethylene carbonate and dimethyl carbonate 1:1 (w/w), with 1 M LiPF₆ (MERCK Selectipur, LP30) unless the dependence of the electrolyte was the aim of the measurement. The water content of the electrolyte was measured using the Karl Fischer method with a 684 KF Coulometer (Metrohm). It never exceeded 10 ppm.

5.4 Cyclic voltammetry

Cyclic voltammetry is a widely used method for studying electrode processes. It is often employed as the first method to characterise new systems. The cell is cycled in a
potential window, where the potential applied on the working electrode is continuously changed with a constant rate (Eq. 5.1):

\[ \Delta E(t) = \Delta E_i \pm vt \]  

(5.1)

\[ \nu = \frac{\Delta E}{\Delta t} \quad [\text{mV/s}] \]  

(5.2)

\( \Delta E_i: \) potential at the beginning \( \nu: \) sweep rate 

\( t: \) time

Other important parameters are the maximum and the minimum potential, which define the potential window. The choice of this potential window must take the stability of the electrolyte into account, so as to avoid its decomposition.

The current that flows is measured and plotted versus the potential (Fig. 5.3). In this plot we observe an increase in the current response at the potential where an electrochemical reaction takes place. For a positive electrode the part of the curve under the zero line is the discharge (or cathodic) curve, the one above the charge (or anodic) curve. The surface under the curve is proportional to the total amount of charge flown. Following the convention of Stockholm [47] a positive sweep rate causes the oxidation of the working electrode, and the resulting current has a positive sign. With a negative sweep rate we have the reduction of the working electrode and a negative current.

Figure 5.3: Example of cyclic voltammetry (oxide: LI\text{Mn}_{0.8}\text{Ni}_{0.3}\text{Al}_{0.2}\text{O}_2) measured with a sweep rate of 50 \mu\text{V/s}. The electrolyte used was 1 M LiPF_6 in EC:DMC 1:1 (w/w).
5.5 Galvanostatic measurements

In a galvanostatic measurement a constant current is applied between the working and the counter electrode. This current is applied until the upper or the lower potential limit is reached. Also in this case a positive current causes the oxidation of the working electrode whereas a negative current causes its reduction. The study of the variation of the potential in time (Fig. 5.4) is also called chronopotentiometry. This method has an important advantage compared to the cyclic voltammetry. As a matter of fact, since the current density is constant, the electrode process is investigated under real working conditions, just like in a battery. However, for new systems the potential range in which the new material is active is not known in advance. For this reason, usually, when investigating unknown systems, a cyclic voltammetry is performed first so as to determine the potential range, which is then used for galvanostatic measurements.

Figure 5.4: Example of a galvanostatic measurement (oxide: LiMn_{0.5}Ni_{0.3}Al_{0.2}O_2) measured with a specific current of 10 \( \mu \text{A/mg active material} \). The electrolyte used was 1 M LiPF_6 in EC:DMC 1:1 (w/w).

For an insertion/de-insertion process

\[ A_iM + \Delta xA^+ + \Delta xe^- \leftrightarrow A_{x/\Delta x}M \]  

(5.3)
the amount of guest can be calculated as follows:

$$\Delta x = \frac{I \Delta t M_r}{zFm}$$  \hspace{1cm} (5.4)

$I$: current  \hspace{2cm} $\Delta t$: time interval

$M_r$: molecular weight  \hspace{2cm} $m$: mass of the active component

The curve obtained by plotting the first derivative of the charge over the potential versus the potential ($dC/dE$ vs. $E$) is called differential specific charge plot. The curve obtained in this way is usually more structured than a common cyclic voltammogram.

### 5.6 Coulometric titration

The coulometric titration is a variation of the galvanostatic experiment. The coulometric titration, which can also be seen as an in-situ investigation, allows us the determination of phase equilibria. We are interested in the dependence of the equilibrium cell voltage with respect to the composition of the working electrode ($A_xM$). A charge transport $\int \text{Idt}$ through the galvanic cell changes the electrode composition according to the Faraday’s law. This time integral of the current is a very precise measure of the variation of the concentration of the electroactive component. This variation in the stoichiometric number $x$ of the electroactive component in the electrode is given in equation (5.4). After a required amount of charge has been passed through the galvanic cell, the current is interrupted and the equilibrium cell voltage is measured. The equilibration process can be followed by recording the time dependence of the cell voltage until it becomes constant. Then, further charge is injected and the equilibrium cell voltage is recorded. In this way the dependence of the equilibrium cell voltage (or the electrode potential) is measured as a function of the working electrode composition. The observation of this equilibrium cell voltage during titration allows getting information on the thermodynamics of the system.
5.7 In-situ methods

A lot of solely electrochemical experiments can be performed in order to understand electrode processes, but they can rarely deliver information on what is happening at a molecular or microscopic level on the electrode surface and/or bulk. In-situ techniques are a powerful tool to investigate electrode processes. The main advantage is that, contrary to most ex-situ methods, the exposure of the working electrodes to moisture, vacuum, air or CO₂, which may change their properties, is avoided. Two in-situ methods were used: differential electrochemical mass spectrometry (DEMS) and in-situ X-ray diffraction.

• **Differential electrochemical mass spectrometry**

Differential electrochemical mass spectroscopy (DEMS, or on-line electrochemical mass spectrometry) detects volatile and gaseous electrochemical products via a quadrupole mass spectrometer. In this system, a porous electrode directly attached to a porous hydrophobic membrane serves as the interface between the electrochemical cell (normal pressure) and the ionisation chamber of the mass spectrometer (vacuum). Volatile and gaseous electrochemical products formed at the electrode go directly through the membrane into the mass spectrometer, where they can be detected [48,49].

The DEMS apparatus used in this work was controlled with a personal computer. The electrochemical cell is directly connected to the vacuum system of the quadrupole mass spectrometer (QMS 200, Balzers), which is evacuated by a turbomolecular pump (TSU 260 D, Balzers). In order to protect this turbomolecular pump, it is necessary to enable a prevacuum, which is reached with a vacuum pump (Balzers).

The electrochemical cell is shown in Fig. 5.5. The cell body was made of polypropylene and the remainder of stainless steel. The cell was sealed using an O-ring. The counter and reference electrode was metallic lithium. The critical point in the cell is the membrane since it must be permeable to volatile reactions products, but at the same time it must minimise the evaporation of volatile electrolyte components. Since the ionisation chamber is pumped continuously, intensity changes in mass signals can be detected as a function of time and/or potential and, thus, can be correlated with current peaks in the cyclic voltammogram or plateaux on galvanostatic charging/discharging curves.
In-situ X-ray diffraction

Diffraction experiments are generally performed using samples prepared well in advance and brought to the diffractometer for measurement. However, there are many circumstances where this cannot be done, for example, when the sample is only formed for a short time in a reactive environment. Then, an in-situ method is required where the formation or transformation of the sample takes place on the diffractometer itself. This method is known as in-situ diffraction. X-ray diffraction is able to detect structural changes, such as phase transitions or lattice expansion, as a result of an electrochemical process. There are many advantages of using in-situ X-ray diffraction. First of all, structure changes due to loss of potential control in an ex-situ analysis are avoided. The chemical reaction due to a change of the environment, as well as the scatter between data from several samples or from repeated mounting, are also avoided. Summing up, small structural changes in function of potential can be investigated reliably.
The cell used was designed by considering previous experiences [50]. Their cell had a window of amorphous PET (Mylar), which is transparent to X-rays, but one of its problems was that it was not absolutely airtight.

Before designing the new cell, a survey of the previous literature was carried out so as to find some improvements [51,52]. The main problem was that all the described cells had a beryllium window, which we did not want to use because of the well-known toxicity of Be compounds. Since the XRD probes the bulk of the particles whereas the potential of the electrode is determined by the concentration of lithium at the surface of the particles, great care must be taken in designing the cell. The electrochemical equilibrium of the electrode should be achieved in a reasonably short time, thus the current density should be uniform and the internal resistance small.

The new electrochemical cell which was developed during this work is shown in Fig. 5.6. The working electrode consists of a thin coated metal foil (Cu or Al) which is used both as current collector and as window for the X-ray beam. The inward side of the metal foil is coated with the electrode mass to be investigated. The electrode is prepared using the spraying method described above (section 5.3.1).

![Diagram of the in-situ X-ray cell](image)

**Figure 5.6: Schematic picture of the in-situ X-ray cell.**

The metal foil is irradiated from outwards. The counter electrode was a disc of metallic lithium pressed onto a cylinder made of stainless steel. A problem we had at the
beginning was the scattering of the metallic cell body. This problem was solved by making the metallic body thinner. Another problem lay in the high intensities detected for the lines of the copper or aluminium foil, as the current collector absorbs a part of the rays reflected from the electrode. In this way the amount of rays that reach the detector is reduced. This problem could be solved by using a foil as thin as possible (usually 12.5-25 μm). Even if the intensity of the current collector lines was high, for graphite the relevant lines could easily be detected (see Fig. 5.7).

![XRD pattern of a copper foil coated with graphite. The (111) and (200) peaks of copper are compared with theoretical lines.](image)

From Fig. 5.7 we see that fortunately the copper peaks do not hide the relevant peaks (002) and (004) of graphite. The position of the (200) line of copper is used as a rough internal standard.
Chapter 6

Electroactive manganese-based materials

6.1 Manganese dioxide

Manganese dioxide (MnO\textsubscript{2}) is an interesting material for battery applications. Moreover, it is an inexpensive, readily available compound. It exists in various phase modifications (\(\alpha\)-MnO\textsubscript{2}, \(\beta\)-MnO\textsubscript{2}, \(\gamma\)-MnO\textsubscript{2}, \(\lambda\)-MnO\textsubscript{2}, ramsdellite-MnO\textsubscript{2}) and well defined samples can be used for many electrochemical applications [36,53,54]. MnO\textsubscript{2} is suitable for the insertion of small ions (H\textsuperscript{+}, Li\textsuperscript{+}):

\[
x\text{Li}^+ + \text{MnO}_2 + xe^- \leftrightarrow \text{Li}_x\text{MnO}_2
\]

The structures can be described in terms of octahedra composed of oxygen atoms with manganese atoms in the centres of the octahedra. All the various structural forms are thus built up by linking such MnO\textsubscript{6} octahedra in various ways. For most of the MnO\textsubscript{2} materials the structures can be described as consisting of parallel chains of edge-linked manganese-oxygen octahedra, linked together in various ways.

The structure of \(\alpha\)-MnO\textsubscript{2} consists of interlinking double chains of MnO\textsubscript{6} octahedra with 1-dimensional channels of dimension (1x1) and (2x2). These parallel chains are large enough to accommodate other species. Several minerals in nature such as cryptomellane (KMn\textsubscript{8}O\textsubscript{16}) and hollandite (BaMn\textsubscript{8}O\textsubscript{16}) show the \(\alpha\)-MnO\textsubscript{2} structure. In these structures, because of the large tunnels, the oxygen framework is not close packed. On the other hand, \(\beta\)-MnO\textsubscript{2} (pyrolusite) show the rutile structure which consists of
single chains connected by corner sharing to other single chains. The structure of \( \alpha \)-MnO\(_2\) and \( \beta \)-MnO\(_2\) is displayed in Fig. 6.1.

**Figure 6.1:** Crystal structure of \( \alpha \)-MnO\(_2\) (left) and \( \beta \)-MnO\(_2\) (right).

Most frequently used in the industry is \( \gamma \)-MnO\(_2\), which can be prepared either chemically (CMD-MnO\(_2\)) or electrochemically (EMD-MnO\(_2\)). \( \gamma \)-MnO\(_2\) is characterised by a tunnel structure, more precisely it has an intergrowth structure consisting of \( \beta \)-MnO\(_2\) domains of relative size (1x1) and ramsdellite-MnO\(_2\) domains of size (2x1). The ramsdellite structure consists of double chains of MnO\(_6\) octahedra connected to other double chains by corner sharing. The resulting channels have relative dimension (2x1). The crystal structure of ramsdellite-MnO\(_2\) is displayed in Fig. 6.2.

**Figure 6.2:** Crystal structure of ramsdellite-MnO\(_2\) form.
Although $\alpha$-MnO$_2$, $\beta$-MnO$_2$, and $\gamma$-MnO$_2$ show an initial specific charge of >200 Ah/kg in the potential range 2-4 V vs. Li/Li$^+$, they all have a strong tendency to lose specific charge on electrochemical cycling. For these reasons they are not considered competitive for use in Li-ion cells [36].

Despite these problems many efforts have been made in order to synthesise a form of MnO$_2$ that could be suitable for reversible lithium insertion and thus for the development of rechargeable, environmental friendly Li-ion batteries. In this respect, particular attention has been devoted to the synthesis of spinel-related manganese dioxide forms. The first who showed that the spinel form is a lithium insertion compound was Hunter [54], who reported about lithium extraction from LiMn$_2$O$_4$ by acid treatment at ambient temperature. The resulting material was identified as $\lambda$-MnO$_2$, where the [Mn$_2$O$_4$] framework structure remains as a spinel structure, but with most of the lithium removed from the tetrahedral sites. As a result, the lattice of $\lambda$-MnO$_2$ allows the insertion and de-insertion of Li$^+$ ions. The conversion of LiMn$_2$O$_4$ to $\lambda$-MnO$_2$ results in some contraction of the lattice. The crystal structure of $\lambda$-MnO$_2$ and that of LiMn$_2$O$_4$ are displayed in Fig. 6.3.

![Figure 6.3: Crystal structure of $\lambda$-MnO$_2$ (left) and LiMn$_2$O$_4$ (right).](image)

Since the lithium spinel Li[Mn$_2$]O$_4$ is of great interest in the system Li-Mn-O let us consider it in more detail.
6.2 LiMn$_2$O$_4$ spinel

The general spinel structure, A[B$_2$]X$_4$, crystallises with the space group $Fd3m$. The anions X ($O^{2-}$, $S^{2-}$) form a closely packed cubic framework (position 32e), while cations A and B occupy tetrahedral and octahedral interstices. In normal spinels, the A atoms occupy tetrahedral positions 8a and the B atoms occupy octahedral position 16d. The crystal structure is shown in Fig. 6.4.

Figure 6.4: Crystal structure of the normal spinel A[B$_2$]O$_4$ (redrawn from [55]). Hatched, solid and open circle refer, respectively, to Li$^+$, Mn$^{3/4+}$, and O$^{2-}$ ions in LiMn$_2$O$_4$ spinel. The numbers refer to the various crystallographic positions in the spinel structure.

The spinel oxides Li$_x$Mn$_2$O$_4$ are at the moment the most investigated manganese oxides for cathode material in Li-ion batteries [56-60]. This is mainly because they offer the highest potential against lithium and moreover, provide a stable cubic framework over a
composition range of \(0 < x < 1\) [61,62]. The transport of \(\text{Li}^+\) is achieved at the residual voids in the \([\text{Mn}_2\text{O}_4]\) sublattice. The potential response of the lithium insertion/de-insertion in \(\text{Li}_x\text{Mn}_2\text{O}_4\) for \(0 < x < 1\) is characterised by two large plateaux at about 4.05 and 4.1 V vs. \(\text{Li}/\text{Li}^+\) at a galvanostatic charging curve. These plateaux correspond to the peaks 2 and 3 in the cyclic voltammogram of Fig. 6.5.

![Cyclic voltammogram](image)

**Figure 6.5**: Typical cyclic voltammogram of \(\text{LiMn}_2\text{O}_4\) measured at a sweep rate of 10 \(\mu\text{V/s}\) in 1 M \(\text{LiPF}_6\;\text{EC:DMC 1:1 (w/w)}\).

In the range of the peak 2, lithium is approximately cycled in the range \(1 > x > 0.5\) and in a second step (range of peak 3) in the range \(0.5 > x > 0\) [61]. The electrochemical reaction can be written as follows:

\[
\text{LiMn}_2\text{O}_4 \leftrightarrow \text{Li}_{1-x}\text{Mn}_2\text{O}_4 + x\text{Li}^+ + xe^- \quad (6.2)
\]

The theoretical specific charge that can be achieved with this reaction is 148 Ah/kg. Practically, since it is difficult to extract all the lithium electrochemically at practical cell voltages, the usable specific charge is limited to about 110-120 Ah/kg.
It is also possible, starting from LiMn$_2$O$_4$, to insert an additional Li$^+$ (peak 1 in Fig. 6.5). This additional insertion results in a big potential drop to a 3 V plateau corresponding to a coexistence of the cubic LiMn$_2$O$_4$ with the tetragonal Li$_2$Mn$_2$O$_4$ phase. The electrochemical reaction can be written as follows:

$$\text{LiMn}_2\text{O}_4 + x\text{Li}^+ + xe^- \leftrightarrow \text{Li}_{1+x}\text{Mn}_2\text{O}_4$$

These two phases show cell volumes which are quite different (about 10% greater for the tetragonal phase). This large anisotropic (increase in the c-parameter) expansion of the unit cell is too severe for the cubic and tetragonal phase to remain as one intergrown structure and mechanical decomposition occurs. The decrease in the potential at $x = 1$ (average Mn oxidation state of 3.5) is caused by the Jahn-Teller distortion, which is caused by the presence of the Mn$^{3+}$ Jahn-Teller ions. This effect is thought to be responsible for the large specific charge fading when Li$_x$Mn$_2$O$_4$ is cycled over both ranges ($0 < x < 2$). This problem makes the spinel be cycleable only in the 4 V range. However, also in this regime specific charge fading is a problem. In fact, at the end of discharge (when $x$ is close to 1) the surface of some particles is more lithiated than the bulk and can reach a Li$_{1+x}$Mn$_2$O$_4$ composition, where the average Mn oxidation state falls below 3.5. This surface-gradient-induced Jahn-Teller distortion is at the origin of the specific charge fading [63,64]. The resulting damaging effect can be suppressed by modifying the composition of the spinel so as to keep the average Mn oxidation state slightly above 3.5 at the end of discharge. This increase can be achieved in several ways [63]:

- by incorporating lithium ions in the manganese position according to the general formula Li[Li$_{8}$Mn$_{2-8}$]O$_4$ with small values of $\delta$, for example $\delta = 0.05$ [65];

- by incorporating other divalent cations (e.g. Mg or Zn [66]) according to the general formula LiM$_{8-2}\delta$Mn$_{2-8}\delta$O$_4$ with small values of $\delta$, for example $\delta = 0 - 0.1$;

- by synthesis of defect structures like Li$_{1-\delta}$Mn$_{2-2\delta}$O$_4$ with small values of $\delta$, for example $\delta = 0.05$ [67].
In general, materials which have an oxidation state of Mn slightly higher than 3.5, can be found in the darkened triangle of the Li-Mn-O phase diagram shown in Fig. 6.6.

Although these “stabilised” spinels offer a slightly inferior specific charge compared to the undoped ones, they show an improvement in the cycling efficiency [68]. However, this is found only at ambient temperature. As a matter of fact, the storage and the electrochemical performance at elevated temperature is mediocre [69-71]. The reason for this poor performance of the spinel in Li-based electrolytes resides in its chemical instability with respect to Mn dissolution [72]. The manganese dissolution is induced by acids formed in the electrolyte (e.g. HF) either through electrolyte decomposition (more relevant at high temperature) by traces of water in the cell, or by chemical reactions occurring at the oxide/electrolyte interface. Manganese disproportionates, thus producing soluble Mn$^{2+}$:

$$2\text{Mn}^{3+} \rightarrow \text{Mn}^{4+} + \text{Mn}^{2+}$$

(6.4)

A possible solution of this problem is to modify the surface of the oxide particles with a protecting surface coating [68,73,74] or by replacing some oxygen by fluorine [74]. The
coating of the oxide particles did not increase the cycling stability significantly [68], whereas the spinels with fluorine (LiAl_{0.2}Mn_{1.2}O_{4.2}F_{2}, 0 < z < 0.5) showed an increased stability [74].

**Due to the numerous problems outlined in this paragraph, much effort has been devoted to yield a manganese oxide with the nominal composition LiMnO\textsubscript{2}.** This, even though it is known that LiMnO\textsubscript{2} does not crystallise in the same structure type as LiNiO\textsubscript{2} or LiCoO\textsubscript{2}. Moreover, the potential range where LiMnO\textsubscript{2} is active is located on a 3 V plateau. Nevertheless, this compound is interesting because it has a theoretical specific charge (285 Ah/kg for complete Li removal) which is twice that of the spinel.

### 6.3 LiMnO\textsubscript{2}

LiMnO\textsubscript{2} is known to exist in several phases. The tetragonal spinel related \( \lambda \)-Li\textsubscript{2}Mn\textsubscript{2}O\textsubscript{4} was discussed in the previous section. A second phase shows an orthorhombic crystal structure. This structure is presented in Fig. 6.7.

![Figure 6.7: Crystal structure of orthorhombic LiMnO\textsubscript{2}.](image)

The Jahn-Teller distortion associated with the Mn\textsuperscript{3+} leads to an orthorhombic rock salt structure. In this structure the oxygen array is distorted with respect to the ideal cubic
close packing. In this compound we have corrugated layers of the \( \text{MnO}_6 \) and \( \text{LiO}_6 \) octahedra that are not parallel to the close-packed oxygen layers. This material exists both in a low- and in a high-temperature modification. The low temperature modification shows an initial specific charge value of about 230 Ah/kg [75] and the high-temperature one an initial specific charge value of about 150 Ah/kg [76]. However, both materials tend to convert into a spinel-like structure upon cycling [75-79], without showing the good cycling performance that can be achieved with the optimised lithium manganese spinels.

Another very interesting phase is a \( \text{LiMnO}_2 \) which is isostructural with \( \text{LiCoO}_2 \), thus crystallising with a layered structure. This compound would have both the advantages of the layered oxides and the economical and ecological benefits of manganese. Unfortunately, solid state syntheses of this phase were unsuccessful since the non-layered structures (spinel and orthorhombic) are thermodynamically favoured. On the contrary, soft-chemistry routes are helpful to achieve metastable compounds. Since \( \alpha\)-\( \text{NaMnO}_2 \) is isostructural to \( \text{LiCoO}_2 \), ion-exchange reactions have been pursued to obtain layered \( \text{LiMnO}_2 \) [80]. Unlike \( \text{LiCoO}_2 \), which is rhombohedral (space group \( R\bar{3}m \)), \( \text{LiMnO}_2 \) is monoclinic (space group \( C2/m \)) because the octahedra, distorted due to the Jahn-Teller effect, are aligned in a specific way. In this oxide the \( \text{Li}^+ \) cations are located in octahedral sites between \( \text{MnO}_6 \) sheets. The crystal structure of monoclinic \( \text{LiMnO}_2 \) is shown in Fig. 6.8.

Figure 6.8: Crystal structure of monoclinic \( \text{LiMnO}_2 \).
Electrochemical and X-ray diffraction experiments, however, showed that also the layered LiMnO$_2$ transforms irreversibly to the spinel upon cycling. Unlike the isostructural LiCoO$_2$, this manganese oxide undergoes a structural breakdown due to a migration of Mn atoms from the Mn layers to the lithium layers. This is due to the fact that the spinel lattice is more stable than the layered lattice for the Li-Mn-O oxides [81,82]. Therefore, if there was a way to thermodynamically stabilise layered LiMnO$_2$, it would be an extraordinarily interesting candidate for cathode material in Li-ion cells.

6.3.1 Doping of LiMnO$_2$

One of the most investigated and potentially attractive dopant is aluminium [83,84]. First of all, owing to its low weight and price, aluminium can significantly increase energy density while reducing cost. Secondly, Aydinol et al. [85] have shown that LiAlO$_2$ has a theoretical insertion potential of $\sim 5$ V vs. Li/Li$^+$. Even if LiAlO$_2$ is electrochemically inactive, solid solutions of LiAlO$_2$ with other lithiated transition metal oxides can potentially increase the insertion potential. This effect was verified for LiCo$_{1-x}$Al$_x$O$_2$ solid solutions [86]. Due to the same crystal structure of LiAlO$_2$ and LiCoO$_2$ (or LiNiO$_2$) the formation of solid solutions is expected to be possible. A more difficult task is to synthesise solid solutions of LiAlO$_2$ with LiMnO$_2$ in the $\alpha$-NaFeO$_2$ structure. If one succeeded in doing so, aluminium, due to its redox inactivity, is expected to reduce the overall distortions arising from the Jahn-Teller distortion of Mn(III) which occurs during lithium insertion and de-insertion cycles.
Chapter 7

Searching for new materials

7.1 How to estimate the optimum chemical composition

A systematic and fundamental approach to materials which have to be employed in Li-ion batteries is possible by considering topotactic electrochemical reactions. A basic question is how to estimate the optimum chemical composition, and what kinds of materials are the most suitable for this purpose. In order to find the optimum composition the following model was postulated [87]:

(a) the reversible reaction during cycling consists of an insertion/de-insertion of lithium ions into/from a solid matrix and of an injection/removal of an electron;

(b) the anions should form a closest packing in the framework of the solid matrix;

(c) the transition metal ions should occupy octahedral positions in the closest-packed anion array;

(d) the intercalated lithium ions should occupy octahedral sites.

The crystal structure of many transition metal oxides and chalcogenides fulfil assumptions (b) and (c). Assumption (a) is also valid for many transition metal oxides and sulphides, whereas assumption (d) was shown to be satisfied for LiMeO$_2$ and Li$_2$MeO$_3$ (Me = transition metal) [87]. Figure 7.1 shows which composition gives the maximum specific charge.
Figure 7.1: Diagram showing which composition gives maximum specific charge (redrawn from [87]). Number of available electron sink and vacant octahedral sites to accommodate lithium ions are crossing at x = 2 in MeO_x, at which maximum specific charge can be obtained.

It can be seen that the maximum specific charge is given for a composition MeO_2 (Me/O = 0.5), thus for metal dioxides. To summarise, we have the following reaction:

$$\begin{align*}
Li^+ + e^- + \square_{\text{oct}} MeO_2 & \leftrightarrow \text{Li}\text{MeO}_2 \\
& \quad \quad \text{oct} \quad \text{cp} \\
& \quad \quad \text{oct} \quad \text{oct} \quad \text{cp}
\end{align*}$$

(7.1)

where \((\text{oct})\) represents the octahedral sites and \((\text{cp})\) denotes the closest-packed oxygen array. These arguments make MeO_2 or LiMeO_2 the most suitable materials for Li-ion batteries.
7.2 The role of the metal-ion and that of the anion

Not only metal oxides show the desired composition MeX₂ (X = O). In fact many compounds with X = S or Se also are capable of lithium insertion (e.g. LiₓTiS₂). Theoretical work showed however that the calculated insertion potential for Li in various LiCoX₂ (X = O, S, and Se) compounds in the α-NaFeO₂ structure is strongly dependent on the anion used. The average insertion potential (V vs. Li/Li⁺) was found to be 3.75 V for X = O, 2.04 V for X = S, and 1.46 V for X = Se [85,88,89]. If energy per unit weight is considered, the sulphides and selenides are much less attractive if one considers the higher anion weight, too.

For these reasons layered transition metal sulphides like TiS₂ and MoS₂ are less interesting. As a result, attention is devoted to oxides containing lithium and light multivalent 3d transition metals. At first, this strong dependence of the anion on the insertion potential of lithium may be surprising. In fact, it is traditionally assumed that when Li inserts, the compensating electron reduces the metal ion. As a consequence, the nature of the metal ion and the strength of its M⁴⁺/M³⁺ redox couple is expected to play a significant role in the insertion potential. It was observed that the calculated insertion potential for LiMO₂ oxides increases while going to the right in the 3d-transition metal series [88].

<table>
<thead>
<tr>
<th>M in LiMO₂</th>
<th>Ti</th>
<th>V</th>
<th>Mn</th>
<th>Co</th>
<th>Ni</th>
<th>Cu</th>
<th>Zn</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>Av. Potential</td>
<td>2.36</td>
<td>3.03</td>
<td>3.35</td>
<td>3.97</td>
<td>3.14</td>
<td>3.88</td>
<td>4.63</td>
<td>5.4</td>
</tr>
</tbody>
</table>

[V vs. Li/Li⁺]

The drop at M = Ni is caused by the Jahn-Teller instability of LiNiO₂. The highest insertion potential was found for LiAlO₂.

The results of these theoretical calculations [85] showed that the net result of Li insertion is electron transfer predominantly to the oxygen and not to metal. The transfer to oxygen is found to increase as M goes to the right in the series from Ti to Zn, correlating well with the increase in the insertion potential. The metal cation can be viewed as a means to stabilise the oxide structure.
The stabilisation of the layered manganese oxide was pursued by a synthesis strategy. The basic concept of this strategy was the fact that highly polarising ions tend to form layered compounds. A classic example is the series of the dichalcogenides structures from three-dimensional octahedral linkages (for example for the alkaline earth cations) to layered structures in case of transition metal or $d^{10}$ cations like Cd$^{2+}$. Inspecting the series of the ternary transition metal (M) oxides, it becomes clear that the layered AMO$_2$ structure type occurs preferentially for the heavier M elements but not for the early ones. Secondly, it is a common observation that large cations A are in favour of a layered packing. There are many examples for this, but only the structural change from LiMn$_2$O$_4$ to NaMnO$_2$ should be mentioned here. As the target is LiMO$_2$ there is only a limited possibility to use larger cations, e.g. as pillaring component between the layers. But this will hardly change the thermodynamics because there should only be very few of the larger cations per Li$^+$, otherwise the specific charge loss would be too large.

We have chosen to introduce polarising cations into the target compounds. These are characterised by one or more of the following parameters:

1. small radius (Be$^{2+}$, B$^{3+}$, Al$^{3+}$, Ti$^{4+}$, Sn$^{4+}$, etc.);

2. high charge (Ti$^{4+}$, Sn$^{4+}$, Zr$^{4+}$, etc.);

3. high effective nuclear charge (Ni$^{2+/3+}$, Cu$^{2+/3+}$, Zn$^{2+}$, Cd$^{2+}$, etc.).

Preferentially, there should be a suitable amount of non-redox active cations to stabilise the structure during the Jahn-Teller distortions of the redox-active metals. This amount must not be too high because it reduces the overall specific charge. This means that these cations may be found in group 1 and 2. In addition, there may be a need for more polarising cations to drive the system to thermodynamic stability. This would then preferentially be done by a group 3 member to preserve as much specific charge as possible.

Our attempts to generate a manganese-based cathode material utilised different cations from either list to achieve the goal.
Chapter 8

Characterisation of commercially available oxides

8.1 Effect pigments

Pigments are materials which are used to impart colour to surfaces, plastics, inks, etc. Many pigments are inorganic in nature. Among the inorganic pigments there are the so-called effect pigments. Effect pigments are always in form of platelets and have, compared to the colour pigments, bigger particle sizes. Colour pigments have a particle size which is comparable to the wave length of visible light, whereas effect pigments have a particle size range from 5 to 35 μm (Fig. 8.1).

Figure 8.1: SEM pictures of a platelet-like monocrystal (see Tab. 8-1). The length of the white line corresponds to 70 μm for left picture and 6 μm for the right picture.
The most important applications are plastics, coatings, printing ink, cosmetics, and automotive paints. Effect pigments can be divided into several groups. A list is given in Tab. 8.1 [90].

<table>
<thead>
<tr>
<th>Pigment type</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metallic platelets</td>
<td>Al, Zn/Cu, Cu, Ni, Au, Ag,...</td>
</tr>
<tr>
<td>Oxide coated metallic platelets</td>
<td>Fe$_2$O$_3$ coated Al platelets,...</td>
</tr>
<tr>
<td>Coated mica platelets</td>
<td>coating: TiO$_2$, SnO$_2$,...</td>
</tr>
<tr>
<td>Platelet-like monocrystals</td>
<td>Al$_x$Mn$<em>y$Fe$</em>{2-x-y}$O$_3$,...</td>
</tr>
</tbody>
</table>

Two pigments (a platelet-like monocrystal and a coated mica platelet) were at our disposal for electrochemical characterisation and are discussed in more detail. The electrochemical activity was checked since their composition is similar to that of one of the insertion compounds for the negative electrode.

8.1.1 Electrochemical characterisation of a platelet-like monocrystal

Among this class of pigments there are flaky iron oxides. These flakes consist of pure iron oxide or mixed phase pigments, e.g. Al$_x$Fe$_{2-x}$O$_3$, Mn$_y$Fe$_{2-y}$O$_3$, or Al$_x$Mn$_y$Fe$_{2-x-y}$O$_2$. The pigment investigated (Paliocrom Kupfer L 3000, produced by BASF AG) had the following composition: Al$_{0.12}$Mn$_{0.03}$Fe$_{1.85}$O$_3$.

The electrode was prepared in form of a pressed pill and consisted of 83 weight percent (wt %) active material, 4 wt % Ensaco soot, 4 wt % SFG6, and 9 wt % PVDF. The mixture was suspended in petroleumether and mixed using a high-speed mixer.

A cyclic voltammogram was recorded in order to see if the material showed any electrochemical activity. The cyclic voltammogram is shown in Fig. 8.2, where we see that the oxide is slightly electroactive in the potential range 0.8-2 V vs. Li/Li$^+$. This is not surprising due to the high amount of iron(III). It can also be observed that the shape of the voltammogram drastically changes upon cycling.
The next figure (8.3) shows the evolution during the first four cycles of the shape of the cyclic voltammogram. During the first discharge process a reduction reaction takes place at 0.5 V vs. Li/Li⁺ and an oxidation reaction at 1.7 V vs. Li/Li⁺. During the second cycle two additional reductions occur at about 0.9 and 1 V vs. Li/Li⁺. The following oxidation remains more or less unaffected. From the third cycle this additional process is no longer divided in two separate peaks. With further cycling the magnitude of the reduction as well as the oxidation process start to lose intensity.

The cycling behaviour of this effect pigment is shown in Fig. 8.4. For the first insertion 330 Ah/kg can be reached. The specific charge increases for the following two cycles, reaching a maximum value of 486 Ah/kg. From this point on, as discussed above, the specific charge dramatically decreases, reaching less than 50 Ah/kg after 8 cycles.
Figure 8.3: Shape evolution of the cyclic voltammogram of $\text{Al}_{0.12}\text{Mn}_{0.88}\text{Fe}_{1.85}\text{O}_3$. 
Chemical lithiation of $\text{Al}_{0.12}\text{Mn}_{0.03}\text{Fe}_{1.85}\text{O}_3$

As already explained in section 3.4, materials which do not contain lithium after their synthesis have to be chemical lithiated before being used in the positive electrode of the Li-ion battery.

The chemical lithiation of the iron oxide was obtained as follows: 0.5 g of the iron oxide were suspended in 25 ml toluene. Then 6.4 ml butyllithium (2.5 M in toluene) were carefully added to this suspension (this amount of butyllithium corresponds to a molar ratio of butyllithium:oxide = 5). The mixture was stirred for a week at a temperature of 80 °C. At the end the solution was filtered and washed thoroughly with toluene and dried. The chemical analysis (ICP-AES) of the lithiated compound gave the composition $\text{Li}_{4.5}\text{Al}_{0.12}\text{Mn}_{0.03}\text{Fe}_{1.85}\text{O}_3$.

The cyclic voltammogram of the lithiated oxide is shown in Fig. 8.5. Little change in the shape of the curves of the unlithiated and the lithiated oxide is observed. The cycling behaviour is shown in Fig. 8.6. Compared to the unlithiated oxide the lithiated one shows a slightly better stability.
Figure 8.5: Cyclic voltammogram of Li$_{4.5}$Al$_{0.12}$Mn$_{0.8}Fe_{1.85}$O$_3$ measured with a sweep rate of 50 $\mu$V/s in the potential range 0.5 - 4.4 V vs. Li/Li$^+$. The electrolyte used was 1M LiPF$_6$ in EC:DMC 1:1 (w/w).

Figure 8.6: Cycling stability of Li$_{4.5}$Al$_{0.12}$Mn$_{0.8}Fe_{1.85}$O$_3$. Data were obtained galvanostatically between 0.5 and 4.4 V vs. Li/Li$^+$ at 10 mA/g. The electrolyte used was 1 M LiPF$_6$ in EC:DMC 1:1 (w/w).

To conclude, it can be said that these kinds of oxides, despite their interesting morphology, are not suitable as electrode materials in high energy lithium batteries.
Both the potential range and the cycling stability are insufficient to have any chance of application.

8.1.2 Electrochemical characterisation of coated mica platelets

The second pigment we had at our disposal consisted of coated mica platelets. These pigments have a coating of transition metal oxides on a mica substrate. The mica substrate is usually made of muskovit (KAl$_2$(OH)$_2$(AlSi$_3$O$_10$)), phlogopit (KMg$_3$(OH)$_2$(Si$_4$O$_10$)) or glass. Examples of coatings are TiO$_2$ (anatase, rutile), ZrO$_2$, and SnO$_2$. This group of pigments have their main application in cosmetic and car industry [90].

The pigment investigated (Flonac ME11, produced by Kemira Oye) was coated with SnO$_2$:TiO$_2$ = 1:9, the TiO$_2$ showing the rutile structure. Even though titanium dioxide is known to be able to insert lithium ions [91], its use as negative electrode in Li-ion batteries is not convenient since its combination with a 4 V cathode material would give a low cell voltage (~1.5 V to ~2 V). In order to understand the fundamental electrochemical properties of such material class we wanted to investigate the electrochemical behaviour of this pigment and test its suitability as electrode material. The first three cycles of the cyclic voltammogram are shown in Fig. 8.7.

The electrode was prepared in form of a pressed pill and consisted of 74 weight per cent (wt %) active material, 18 wt % XC72 soot, 6 wt % SFG6, and 2 wt % oppanol.

![Figure 8.7: Cyclic voltammogram of the coated mica platelets measured with a sweep rate of 50 µV/s in the potential range 0.1 – 4.4 V vs. Li/Li$^+$. The electrolyte used was 1 M LiPF$_6$ in EC:DMC 1:1 (w/w).](image-url)
In the first cycle three reduction peaks are observed. The first at 1.3, the second at 1 and the third at 0.7 V. Only one oxidation process is observed at about 2 V. The reduction occurring at 100 mV and the corresponding oxidation at 250 mV are due to the carbon present in the electrode. In the second cycle a new reduction peak appears at 1.5 V, whereas the three peaks observed during the first cycle are reduced to one centred at 770 mV. On the other hand, the oxidation reaction still occurs at 2 V. For the following cycles the electrochemical behaviour of the oxide does not change any more. The cycling behaviour of this material is shown in Fig. 8.8. Here it can be seen that after the first charge, where the irreversible specific charge is high, the material shows a quite good reversibility towards lithium insertion and de-insertion reaching a specific charge of about 120 Ah/kg.
To conclude it can be said that the coated mica platelets show electrochemical activity in the potential range 0.5-2 V vs. Li/Li'. Although the cycling stability of the pigment is good, the low potential does not render them competitive as cathode material if compared to other oxides. They are also not suitable for the negative electrode due to the higher potential and lower specific charge compared to graphite.
Chapter 9

Oxidation of intermetallic phases

In order to generate a compound with a nominal composition LiMnO₂ stabilised with a more polarising metal cation, a reaction involving lithiumpermanganate as reactant was used.

The strong oxidising nature of the ready available permanganate ion could be exploited to obtain new manganese oxides [92-94]. The reduction of AMnO₄ (A = Li, Na, and K) with water under hydrothermal conditions led to a layered manganese oxide AₓMnO₂•H₂O [94]. Although the hydrated oxides show high specific charge (> 200 Ah/kg between 2-4 V vs. Li/Li⁺) they strongly tend to lose it upon cycling. Electrochemical experiments on the dehydrated oxides also revealed a strong specific charge fading. This fading was observed especially for the lithium compound. The specific charge fading was attributed to the transformation to the more stable spinel structure. In addition, all the reductions reported were made in the presence of water, which may be undesirable for lithium cells because of unavoidable incorporation of H⁺ in the structures. The positive effect of working in absence of water was reported by Manthiram et al. [92], who presented a metastable amorphous manganese oxyiodide with 260 Ah/kg with a mid-discharge potential of 2.6 V vs. Li/Li⁺.

9.1 Oxidation of LiAl with lithiumpermanganate

Due to the problem of water, a solid state route was tested in this study. The reaction consists of the oxidation of the intermetallic phase LiAl with lithium permanganate.
Since lithium permanganate is not commercially available, it had to be synthesised. The overall reaction is shown in equation (9.1):

\[ x\text{LiAl} + (1-x)\text{LiMnO}_4 \rightarrow \text{"LiMn}_{1-x}\text{Al}_x\text{O}_2" + (1-2x)\text{O}_2 \]  

(9.1)

9.1.1 Synthesis of the reactants

Synthesis of LiAl [95]

For the synthesis of LiAl 0.3413 g (50 mmol) lithium and 1.2295 g (45 mmol) aluminium were put in a niobium tube, which was then heated in a tube furnace for 48 h at a temperature of 500 °C. The heating and cooling rate was 50 °C/h. The product was single phase, based on X-ray powder diffraction.

Synthesis of LiMnO₄

For the synthesis of LiMnO₄ 10.6 g (67 mmol) of KMnO₄ and 7.13 g (67 mmol) of LiClO₄ were dissolved in an as small as possible quantity of distilled water. The separation of the products was performed exploiting the different solubility of KClO₄ (0.75 g/100 ml) and LiMnO₄ (71 g/100 ml). The solution was filtered several times at 0 °C, reducing the quantity of water after each filtration so as to allow the precipitation of KClO₄. A quite high purity degree was achieved, as confirmed by X-ray diffraction. The product was identified as LiMnO₄•3H₂O and was used in the hydrated form since the water it contained could not be removed without decomposing the material.

9.1.2 Synthesis of the oxides

Stoichiometric amounts of LiAl and LiMnO₄•3H₂O were mixed together in a ball mill for 15 minutes, transferred into a crucible and then treated in the furnace oven. DTA experiments revealed that a reaction temperature of 200 °C was high enough.

9.1.3 Electrochemical characterisation

The electrode was prepared in form of a pressed pill by mixing together the active material and carbon black (XC72) in a weight ratio 1:1 and with 2 wt % of Teflon as binder. The mixture was suspended in hexane and milled in the ball mill for 5 minutes.
First experiments \((T = 250, 300, 500 \, ^\circ C, \ x = 0.25 \, \text{in LiAl}_x\text{Mn}_{1-x}\text{O}_2, \text{reaction time} < 1 \, \text{h})\) gave electroinactive materials, due probably to the too short reaction time. This was confirmed by XRD, as most diffraction lines were identified as being still the starting materials. For these materials a specific charge of about 200 Ah/kg was obtained for the first charge cycle, with most of the lithium coming presumably from the lithiumpermanganate. For the following discharge process only 20 Ah/kg could be reached. As an example, the first cycle of a sample calcined at 250 \, ^\circ C is displayed in Fig. 9.1.

![Cyclic voltammogram of a sample with \(x = 0.25\) in \(\text{LiAl}_x\text{Mn}_{1-x}\text{O}_2\) calcined at 250 \, ^\circ C for a reaction time < 1 h. The sweep rate was 50 \, \mu V/s. The electrolyte used was 1 M \text{LiPF}_6 in EC:DMC 1:1 (w/w).]

This figure shows that the electrochemical process occurring at about 4 V vs. \(\text{Li/Li}^+\) on charging is irreversible, indicating quite certainly that a structural transformation has occurred, giving rise to a material without ability to intercalate and de-intercalate lithium ions.

When the reaction time was increased to about one hour, the materials showed electrochemical activity. The XRD patterns of these materials were quite complex and presented several phases (amorphous and crystalline ones), which could not always be completely identified. The electrochemical activity is thought to arise from the amorphous material. Since the activity was still too low, the reaction time was increased
from 12 to 48 hours (see Tab. 9-1) to check if the performance could be increased. The stoichiometry, $x = 0.25$ in LiAl$_x$Mn$_{1-x}$O$_2$, was kept constant.

Table 9-1: Synthesis conditions for oxides with $x = 0.25$.

<table>
<thead>
<tr>
<th>Sample number</th>
<th>Temp. [°C]</th>
<th>Time [h]</th>
<th>Atmosphere</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>250</td>
<td>12</td>
<td>Ar</td>
</tr>
<tr>
<td>2</td>
<td>250</td>
<td>24</td>
<td>Ar</td>
</tr>
<tr>
<td>3</td>
<td>250</td>
<td>48</td>
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</tr>
<tr>
<td>4</td>
<td>500</td>
<td>48</td>
<td>Ar</td>
</tr>
<tr>
<td>5</td>
<td>800</td>
<td>48</td>
<td>Ar</td>
</tr>
</tbody>
</table>

In the next figure the XRD patterns of the synthesised materials are shown.

Figure 9.2: Powder XRD patterns of LiMn$_{0.75}$Al$_{0.25}$O$_2$ calcined at various temperatures for various reaction times. The numbers refer to the sample number in Tab. 9-1. The asterisks refer to unreacted LiMnO$_4$·3H$_2$O.
As expected, both the reaction time and the temperature play an important role for the degree of cristallinity. A more detailed discussion of the XRD patterns will be given later in this chapter.

The cyclic voltammogram of one of these samples, namely sample 2, is shown in Fig. 9.3.

![Cyclic Voltammogram](image)

**Figure 9.3:** 1st, 5th, and 15th cycle of sample 2. The sweep rate was 50 µV/s.
The electrolyte used was 1 M LiPF₆ in EC:DMC 1:1 (w/w).

By comparing Fig. 9.1 and Fig. 9.3 we can see that electrochemical activity is now formed for sample 2. Here a reduction process takes place at about 2.8 V and the corresponding re-oxidation reaction occurs at 3 V vs. Li/Li⁺. In the range from 3.3 to 4.4 V the current response is not zero, indicating that some electrochemical activity is present. It can also be seen that the irreversible peak centred at 4 V, which was responsible for the destruction of the material calcined for t < 1 hour, is not occurring any more. It is also noteworthy that the polarisation in the 3 V region increases dramatically upon cycling. As a matter of fact, while in the first cycle the two peaks are separated by 250 mV, in the fifteenth cycle the difference is 355 mV. The cycling behaviour of sample 2 is displayed in Fig. 9.4, which shows that the specific charge for discharge increases progressively with further cycling from a value of 86 Ah/kg in the first cycle to 155 Ah/kg in cycle number 6. From this point on the specific charge
rapidly decreases reaching 100 Ah/kg after 15 cycles. Such behaviour was observed for an orthorhombic LiMnO₂, as well [79]. Fig. 9.4 also shows a remarkably high irreversible specific charge.

![Figure 9.4: Specific charge vs. cycle number for sample 2. Data were obtained galvanostatically between 2.5 and 4.4 V vs. Li/Li⁺ at 10 mA/g. The electrolyte used was 1 M LiPF₆ in EC:DMC 1:1 (w/w).](image)

In Fig. 9.3 it can also be seen that on further cycling the specific charge in the 3 V region decreases, while that in the 4 V region is increasing. This fact is displayed in Fig. 9.5, where the total specific charge is divided into a 3 V plateau (between 2.5 and 3.3 V vs. Li/Li⁺) and a 4 V plateau (between 3.3 and 4.4 V vs. Li/Li⁺). The ratio of 3 V specific charge to 4 V specific charge is plotted in Fig. 9.6.

Figure 9.5 shows that the specific charge in the 3 V region is higher than that in the 4 V region for about the first 10 cycles. As a matter of fact, the specific charge in the 4 V region increases upon cycling, while the specific charge in the 3 V region rapidly decreases after a few cycles. The ratio 3 V/4 V displayed in Fig. 9.6 shows this effect once more. The curve starts from a ratio of about 3 and decreases in a parabolic way to a value of 0.8 after 15 cycles. The reason for this behaviour will be discussed later in this chapter.
Figure 9.5: 4 and 3 V plateau specific charge for discharge vs. cycle number for sample 2. The 4 and 3 V specific charges were calculated in the potential ranges of 3.3 to 4.4 V and 2.5 to 3.3 V vs. Li/Li⁺, respectively.

Figure 9.6: Ratio of 4 and 3 V plateaux specific charges for discharge vs. cycle number for sample 2. The 4 and 3 V specific charges were calculated in the potential ranges of 3.3 to 4.4 V and 2.5 to 3.3 V vs. Li/Li⁺, respectively.
Although the electrochemical performance of these oxides is not satisfying if compared to other oxides, this system seemed to have some potential, so that we decided to investigate it in more detail. Four more samples (see Tab. 9-2) were prepared by increasing the reaction time to one week and by varying the Mn/Al ratio. Two temperatures were chosen.

Table 9-2: Synthesis conditions for oxides with \( x = 0.25 \) and \( x = 0.10 \).

<table>
<thead>
<tr>
<th>Sample number</th>
<th>Temp. [°C]</th>
<th>( x )</th>
<th>Time [d]</th>
<th>Atmosphere</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>250</td>
<td>0.10</td>
<td>7</td>
<td>Ar</td>
</tr>
<tr>
<td>7</td>
<td>350</td>
<td>0.10</td>
<td>7</td>
<td>Ar</td>
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<td>0.25</td>
<td>7</td>
<td>Ar</td>
</tr>
<tr>
<td>9</td>
<td>350</td>
<td>0.25</td>
<td>7</td>
<td>Ar</td>
</tr>
</tbody>
</table>

The XRD patterns of the four samples are displayed in Fig. 9.7. The identification of the presumed electroactive phase was not so easy. As a matter of fact, the XRD patterns of all the possible phases were very similar. Up to now the phases found in the system Li/Mn/O or Li/Mn/Al/O are: cubic LiMn\(_2\)O\(_4\) spinel, orthorhombic LiMnO\(_2\) [79], and monoclinic LiMnO\(_2\) [80,82]. A further phase in this system is the tetragonal Li\(_2\)Mn\(_2\)O\(_4\) spinel.

As we will see from the electrochemical results, the synthesised phase can not be a LiMn\(_2\)O\(_4\) spinel. The orthorhombic phase could also be excluded, since the strongest peak of this oxide is located at \(-16° \ 2\Theta\). For a more detailed examination, the XRD patterns of the two remaining phases, the monoclinic LiMnO\(_2\) and the tetragonal Li\(_2\)Mn\(_2\)O\(_4\) spinel, were simulated. The data for the monoclinic phase were taken from [80] and the ones for the tetragonal spinel from the ICSD database. In addition, a hypothetical hexagonal LiMn\(_{0.75}\)Al\(_{0.25}\)O\(_2\) with the same crystallographic data as LiNiO\(_2\) was calculated. In this case a completely ordered \(\alpha\)-NaFeO\(_2\) structure was assumed, except for the substitution of 25% of the Mn by Al. These three simulated patterns are shown in Fig. 9.8. It can be noticed at first sight that the monoclinic and the tetragonal patterns are very similar.
Figure 9.7: Powder XRD patterns of LiMn$_{1-x}$Al$_x$O$_2$ oxides calcined at different temperatures for one week. The asterisks refer to an unidentified phase, while the Miller indexes are given assuming a hexagonal lattice (see discussion below).
Figure 9.8: Simulated XRD patterns for monoclinic-LiMnO₂, tetragonal Li₃Mn₂O₄ spinel and hypothetical hexagonal LiMn₀.₇₅Al₀.₂₅O₂.

Some differences are visible in the 58-69° 2Θ range (Fig. 9.9). The monoclinic phase exhibits (202), (310) and (020) peaks at 65.1, 66.2 and 66.6°, respectively. On the other hand, the tetragonal phase has (400) and (323) peaks at 66.0 and 66.8°, respectively. In this range the hexagonal phase has (018), (110), and (113) peaks at 64.4, 64.7, and 68.0°, respectively. Fig. 9.10 shows the expansion of the 58-69° 2Θ range for sample 6. The previous considerations allow us to exclude the tetragonal phase since our oxide shows a strong peak at 65°, while the tetragonal Li₃Mn₂O₄ does not. By comparing our sample with the monoclinic phase we observe important differences, not only in the 30-40°, but also in the 61-62° 2Θ range. While in this range the monoclinic phase has two peaks, (31 1) and (11 3), our sample does not.
Figure 9.9: Simulated XRD patterns for monoclinic-LiMnO$_2$, tetragonal Li$_2$Mn$_2$O$_4$ spinel and hypothetical hexagonal LiMn$_{0.75}$Al$_{0.25}$O$_2$. Enlargement of the 58-69° 2Θ range.

Figure 9.10: Enlargement of the 58-69° 2Θ range for sample 6.
All the diffraction patterns of samples 6 to 9 fit to the hexagonal phase. Indexing and refinement gave the following lattice constants: $a = 2.85 \text{ Å}$, $c = 14.16 \text{ Å}$. **To conclude this discussion it can be stated that all the synthesised oxides show the $\alpha$-NaFeO$_2$ structure, and are thus layered.** A big difference between the patterns of sample 6 and that of the hypothetical compound LiMn$_{0.75}$Al$_{0.25}$O$_2$ resides in the different intensity ratio of the peaks (003) and (104). The intensity ratio (003)/(104) is a very sensitive indicator of cation mixing [96]. Cation mixing means that lithium ions migrate from the lithium layers to the transition metal layer and these migrate into the lithium layers. As the degree of cation mixing increases, the intensity of the (003) peak decreases relative to that of the (104) peak. These considerations suggest that our material has quite a high degree of cation mixing, since the (003)/(104) ratio is low.

In the next figure the evolution of the specific charge (discharge) for the four samples (6 to 9) is shown.

![Figure 9.11: Specific charge for discharge vs. cycle number for samples 6 to 9.](image)

Data were obtained galvanostatically between 2.5 and 4.4 V vs. Li/Li$^+$ at 10 mA/g. The electrolyte used was 1 M LiPF$_6$ in EC:DMC 1:1 (w/w).

As one can see in Fig. 9.11, the specific charge of sample 7 ($350 \text{ °C}, x = 0.10$) increases for the first cycles reaching a maximum of 120 Ah/kg after 10 cycles. From this point
on the specific charge decreases rapidly with a loss of about 1.3 Ah/kg per cycle. The same specific charge loss rate was observed for an orthorhombic LiMnO$_2$ [77]. Sample 9 (350 °C, $x = 0.25$) presents a very similar behaviour. In this case the highest specific charge (103 Ah/kg) is reached after 15 cycles and from this point on the material shows the same specific charge loss rate as sample 7.

By comparing these two oxides we can infer that the higher amount of aluminium present in sample 9 probably has a slightly beneficial effect since the decrease of the specific charge is delayed. On the other hand, the maximum value of sample 9 is lower due to the higher amount of the electroinactive aluminium.

The cycling behaviour of sample 6 (250 °C, $x = 0.10$) is comparable to that of the previous two for the first cycles. As a matter of fact, the specific charge increases for the first 12 cycles to a maximum value of 100 Ah/kg. The difference lies in the specific charge retention. This material shows a specific charge loss of only 0.4 Ah/kg per cycle. The performance of sample 8 is even better. As far as this oxide is concerned, the maximum value (96 Ah/kg) is reached after 17 cycles and during the following cycles a constant specific charge of ~90 Ah/kg is retained, without any significant losses for 50 cycles.

The same remarks made for the previous two oxides (i.e. samples 7 and 9) can also be made here. As a matter of fact, sample 8 ($x = 0.25$) reaches its maximum value in a later cycle than sample 6 ($x = 0.10$). Moreover, in this case the cycling stability is slightly increased by the higher amount of aluminium.

In addition, the role played by the reaction temperature seems to be more important than the role played by the aluminium amount: while the two samples calcined at 350 °C show a strong fading, which is independent of the amount of aluminium, the two samples calcined at 250 °C are definitely more stable.

For the following discussion the two samples with $x = 0.10$, namely sample 6 and 7, were chosen. Figure 9.12 displays the first charge-discharge curve for samples 6 and 7, while Fig. 9.13 shows the corresponding differential specific charge plot for sample 7. The curves were measured between 2.5 and 4.3 V vs. Li/Li$^+$ at 10 mA/g rate. Both materials show a single charging potential plateau at about 4.1 V. As far as sample 6 is concerned, an initial specific charge for charge of 96 Ah/kg was obtained, while
93 Ah/kg could be inserted during the following discharge process. For sample 7, on the other hand, a specific charge of 140 Ah/kg was obtained during the first charge, while only 113 Ah/kg were reached on discharge. This high specific charge loss during the first cycle, especially for sample 7, was also observed in the past [79,97].

Figure 9.12: First charge-discharge curve for sample 6 and 7. The electrolyte used was 1 M LiPF$_6$ in EC:DMC 1:1 (w/w).

Figure 9.13: Differential specific charge plot for the first charge-discharge cycle for sample 7. $C$ and $E$ represent the specific charge and potential, respectively.
Another important aspect that can be seen in Fig. 9.12 and 9.13 is that, while the lithium ions are removed from the oxides over a plateau centred at 4.1 V during the first charge, the following insertion occurs mainly below 3 V. These results indicate that the materials undergo a structural transformation during the first cycle.

In the next figure (9.14) the evolution of the charge-discharge curves upon cycling for samples 6 and 7 is displayed. The potential profiles for the 2\textsuperscript{nd}, 10\textsuperscript{th}, 20\textsuperscript{th}, 30\textsuperscript{th}, and 40\textsuperscript{th} cycle are shown. It can be seen that with further cycling, potential plateaux develop at about 4.1 V and 2.9 V, respectively. This indicates that lithium inserts at two different sites. This behaviour is characteristic of the spinel phase \( \text{Li}_x\text{Mn}_2\text{O}_4 \), where lithium is inserted into the tetrahedral positions at the 4 V plateau, corresponding to \( 0 < x < 1 \), and into the octahedral positions at the 3 V plateau, corresponding to \( 1 < x < 2 \) (see section 6.2). It must also be noticed that after the 20\textsuperscript{th} cycle the plateau centred at 4.1 V splits into two steps. The first one is centred at 4.05 V and the second at 4.2 V during charge and at 4.15 V and 4 V during discharge. This phenomenon is also typical of \( \text{Li}_x\text{Mn}_2\text{O}_4 \) spinels.

These results clearly show that this material transforms to the spinel phase upon cycling.

The formation of the 3 and 4 V potential plateaux can also be observed in Fig. 9.15, which show the differential specific charge plots for samples 6 and 7. These figures also show that the 3 V plateau exhibits a larger polarisation than the 4 V plateau. This can be seen from the differences in potential of the differential specific charge peaks. As a matter of fact, while the peaks in the 3 V region are separated by 150 mV, the separation in the 4 V region is much less pronounced.

The fact that these materials convert to the spinel phase is further supported by an examination of the evolution of the specific charge in the two potential plateaux upon cycling. The potential plateaux were separated into a 4 V plateau (between 3.3 and 4.3 V vs. \( \text{Li}/\text{Li}^+ \)) and a 3 V plateau (between 2.5 and 3.3 V vs. \( \text{Li}/\text{Li}^+ \)). These potential limits correspond to minimum values of the differential specific charge \( (dC/dE) \) (Fig. 9.15) and clearly separate the potential plateaux.
Figure 9.14: Evolution of the charge-discharge curves upon cycling for sample 6 (top) and 7 (bottom). Potential profiles are shown for the 2nd, 10th, 20th, 30th, and 40th cycle.
Figure 9.15: Evolution of differential specific charge plots upon cycling for sample 6 (top) and 7 (bottom). Results are shown for the 2nd, 10th, 20th, 30th, and 40th cycle. C and E represent the specific charge and potential, respectively.
Figure 9.16 shows the evolution of the 3 and 4 V plateaux for sample 6. It can be seen that the specific charge in the 3 V plateau is always higher during the first 40 cycles, which indicates that the lithium ions are preferably inserted into the octahedral than into the tetrahedral sites. This limited insertion into the tetrahedral sites may suggest that these are occupied with manganese ions. If upon cycling these manganese ions migrate to the spinel octahedral sites (16d), the 3 V specific charge should then decrease relative to the 4 V specific charge. This is exactly what happens (Fig. 9.17).

![Figure 9.16: 4 and 3 V plateaux specific charge for discharge vs. cycle number for sample 6. The 4 and 3 V specific charges were calculated in the potential ranges of 3.3 to 4.3 V and 2.5 to 3.3 V vs. Li/Li⁺, respectively.](image)

In Fig. 9.17, which shows the ratio 3 V/4 V, we can see what previously discussed. At the beginning the ratio is about 4 and decreases in a parabolic way until it saturates to a value of about 1. This is a further confirmation that our material converts to a spinel phase.
Figure 9.17: Ratio of 4 and 3 V plateaux specific charges on discharge vs. cycle number for sample 6. The 4 and 3 V specific charges were calculated in the potential ranges of 3.3 to 4.3 V and 2.5 to 3.3 V vs. Li/Li⁺, respectively.

A similar behaviour is observed for sample 7 (Fig. 9.18 and 9.19). In this case the specific charge in the 3 V region is higher only during the first 30 cycles. The specific charge loss rate in the 3 V plateau was 1.7 Ah/kg for sample 7, whereas it was only 0.7 Ah/kg for sample 6. These facts seem to suggest that sample 7 converts to the spinel phase more rapidly than sample 6. This interpretation is also supported by the analysis of the behaviour of the 4 V plateau. As we said before, the 4 V plateau originates from the insertion of the lithium ions in the tetrahedral sites, which at the beginning are occupied by manganese ions. The spinel is then formed if these manganese ions migrate to the octahedral sites. By comparing the 4 V plateaux of the two samples under discussion it can be seen that both increase exponentially, but sample 7 reaches a saturation earlier than sample 6. This indicates that in sample 7 the tetrahedral sites are left free at an earlier stage.

The ratio 3 V/4 V for sample 7 is shown in Fig. 9.19. The remarks made for sample 6 are also valid here: once again the ratio is quite high at the beginning and decreases in a parabolic way until it saturates to a value of 0.9.
Figure 9.18: 4 and 3 V plateau specific charge for discharge vs. cycle number for sample 7. The 4 and 3 V specific charges were calculated in the potential ranges of 3.3 to 4.3 V and 2.5 to 3.3 V vs. Li/Li⁺, respectively.

Figure 9.19: Ratio of 4 and 3 V plateaux specific charge for discharge vs. cycle number for sample 7. The 4 and 3 V specific charges were calculated in the potential ranges of 3.3 to 4.3 V and 2.5 to 3.3 V vs. Li/Li⁺, respectively.
In order to see if more specific charge can be obtained from these oxides, electrochemical experiments were made, up to a final potential of 4.8 V vs. Li/Li+. Figure 9.20 shows the first two cyclic voltammograms of sample 6. A big irreversible peak is present at 4.65 V, which could be responsible for the phase transformation or could be due to some electrolyte decomposition. The following cycles did not present this peak. The figure also shows that an additional amount of specific charge could be obtained from the oxide.

![Cyclic voltammograms of sample 6](image)

**Figure 9.20:** 1st and 2nd cycle of sample 2 measured between 2.5 and 4.8 V vs. Li/Li+. The sweep rate was 50 μV/s. The electrolyte used was 1 M LiPF$_6$ in EC:DMC 1:1 (w/w).

In the next figure (9.21) the cycling behaviour of the four samples (6 to 9) is displayed. It can be seen that effectively more specific charge could be obtained. For sample 6 the initial specific charge for discharge was 135 Ah/kg, but it decreased to 118 Ah/kg after only 6 cycles. The highest specific charge was obtained with sample 7, which showed 170 Ah/kg for the first discharge. In this case as well, the specific charge could not be retained and dropped to 145 Ah/kg after 6 cycles. A similar behaviour can be observed for the other two samples. It seems that charging the materials up to 4.8 V has a detrimental effect on the stability. The explanation could be that when too many lithium ions are removed from the structure, the latter tends to lose its integrity, and thus the ability to insert lithium ions in a reversible way.
Figure 9.21: Specific charge vs. cycle number for samples 6 to 9. Data were obtained galvanostatically between 2.5 and 4.8 V vs. Li/Li⁺ at 10 mA/g. The electrolyte used was 1 M LiPF₆ in EC:DMC 1:1 (w/w).
9.1.4 Conclusions

Electroactive doped layered lithium manganese oxides with the α-NaFeO₂ structure were synthesised at a low temperature by oxidising the intermetallic phase LiAl with lithiumpermanganate. After the first cycle all the materials tended to transform into the more stable spinel phase. This fact became evident when we analysed the behaviour of the 3 and 4 V plateaux upon cycling. At the beginning the specific charge in the 3 V region was higher than that in the 4 V region, suggesting cation disorder in the structure. This cation disorder was confirmed by the low ratio of the (003) to the (104) peak in the XRD patterns. A specific charge for discharge of ~90 Ah/kg for 50 cycles was obtained for a sample containing 25% aluminium calcined at 250 °C.

9.2 Oxidation of LiAl and CaNi₂ with lithiumpermanganate

In the previous section the synthesis of aluminium doped LiMnO₂ was described. The materials synthesised had a too small specific charge and tended to lose it upon cycling. Furthermore, the tendency to convert to the spinel phase was evident. To avoid the specific charge drop, the incorporation of additional stabilising cations was performed and the resulting materials were characterised electrochemically.

In addition to aluminium, other elements which could be helpful to stabilise the layered structure are, for example, calcium and nickel. While calcium is thought to replace lithium and so to act as an interlayer stabiliser which is not exchanged, nickel stabilises the layered arrangement, as it does in LiNiO₂. Here the reaction consists of the oxidation of two intermetallic phases with lithiumpermanganate. The overall reaction is consistent with the equation:

\[ xLiAl + xCaNi₂ + (1-3x)LiMnO_4 \rightarrow Li_{1-x}Ca_{x}Mn_{1-2x}Ni_{2x}Al_{x}O_2 + (1-6x)O_2 \quad (9.2) \]

9.2.1 Synthesis of the reactants

Synthesis of CaNi₂

For the synthesis of CaNi₂ 0.753 g (18.8 mmol) calcium and 2.208 g (37.6 mmmol) nickel were put into a tantalum tube. The tube was then heated in a tube furnace for three days at a temperature of 900 °C. The heating and cooling rate was 50 °C/h.
9.2.2 Synthesis of the oxides

Stoichiometric amounts of LiAl, CaNi₂ and LiMnO₄•3H₂O were mixed together in a ball mill for 30 minutes, transferred into a crucible and then put into the furnace oven. Four syntheses with \( x = 0.05 \) were performed at different temperatures (see Tab. 9-3).

<table>
<thead>
<tr>
<th>Sample number</th>
<th>Temp. [°C]</th>
<th>Time [h]</th>
<th>Atmosphere</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>300</td>
<td>24</td>
<td>Ar</td>
</tr>
<tr>
<td>11</td>
<td>500</td>
<td>24</td>
<td>Ar</td>
</tr>
<tr>
<td>12</td>
<td>700</td>
<td>48</td>
<td>Ar</td>
</tr>
<tr>
<td>13</td>
<td>900</td>
<td>48</td>
<td>Ar</td>
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</tbody>
</table>

Table 9-3: Synthesis conditions for oxides with \( x = 0.05 \). After 24 h sample 3 and 4 were not homogeneous and therefore calcined for an additional 24 h.

Figure 9.22: Powder XRD patterns of \( \text{Li}_{0.95}\text{Ca}_{0.05}\text{Al}_{0.85}\text{Mn}_{0.85}\text{Ni}_{0.15}\text{O}_2 \) calcined at different temperatures: (a) 300 °C, (b) 500 °C, (c) 700 °C, and (d) 900 °C. • refers to the electroactive phase (layered or spinel), * to an unknown phase and ° to \( \text{Li}_2\text{MnO}_3 \).
Figure 9.22 shows the XRD pattern of the prepared oxides. Once again the identification of the different phases was not easy. As far as samples 10 and 11 are concerned, we thought to be confronted with the same phase as the one obtained in the previous section, namely a layered phase. As concerns samples 12 and 13 the electrochemical results seemed to indicate that the oxides are crystallised in the spinel symmetry. By looking at the two oxidation reactions we can infer that at low temperatures we tend to have the layered form, while at temperatures above 700 °C the spinel phase is more stable. In all the samples there were lines belonging to other phases that could not be identified. The presence of several phases is not surprising since in a system consisting of six elements it is highly unlikely that only one phase can be formed. The phase which started to form at 700 °C could be identified as Li$_2$MnO$_3$.

As remarked above, it was not possible to decide to which phase the electroactive phase belonged by looking only at the XRD patterns. This is for a simple reason: the distinction between the layered and the spinel phase is very difficult as one can see in Fig. 9.23, where very slight differences in the intensities are present. As a consequence we had to take a decision by considering the electrochemical results.

![Figure 9.23: Comparison between the calculated XRD patterns of the cubic spinel and the hexagonal layered phase.](image-url)
9.2.3 Electrochemical characterisation

Fig. 9.24 and 9.25 show the cyclic voltammogram of samples 10 and 13. When looking at the first picture we notice that sample 10 behaves in a way similar to the oxides synthesised by the oxidation of LiAl. As a matter of fact, this sample shows a big irreversible peak during the first charge process located in the 4 V region. This irreversible peak may be the result of a structural change of the material during the first charge, as was the case in the previous oxides. The performance in the 3 V region is also similar. The oxidation and the corresponding reduction take place at 3.05 and 2.7 V, respectively. **This behaviour may suggest that the sample prepared at 300 °C has the same structure as samples 6 to 9, namely a layered structure.** With further cycling this material showed the formation of two peaks in the 4 V region, which are characteristic of the spinel phase. The two single steps (4.05 and 4.15 V on charging, 3.95 and 4.05 V on discharging) are clearly visible already during the 10th cycle. **These results indicate that also this oxide converts into the spinel phase upon cycling.**

![Cyclic voltammogram of samples 10 and 13](image.png)

**Figure 9.24: 1st and 10th cycle of sample 10. The sweep rate was 50 μV/s. The electrolyte used was 1 M LiPF6 in EC:DMC 1:1 (w/w).**

Quite different is the cyclic voltammogram of sample 13 (Fig. 9.25). In this case we do not observe any irreversible peak, which suggests that this oxide does not undergo a
structural modification. As a matter of fact, the cyclic voltammogram shows the characteristics for the spinel peak splitting (maxima at 4.05 and 4.20 V on charging) already during the first charging process, and this indicates that the lithium ions are inserted into the tetrahedral positions from the beginning. The reversible process observed at 4.75 and 4.65 V is also characteristic of the spinel phase. These results seem to suggest that the sample prepared at 900 °C has the spinel phase from the beginning.

By carefully analysing the shape of the cyclic voltammogram of the 10th cycle we see that an additional electrochemical process is detectable. As a matter of fact, we observe an oxidation peak located at 3.75 V and we notice that the corresponding reduction takes place at 3.25 V. The presence of an oxidation peak at 3.7 V was already observed by [79], even if they did not observe any reduction peak. The meaning of these peaks remains to be cleared.

![Figure 9.25: 1st, and 10th cycle of sample 13. The sweep rate was 50 μV/s. The electrolyte used was 1 M LiPF₆ in EC:DMC 1:1 (w/w).](image)

Fig. 9.26 displays the charge-discharge behaviour of samples 10 to 13. The curves were measured galvanostatically between 2.5 and 4.8 V vs. Li/Li⁺ with a specific current of 10 mA/g.
Figure 9.26: Specific charge vs. cycle number for samples 10 to 13 measured galvanostatically between 2.5 and 4.8 V vs. Li/Li⁺ with a specific current of 10 mA/g.

Sample 10 has an initial specific charge for discharge of 141 Ah/kg, which then increases and reaches 154 Ah/kg after three cycles. From this point on the specific charge rapidly decreases, so that after 10 cycles only 108 Ah/kg were obtained. A definitely better performance is shown by sample 11. Although the initial specific
charge for discharge is lower (123 Ah/kg), this amount is increased by further cycling and reaches its maximum after 5 cycles with 150 Ah/kg. This specific charge is then retained without losses. The cycling behaviour of samples 12 and 13 is somehow similar. Both materials showed an initial specific charge for discharge of about 80 Ah/kg which increased upon cycling and reached 100 Ah/kg after 10 cycles. As a general remark it can be said that in this system, materials with a more stable cycling behaviour are obtained by increasing the synthesis temperature. On the contrary, the specific charge decreases when increasing the synthesis temperature.

### 9.2.4 Conclusions

Starting from the results obtained in the previous section we tried to incorporate additional elements in the structure LiMn$_{1-x}$Al$_x$O$_2$. By oxidising LiAl and CaNi$_2$ with lithiumpermangante, electroactive layered materials with the α-NaFeO$_2$ structure were obtained at a low temperature synthesis (300 °C) and spinel materials at a high temperature (900 °C).

After the first cycle the layered materials tended to transform into the more stable spinel phase. A specific charge for discharge of 150 Ah/kg for 10 cycles was obtained for a sample calcined at 500 °C.
Ion-exchange reactions belong to the family of soft-chemistry reactions. Soft-chemistry is regarded as the most appropriate technique for the formation of metastable phases through nonreconstructive phase transformations (topochemistry) and utilisation of low reaction temperatures. Such transformations are ideal for preserving the topotacticity and reversibility of the reaction [36].

As already discussed in section 6.3, LiMnO₂ does not adopt the layered structure exhibited by other LiMO₂ (M = Co and Ni) compounds. On the other hand, α-NaMnO₂ is isostructural with LiCoO₂. Accordingly, ion-exchange reactions with α-NaMnO₂ have been performed in order to obtain layered LiMnO₂ [80,81,98,99]. Ion exchange reactions with molten LiCl, LiBr, or LiI at 450-650 °C yield the lithiated spinel Li₂Mn₂O₄ and orthorhombic LiMnO₂ [98]. On the other hand, exchange reactions with LiCl or LiBr in hexanol [80] or in methanol [81] at low temperatures (T ~150 °C) lead to the layered LiMnO₂. Electrochemical studies showed that this layered LiMnO₂ is unstable towards lithium extraction/insertion and transforms into a spinel-related modification on cycling. This irreversible transformation is due to a migration of the Mn atoms from the Mn layers to the lithium layers [81].

Our idea was to try to avoid this transformation by doping the LiMnO₂ with a stabilising cation such as Al³⁺. We thought that in this way the Jahn-Teller effect, which is responsible for the structural instability, could be suppressed to a certain extent.
10.1 Synthesis of LiMnO₂ and LiMn₁₋₅AlₓO₂

The synthesis of the metastable layered lithium manganese oxide was performed in two steps, i.e. the synthesis of α-NaMnO₂ and α-NaMn₁₋₅AlₓO₂ and the sodium exchange with lithium ions under soft chemistry conditions.

*Synthesis of α-NaMnO₂ and α-NaMn₁₋₅AlₓO₂*

Stoichiometric amounts of MnCO₃, Na₂CO₃, and when needed α-Al₂O₃, were mixed thoroughly and heated at 700-750 °C in a tube furnace under flowing nitrogen for 18 hours. After 9 hours an intermediate grinding was done. The heating and cooling rate was 100 °C/h.

*Ion exchange*

The ion exchange was performed by heating α-NaMnO₂ or α-NaMn₁₋₅AlₓO₂ in a solution of lithium chloride in n-hexanol at 145-155 °C for 6-8 hours. The total amount of LiCl corresponded to a fivefold excess of the amount required for the full exchange of Na with Li. The slurry was then filtered and the precipitate washed with n-hexanol and methanol. Finally, the product was dried overnight at 80 °C.

10.2 Electrochemical characterisation

The electrodes were prepared in form of a pressed pill by mixing together the active material with carbon black (XC72) in a weight ratio 1:1 and with 2 wt % of Teflon as binder. The mixture was suspended in hexane and milled in the ball mill for 5 minutes.

Fig. 10.1 shows the 1st, 2nd, 3rd, and 10th cycle of LiMnO₂ measured between 2.5 and 4.4 V vs. Li/Li⁺. When cycled in this range, two pairs of peaks are visible, one centred around 4 V and one around 3 V. The most important feature is the difference between the first and the following cycles. On the first charge there is a big peak located at about 4 V, which disappears during the second cycle. This fact suggests that a change occurs during the first charge. On the second charge we have an oxidation process at 3.25 V and one at 4.1 V. The reduction processes show only a small change on cycling. The
presence of peaks at both the 4 V and at 3 V in the cyclic voltammogram shows that two essentially different types of lithium sites are present, and this is not to be expected for a layered structure. **In other words, the LiMnO₂ probably converts into the spinel structure.**

![Cyclic Voltammogram](image)

**Figure 10.1:** 1ˢᵗ, 2ⁿᵈ, 3ʳᵈ, and 1⁰ᵗʰ cycle of LiMnO₂. The sweep rate was 50 μV/s.

The electrolyte used was 1 M LiPF₆ in EC:DMC 1:1 (w/w).
These results are in reasonable agreement with the work of Armstrong and Bruce [80,100], however, the large specific charge reported by them could not be recovered. The cycling behaviour of LiMnO₂ is shown in Fig. 10.2.

The first charge is associated with a specific charge of 180 Ah/kg but this falls significantly to only 114 Ah/kg on the subsequent discharge. Thereafter, the specific charge for charge and discharge are quite similar and reach 105 Ah/kg. The same results were obtained by Vitins and West [81]. Thus, the challenge here is to modify LiMnO₂ in order to avoid this structure modification while retaining the layered structure. This was tried by doping the precursor α-NaMnO₂ with aluminium. The next figure (10.3) shows the 1<sup>st</sup>, 2<sup>nd</sup>, 3<sup>rd</sup>, and 10<sup>th</sup> cycle of LiMn₀.₉Al₀.₁O₂.

First of all, one can see that the cyclic voltammogram of this oxide is substantially different from that of LiMnO₂. Secondly, the figure shows that also in this case there is a big difference in the first cycle compared to the following ones. During the first charging an irreversible process takes place at the 4 V plateau, which suggests that a
change occurs. On the second charging there is an oxidation process at 3.15 V and the corresponding reduction at 3.1 V. The following cycles show only small changes and, above all, no formation of 3 and 4 V plateaux. This may suggest that the oxide has only one site available for lithium ions, compared with two different sites in the spinel phase.

Figure 10.3: 1\textsuperscript{st}, 2\textsuperscript{nd}, 3\textsuperscript{rd}, and 10\textsuperscript{th} cycle of LiMn\textsubscript{0.5}Al\textsubscript{0.1}O\textsubscript{2}. The sweep rate was 50 µV/s. The electrolyte used was 1 M LiPF\textsubscript{6} in EC:DMC 1:1 (w/w).
Figure 10.4 shows the cycling behaviour of LiMn$_{0.9}$Al$_{0.1}$O$_2$. The first charge has a specific charge of 146 Ah/kg, but this falls considerably to only 59 Ah/kg on the subsequent discharge. Thereafter, the specific charge for charge and discharge are quite similar and reach 65 Ah/kg. Similar results were obtained by Dahn [101] with the compound Li$_{2/3}$[Li$_{1/6}$Mn$_{5/6}$]O$_2$.

![Figure 10.4: Cycling stability of LiMn$_{0.9}$Al$_{0.1}$O$_2$. Data were obtained galvanostatically between 2.5 and 4.4 V vs. Li/Li$^+$ at 10 mA/g. The electrolyte used was 1 M LiPF$_6$ in EC:DMC 1:1 (w/w).](image)

10.3 Conclusions

The synthesis of layered LiMnO$_2$ and LiMn$_{0.9}$Al$_{0.1}$O$_2$ by ion-exchange reactions from NaMnO$_2$ and NaMn$_{0.9}$Al$_{0.1}$O$_2$ was performed. It was shown that lithium extraction from and re-insertion into the undoped layered manganese oxide is not a reversible intercalation reaction. This conclusion was supported by electrochemical experiments that presented the formation of two peaks, one centred at 3 and the second at 4 V. In other words, the undoped lithium manganese oxide converted to the spinel phase. The
behaviour of the doped LiMn_{0.9}Al_{0.1}O_2 was somehow different. The material did not show the development of the two peaks, but it seemed that the lithium ions were inserted and removed in a single process. These facts suggested that the doped lithium manganese oxide did not assume the spinel structure upon cycling. These results were also supported by new literature data which reported about lithium insertion and extraction from Li_{2/3}[Li_{1/6}Mn_{5/6}]O_2 [101].
Chapter 11

Coprecipitation of Al- and Mn-nitrate

The main advantage of the coprecipitation method is that the starting materials are mixed well so that a high homogeneity of the products can be reached.

11.1 Synthesis

A solution of 1.120 g (3 mmol) $\text{Al(NO}_3\text{)}_3\cdot9\text{H}_2\text{O}$ and one of 3 g (12 mmol) $\text{Mn(NO}_3\text{)}_2\cdot4\text{H}_2\text{O}$ were mixed together. After adding a solution of 0.660 g (15.7 mmol) $\text{LiOH}\cdot\text{H}_2\text{O}$, a yellow-pink precipitate was observed. A slight excess of lithium (5%) was used. The precipitate was dried for 3-4 days at 80 °C and was subsequently heated in a tube furnace at 700 °C. Two reaction times (12 and 24 h) and different stoichiometries were used. The heating and cooling rate was 100 °C/h. The reaction with 20% aluminium is shown as an example:

$$\text{LiOH} \cdot \text{H}_2\text{O} + 0.2\text{Al(NO}_3\text{)}_3 \cdot 9\text{H}_2\text{O} + 0.8\text{Mn(NO}_3\text{)}_2 \cdot 9\text{H}_2\text{O} \rightarrow \text{LiAl}_{0.2}\text{Mn}_{0.8}\text{O}_2$$ (11.1)

11.2 Electrochemical characterisation

The electrode was prepared in form of a pressed pill and consisted of 74 weight per cent (wt %) active material, 18 wt % XC72 soot, 6 wt % SFG6, and 2 wt % oppanol.

The cyclic voltammogram shown in Fig. 11.1 has the typical shape of the lithium manganese spinel oxide but with some important differences in the 4 V region. The reduction peak at 2.7 V can be assigned to the insertion of lithium ions in the octahedral
position 16c of the spinel lattice. The potential response of the lithium insertion/deinsertion in the 4 V region is not structured, which may indicate that the lithium insertion does not proceed as in the spinel, where the lithium ions are intercalated in two different steps (see section 6.2). This absence of structure in the curve of the cyclic voltammogram could be assigned to defects in the spinel structure which may be correlated to the slightly greater cell constant of this oxide found by XRD analysis.

![Cyclic voltammogram of “LiAl₅Mn₄O₂” measured between 2.5 and 4.4 V vs. Li/Li⁺ with a sweep rate of 50 μV/s. The electrolyte used was 1 M LiPF₆ in EC:DMC 1:1 (w/w).](image)

Figure 11.1: Cyclic voltammogram of “LiAl₅Mn₄O₂” measured between 2.5 and 4.4 V vs. Li/Li⁺ with a sweep rate of 50 μV/s. The electrolyte used was 1 M LiPF₆ in EC:DMC 1:1 (w/w).

In Fig. 11.2 the cycling behaviour of “LiAl₅Mn₄O₂” is shown. In the first reduction cycle about 86 Ah/kg were obtained, whereas for the following cycles about 125 Ah/kg could be reversibly cycled between 2.5 and 4.4 V. It is known that spinels cycled over both the 3 and the 4 V plateaux show high specific charge fading. In this case, however, the cycling stability is quite good even if the oxide is cycled over both the 3 and the 4 V plateaux. Even though the cycling stability is good, the amount of specific charge is quite low for a spinel cycled over both the 3 and the 4 V plateaux. Moreover, most of this specific charge is achieved in the 3 V region. A comparison with the 110-115 Ah/kg
achieved for pure manganate spinels shows that this oxide is less suitable as positive electrode.

Figure 11.2: Cycling stability of \( \text{LiAl}_{0.2}\text{Mn}_{0.8}\text{O}_2 \). Data were obtained galvanostatically between 2.5 and 4.4 V vs. Li/Li\(^+\) at 10 mA/g. The electrolyte used was 1 M LiPF\(_6\) in EC:DMC 1:1 (w/w).

In conclusion this synthesis route led to the thermodynamic stable spinel phase for all the samples prepared.
Doped manganese nickel oxides $\text{LiMn}_{1-x}\text{Ni}_x\text{O}_2$

12.1 Introduction

From the work described in the previous chapters we concluded that the main problem associated with the performance of layered manganese oxides was the gradual conversion to the spinel phase and the unsatisfactory specific charge. Previous work of Spahr [39] showed that the layered structure can be stabilised if at least 50% of manganese is substituted by nickel. In this part, the attention will therefore be focused on layered mixed oxides of the type $\text{LiMn}_{1-x}\text{Ni}_x\text{O}_2$.

Previous work on layered mixed Mn/Ni oxides synthesised on a wet chemical route represents a promising starting point for our investigation [39]. The following consideration was made: for the system $\text{LiMn}_{1-x}\text{Ni}_x\text{O}_2$ the material showed the layered structure if the amount of manganese was less than or equal to 50% ($x \geq 0.5$). When $x < 0.5$ the compound converted into the spinel type, which was not at the centre of our interest. Since we are aiming at a material with the highest possible amount of manganese, the starting material for our investigation was $\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$ under such boundary conditions.

12.2 Synthesis of the doped $\text{LiMn}_{1-x}\text{Ni}_x\text{O}_2$ oxides

The preparation started by weighing out appropriate quantities of Mn(II)-, Ni(II)-, and, if needed, Al(III)-nitrate, and dissolving the salts in a 250 ml round-bottomed flask
containing 220 ml of CO₂-free distilled water. This solution was slowly added, under vigorous stirring, to a solution of LiOH/Br₂ dissolved in 135 ml CO₂-free distilled water. The resulting precipitate was then filtered under suction and suspended in a 1.2 equivalent solution of LiOH in distilled water. In addition to that, for the boron-doped oxides another aqueous solution containing H₃BO₃ or B₂O₃ (5 to 50-mole% to the sum of Mn+Ni) was added. The solution was put in an oven set at 80 °C overnight allowing water to evaporate. The resulting solid was then ground in an agate mortar and subsequently transferred to a crucible and heated in a furnace between 750 and 850 °C for 10 hours in flowing oxygen. After cooling the samples were removed from the furnace to room temperature. For the treatment with LiBH₄ the oxides were synthesised as described above. Then, oxide and LiBH₄ were suspended in a round-bottomed flask containing water-free diethyl ether. The suspension was then stirred at room temperature for one week and finally filtered under suction and dried overnight in an oven at 80 °C (see section 12.5.1 for explanation).

12.3 Electrochemical performance of LiMn₀.₅Ni₀.₅O₂

The electrochemical performance of this oxide can be seen in Fig. 12.1 and 12.2.

![Cyclic voltammogram (2nd cycle) of LiMn₀.₅Ni₀.₅O₂ at 50 μV/s in 1 M LiPF₆ EC:DMC 1:1 (w/w).](image)

Figure 12.1: Cyclic voltammogram (2nd cycle) of LiMn₀.₅Ni₀.₅O₂ at 50 μV/s in 1 M LiPF₆ EC:DMC 1:1 (w/w).
Fig. 12.1 shows that this oxide has very interesting electrochemical properties. As a matter of fact, the material is active in the 4 V region and, compared to other manganese oxides, there is no electrochemical activity in the 3 V region. The reversible process that takes place in the 4 V region could be described with the de-insertion from and re-insertion into the octahedral sites of the layered oxide of lithium ions according to the following reaction:

\[
\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2 \leftrightarrow \text{Li}_{1-y}\text{Mn}_{0.5}\text{Ni}_{0.5}\text{O}_2 + y\text{Li}^+ + ye^-
\]

Unfortunately, as one can see in Fig. 12.2, the cycling stability is not satisfactory.

Figure 12.2: Cycling stability of LiMn$_{0.5}$Ni$_{0.5}$O$_2$. Data were obtained galvanostatically between 2.5 and 4.4 V vs. Li/Li$^+$ at 10 mA/g. The electrolyte used was 1 M LiPF$_6$ in EC:DMC 1:1 (w/w).

12.4 DEMS investigations on LiMn$_{0.5}$Ni$_{0.5}$O$_2$

Another aspect that made this oxide very attractive as starting material for our investigations was related to the safety aspects of the Li-ion cell. It is known that all commonly used lithium metal oxides become highly oxidising if they are delithiated.
Such delithiated oxides can then oxidise the lithium salt and/or the solvent. When using organic carbonates as solvent we must expect the release of CO₂. This gas evolution increases the internal pressure of the cell and leads to serious safety problems. The release of gases can be easily detected by Differential Electrochemical Mass Spectrometry (DEMS). Using this method Imhof et al. detected CO₂ evolution at LiNiO₂, LiCoO₂ and LiMn₂O₄ electrodes when propylene carbonate (PC) was the solvent. On the contrary, when using ethylene carbonate/dimethylcarbonate (EC/DMC), CO₂ evolution was only detected at LiNiO₂ [102]. Thus, both LiCoO₂ and LiMn₂O₄ are safer than LiNiO₂ as concerns the problem of gas evolution. Starting from these considerations it was interesting to investigate the behaviour of the mixed oxide LiMn₀.₅Ni₀.₅O₂ on overcharge. As a matter of fact, the presence of nickel in this oxide could be critical for the reasons reported above.

12.4.1 Experimental

Two different electrolytes were used, based on PC and a 1:1 w/w mixture of EC/DMC, both with 1 M LiPF₆ as the electrolyte salt. The electrode was prepared as follows. The oxide (45 wt %), carbon black XC72 (45 wt %), and PVDF (10 wt %) were suspended in 1-methyl-2-pyrrolidinone and then mixed. About 0.5 mg of this mixture were deposited onto a 60 μm thick GORE-TEX ePTFE pV 9008 membrane (pore size 0.02 μm) using an airbrush. Metallic lithium was used as the counter and reference electrode. The measurements were carried out potentiodynamically by cycling the working electrode between 3.5 and 5.5 V vs. Li/Li⁺ with a scan rate of 0.4 mV/s.

12.4.2 Results

Fig. 12.3 shows mass spectrometric cyclic voltammograms of mass m/z = 44, representing CO₂, recorded for the oxide LiMn₀.₅Ni₀.₅O₂ in the two different electrolytes. One can observe that when the PC based electrolyte was used, an evolution of CO₂ (and other decomposition products such as propanal and 2-ethyl-4-methyl-1,3-dioxolane, not displayed in the figure) were detected. This behaviour is not different from the one observed when using other oxides, i.e. LiNiO₂, LiCoO₂ and LiMn₂O₄.
On the contrary, with EC/DMC as electrolyte no gas evolution was detected. Thus, these results underline the suitability of this mixed oxide as a material in the positive electrode of the Li-ion battery.

Figure 12.3: Mass spectrometric cyclic voltammograms of mass m/z = 44, representing CO₂ recorded at LiMn₀.₅Ni₀.₅O₂ electrodes in 1 M LiPF₆ in PC (a) and 1 M LiPF₆ in EC:DMC 1:1 (w/w) (b).
12.4.3 Conclusions

Although both, electrochemical cycling and the DEMS experiments showed that this oxide is promising as electrode material, further improvements had to be made. As a matter of fact, it can be clearly seen from figures 12.1 and 12.2 that despite having an activity in the 4 V region, the material does not show a stable behaviour towards electrochemical cycling. A specific charge of 120 Ah/kg was obtained during the first discharge cycle but this specific charge continuously dropped upon cycling, reaching about 80 Ah/kg after 15 cycles. Therefore, we attempted to improve the cycling stability of the mixed oxide via doping with additional elements.

12.5 Doping of LiMn$_{0.5}$Ni$_{0.5}$O$_2$

12.5.1 What kind of doping?

The primary task was to elucidate how the cycling stability could be stabilised without losing too much in specific charge and without destroying the layered structure. Three methods were found that, at least theoretically, could improve the cycling stability of the material:

- doping by aluminium
- doping by boric acid
- treatment by LiBH$_4$

The expected positive effects of the aluminium doping were already discussed in section 6.3.1.

Boron doped oxides are already known. Several patents reported about batteries with boron-doped LiCoO$_2$ as the active cathode material [103-105]. In all the cases, a small amount of cobalt was replaced by boron. In this research boron was used, but in a different way. The boron doping was performed since borate groups are supposed to stabilise the redox-active parts of the structure against decomposition, both under the cation movements and under the Jahn-Teller distortions. This effect is clearly visible in Fig. 12.4, where the structure of the mineral Pinakiolite is shown. In this compound, the
manganese octahedra are held together by the borate groups BO₃ which render this structure quite flexible.

A first attempt to introduce boron consisted in a treatment of the precipitated and tempered oxide with H₃BO₃ (or B₂O₃) at different temperatures, while a second attempt consisted in the treatment of the oxide with LiBH₄. We used lithiumhydridoborate since we know that oxides synthesised by a wet chemistry route may exchange Li⁺ against protons and this phenomenon would degrade the electrode. We believed that LiBH₄ could act as a bifunctional reactant since the hydride-ion H⁻ can remove the protons. At the same time, the presence of borate-groups could introduce a geometrical stabilisation.

12.5.2 Electrochemical measurements

The electrodes were prepared in form of a pressed pill and consisted of 74 weight per cent (wt %) active material, 18 wt % XC72 soot, 6 wt % SFG6, and 2 wt % oppanol. All measurements were performed in ethylene carbonate:dimethyl carbonate (EC:DMC) 1:1 (w/w) with LiPF₆ 1M. If not specified otherwise, we used a specific current of 10 mA/g of active material (corresponding to about C/10). For cyclic voltammetry experiments a scan rate of 50 μV/s was applied.
12.5.3 Results and discussion

12.5.3.1 Doping by aluminium

X-ray analysis

In this case the idea was to replace a small amount of the electroactive transition metal (Mn or Ni) by the redox inactive aluminium.

Table 12-1 shows the composition of the prepared aluminium doped LiMn_{1-x-y}Ni_{x}Al_{y}O_{2} oxides.

Table 12-1: Nominal composition of the oxides prepared.

<table>
<thead>
<tr>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiMn_{0.5}Ni_{0.4}Al_{0.1}O_{2}</td>
</tr>
<tr>
<td>LiMn_{0.5}Ni_{0.3}Al_{0.2}O_{2}</td>
</tr>
<tr>
<td>LiMn_{0.4}Ni_{0.4}Al_{0.2}O_{2}</td>
</tr>
<tr>
<td>LiMn_{0.4}Ni_{0.5}Al_{0.1}O_{2}</td>
</tr>
<tr>
<td>LiMn_{0.3}Ni_{0.5}Al_{0.2}O_{2}</td>
</tr>
</tbody>
</table>

For all the compositions three different temperatures were applied: 750, 800 and 850 °C. The XRD patterns of the products prepared at 800 °C are shown in Fig. 12.5.

The XRD patterns show that single-phase LiMn_{1-x-y}Ni_{x}Al_{y}O_{2} compounds were obtained. The patterns of the different oxides, showing the typical diffraction peaks of the α-NaFeO_{2}-type, were indexed in the hexagonal crystal system (space group R 3m). According to this hexagonal symmetry, the corresponding a and c cell parameters were calculated (see Tab. 12-2).
Figure 12.5: XRD patterns for LiMn$_{1-x}$Ni$_x$Al$_2$O$_4$ for different x and y values prepared at 800 °C. The indexes refer to a hexagonal symmetry (space group $R\bar{3}m$).
Table 12-2: Crystallographic cell parameters obtained from XRD experiments for LiMn$_{1-x}$Ni$_x$Al$_y$O$_2$ sintered at 800 °C.

<table>
<thead>
<tr>
<th>x</th>
<th>y</th>
<th>a [Å]</th>
<th>c [Å]</th>
<th>V [Å$^3$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>0.0</td>
<td>2.89</td>
<td>14.28</td>
<td>103.6 ± 0.1</td>
</tr>
<tr>
<td>0.4</td>
<td>0.1</td>
<td>2.86</td>
<td>14.21</td>
<td>100.7 ± 0.1</td>
</tr>
<tr>
<td>0.4</td>
<td>0.2</td>
<td>2.85</td>
<td>14.18</td>
<td>99.7 ± 0.1</td>
</tr>
<tr>
<td>0.5</td>
<td>0.1</td>
<td>2.87</td>
<td>14.18</td>
<td>101.1 ± 0.1</td>
</tr>
<tr>
<td>0.3</td>
<td>0.2</td>
<td>2.86</td>
<td>14.24</td>
<td>100.9 ± 0.1</td>
</tr>
<tr>
<td>0.5</td>
<td>0.2</td>
<td>2.87</td>
<td>14.24</td>
<td>101.6 ± 0.1</td>
</tr>
</tbody>
</table>

As a general remark it can be said that by doping LiMn$_{0.5}$Ni$_{0.5}$O$_2$ with aluminium a decrease in the cell volume was observed. This decrease in the cell volume was larger when aluminium replaced nickel. The decrease in the c-direction implies a decrease in the distance between the layers of the transition metal octahedra. This stronger attraction between the layers could render the doped oxides more stable for lithium insertion and extraction. Electrochemical experiments should bring more detailed information.

**Summing up, doping by aluminium was achieved in homogeneous phase under preservation of the layered structure of LiMn$_{0.5}$Ni$_{0.5}$O$_2$.**

*Electrochemical behaviour in function of the oxide composition*

Fig. 12.6 shows cyclic voltammograms of LiMn$_{1-x-y}$Ni$_x$Al$_y$O$_2$. In all the oxides prepared, a reversible lithium insertion/de-insertion process occurs between 3 and 4.4 V vs. Li/Li$^+$. In these potentiodynamic experiments a specific charge of about 120-130 Ah/kg was obtained for LiMn$_{0.5}$Ni$_{0.5}$O$_2$, LiMn$_{0.5}$Ni$_{0.4}$Al$_{0.1}$O$_2$, and LiMn$_{0.5}$Ni$_{0.3}$Al$_{0.2}$O$_2$. For the other three oxides, LiMn$_{0.4}$Ni$_{0.4}$Al$_{0.2}$O$_2$, LiMn$_{0.4}$Ni$_{0.5}$Al$_{0.1}$O$_2$, and LiMn$_{0.3}$Ni$_{0.5}$Al$_{0.2}$O$_2$, a specific charge of 60, 80 and 100 Ah/kg was obtained, respectively. In order to decide which oxides were worth investigating in more detail, galvanostatic measurements were made and the specific charge after 5 cycles was compared. The results are shown in Fig. 12.7 as a function of the calcination temperature.
Figure 12.6: Cyclic voltammograms (first cycle) of LiMn$_{1-x,y}$Ni$_x$A$_y$O$_2$ prepared at 800 °C at 50 μV/s in 1 M LiPF$_6$ EC:DMC 1:1 (w/w).
Figure 12.7: Specific charge (discharge) obtained after 5 cycles for LiMn$_{1-x}$Ni$_{y}$Al$_{z}$O$_2$ in function of the calcination temperature. Data were obtained galvanostatically between 2.5 and 4.4 V vs. Li/Li$^+$ at 10 mA/g. The electrolyte used was 1 M LiPF$_6$ in EC:DMC 1:1 (w/w).

These results confirm the previous impressions obtained with potentiodynamical experiments. As a matter of fact, the highest specific charge was achieved with an oxide doped with 10% aluminum (x = 0.4, y = 0.1) calcined at 800 °C. A calcination temperature of 800 °C gave the best results in most cases and was therefore chosen as the optimal calcination temperature for further syntheses.

Furthermore, one can see from Fig. 12.7 that the two oxides with 50% manganese in the structure presented the best performance, which seems to indicate a particular stability of these compositions. This phenomenon may be related to the fact that in this mixed metal oxide the manganese is oxidised first [39]. The fact that these two oxides showed the best performance was really a success, since at the end we wanted a material with the highest possible amount of manganese. The samples with a manganese content inferior to 50% yielded specific charges which were too low and were not investigated in more detail. Starting from these considerations we decided to
further investigate the two oxides with 50% manganese \((x = 0.3, y = 0.2; x = 0.4, y = 0.1)\).

**Investigations on \(LiMn_{0.5}Ni_{0.3}Al_{0.2}O_2\)**

Fig. 12.8 shows the cycling stability of \(LiMn_{0.5}Ni_{0.3}Al_{0.2}O_2\) prepared at different temperatures. For this composition no significant influence of the calcination temperature was observed, neither on the cycling stability nor on the specific charge obtained.

![Figure 12.8](image)

**Figure 12.8:** Specific charge for discharge of \(LiMn_{0.5}Ni_{0.3}Al_{0.2}O_2\) prepared at different temperatures. Data were obtained galvanostatically between 2.5 and 4.4 V vs. Li/Li\(^+\) at 10 mA/g. The electrolyte used was 1 M LiPF\(_6\) in EC:DMC 1:1 (w/w).

Fig. 12.9 shows the coulometric titration curve for \(LiMn_{0.5}Ni_{0.3}Al_{0.2}O_2\) in the potential range between 3.3 and 4.4 V vs. Li/Li\(^+\). In this galvanostatic experiment, constant current pulses of 7 mA/g were let pass through the cell for 300 s. After each pulse the current was switched off and the cell relaxed until the cell voltage reached equilibrium conditions. In this experiment equilibrium was defined as the situation when the cell voltage did not change more than 1 mV per hour or after 20000 s.
Figure 12.9: Coulometric titration curve for LiMn_{0.5}Ni_{0.3}Al_{0.2}O_2 using 1 M LiPF_6 in EC:DMC 1:1 (w/w) as electrolyte. Pulses of 300 s with a specific current of 7 mA/g were applied.

The equilibrium potential rises rapidly up to 3.8 V vs. Li/Li^+, corresponding to a lithium extraction of x = 0.1. From this point onwards the equilibrium potential rises gradually until it reaches 4.4 V vs. Li/Li^+ at a lithium content of x = 0.6, corresponding to a specific charge of 185 Ah/kg.

In order to verify the positive effect of the aluminium doping, long time experiments were made. Figure 12.10 shows the cycling performance of the LiMn_{0.5}Ni_{0.3}Al_{0.2}O_2 oxide. These results were measured galvanostatically in the potential window 2.5-4.4 V vs. Li/Li^+ with a specific current of 10 mA/g.

The curve shown in the figure demonstrates the excellent cycling behaviour of this oxide. The material showed an initial specific charge of 123 Ah/kg, which still reached 113 Ah/kg after 200 cycles. This means that there was a loss of 5 Ah/kg for 100 cycles. To our best knowledge such an excellent performance was never achieved before for mixed manganese nickel oxides.
Figure 12.10: Cycling stability of LiMn$_{0.5}$Ni$_{0.3}$Al$_{0.2}$O$_{2}$. Data were obtained galvanostatically between 2.5 and 4.4 V vs. Li/Li$^+$ at 10 mA/g. The electrolyte used was 1 M LiPF$_6$ in EC:DMC 1:1 (w/w).

Figure 12.11: Discharge curves for the 1$^{st}$, 10$^{th}$, 50$^{th}$, 100$^{th}$ and 200$^{th}$ cycle of LiMn$_{0.5}$Ni$_{0.3}$Al$_{0.2}$O$_{2}$. The electrolyte used was 1 M LiPF$_6$ in EC:DMC 1:1 (w/w).
This remarkable reversibility upon cycling is also shown in Fig. 12.11, where the discharge curves for the 1st, 10th, 50th, 100th and 200th cycle are displayed. From the picture one can see that the lithium ions were mainly inserted between 3.7 and 4.3 V vs. Li/Li⁺ and that no electrochemical reaction occurred below 3 V. This is a very different behaviour from the one of the other doped oxides discussed in the previous chapters. These, in fact tended to convert from a layered to a spinel structure.

The absence of any structural change is one of the reasons that make this oxide a good candidate for the positive electrode in Li-ion batteries. To confirm the preservation of the layered structure, differential specific charge plots were calculated from the galvanostatic experiments reported in Fig. 12.10. Fig. 12.12 shows these results. The simple charge-discharge process did not change significantly upon cycling. The only change was a very small decrease in the magnitude of the oxidation and reduction peaks. A stronger reduction of the magnitude of these peaks would indicate a gradual structural change of the oxide to an amorphous state due to a high cationic disorder or to a Jahn-Teller distortion of the manganese octahedra. Since this was not the case with this oxide, it can be said that aluminium proved, as expected, to have an enormously positive effect on the cycling behaviour of the LiMn₀.₅Ni₀.₅O₂ oxide.

![Figure 12.12: Differential specific charge plots calculated from the galvanostatic experiments shown in Fig. 12.10. The electrolyte used was 1 M LiPF₆ in EC:DMC 1:1 (w/w).](image-url)
Experiments with different specific currents were performed in order to test how fast the oxide can be charged and discharged. As a matter of fact, for use in practical applications an electrode material should also work at high current densities without losing too much specific charge. Fig. 12.13 shows the dependence of the specific charge of the oxide on the specific current applied (10 mA/g, 50 mA/g and 100 mA/g corresponding to C/10, C/2 and C/1, respectively). It can be observed that by increasing the specific current, the specific charge obtained is still a large fraction of the specific charge obtained by cycling at low rate. For a discharge rate of C/2 110 Ah/kg were obtained, while discharging at C/1 gave a specific charge of 100 Ah/kg. In one experiment a cell was charged and discharged at a C/2 rate for 200 cycles and delivered at the end 80 Ah/kg. By subsequently cycling the same cell at C/10, the specific charge obtained was 110 Ah/kg, which indicated that the oxide remained unaffected by the rather high specific current applied for the first 200 cycles.

![Figure 12.13: Specific charge for discharge of LiMn0.5Ni0.3Al0.2O2 prepared at 800 °C at different current densities. Data were obtained galvanostatically between 2.5 and 4.4 V vs. Li/Li+. The electrolyte used was 1 M LiPF6 in EC:DMC 1:1 (w/w).](image-url)
Figure 12.14: Discharge curves of LiMn$_{0.5}$Ni$_{0.5}$Al$_{2.5}$O$_2$ prepared at 800 °C at different current densities. The electrolyte used was 1 M LiPF$_6$ in EC:DMC 1:1 (w/w).

Figure 12.15: Comparison between the cycling stability of the undoped oxide (LiMn$_{0.5}$Ni$_{0.5}$O$_2$) and the oxide with 20 % aluminium (LiMn$_{0.5}$Ni$_{0.5}$Al$_{2.5}$O$_2$). Data were obtained galvanostatically between 2.5 and 4.4 V vs. Li/Li$^+$ at 10 mA/g. The electrolyte used was 1 M LiPF$_6$ in EC:DMC 1:1 (w/w).
Fig. 12.14 shows the discharge curves for the three different specific currents investigated. The decrease in potential with increasing discharge current is obviously due to the internal resistance of the cell.

To underline the beneficial effect of the aluminium doping once more, the comparison of the specific charge obtained with the oxide without aluminium and the one with 20% aluminium is shown in Fig. 12.15. As one can see, the drop in the specific charge for the undoped oxide was dramatic, and took place after few cycles, while the oxide containing aluminium did not lose specific charge significantly.

A big problem encountered with some transition metal oxides used for the cathode material in Li-ion batteries is their tendency to react with the surrounding atmosphere so that their electrochemical performance is negatively affected. For example, LiNiO$_2$ reacts quite rapidly with air and builds Li$_2$CO$_3$ on the particle surface. This coating on the particle surface is detrimental for the performance of an electrode made with this oxide. For this reason, the storage capability of the oxide to be used in Li-ion batteries should be good. In order to investigate if our oxide deteriorated significantly or not, a first sample was prepared and measured immediately, while a second sample was kept in an air atmosphere for one month and then measured. Fig. 12.16 shows the discharge curves of these two samples.

![Discharge curves](image)

**Figure 12.16: Discharge curves (1st cycle) of LiMn$_{0.5}$Ni$_{0.3}$Al$_{0.2}$O.** One curve was measured immediately after the sample preparation, the other curve after leaving the sample for one month in an air atmosphere. The electrolyte used was 1 M LiPF$_6$ in EC:DMC 1:1 (w/w).
Interestingly enough, no changes in the shape or in the specific charge obtained were observed. This behaviour, which is different from the one obtained for LiNiO₂, is another point in favour of the doped oxides.

Another aspect to be considered in evaluating the suitability of a material to be used in the positive electrode of the Li-ion battery is their electrochemical performance at elevated temperatures. As a matter of fact, Li-ion batteries may be subjected to storage at elevated temperatures in unventilated consumer products. This problem stands in the way of the wider use of the lithium manganese spinel as cathode material. One of the reasons for this poor performance at high temperatures was attributed to the chemical instability of the spinels towards manganese dissolution [71]. This manganese dissolution was found to be induced by traces of acids (e.g. HF) in the electrolyte [106]. Lanz et al. found that at 55 °C (which is the temperature normally used when the high temperature effect is investigated) the specific charge fading of most spinels, related to the cycle number, occurs 5 to 10 times faster than at 25 °C (room temperature). While at 25 °C the best spinel still had 80 % of its initial specific charge after 200 cycles, the same spinel cycled at 55 °C reached 80 % of its initial specific charge after only about 60 cycles [68].

Figure 12.17: Specific charge for discharge of LiMn₀.₅Ni₀.₃Al₀.₂O₂ at room temperature and at 55 °C. Data were obtained galvanostatically between 2.5 and 4.4 V vs. Li/Li⁺ at 10 mA/g. The electrolyte used was 1 M LiPF₆ in EC:DMC 1:1 (w/w).
Fig. 12.17 shows the evolution of the specific charge for discharge of the LiMn$_{0.5}$Ni$_{0.3}$Al$_{0.2}$O$_2$ oxide at room temperature and at 55 °C. As one can see, the cycling stability at 55 °C is as good as the one measured at room temperature. In addition, due to the higher temperature the kinetics are faster, allowing to get a higher specific charge. Once more this oxide turned out to have very interesting properties when compared to other oxides (e.g. LiMn$_2$O$_4$).

Summing up, the expected beneficial effect of the aluminium doping in the oxide LiMn$_{0.5}$Ni$_{0.5}$O$_2$ was confirmed. An aluminium content of 20 % did not affect the layered structure of the starting oxide LiMn$_{0.5}$Ni$_{0.5}$O$_2$. The electrochemical experiments performed on the doped oxide revealed the enormous positive effect of aluminium on the cycling stability. More than 200 cycles were demonstrated with a specific charge loss of 4 % every 100 cycles. Differential specific charge plots were calculated and revealed that this doped oxide did not undergo structural modification. This structural stability may be due to counteracting the Jahn-Teller distortions of the redox active centres by the aluminium atoms present in the transition metal layers. Measurements were performed in order to check if high temperatures have the same negative effect on the cycling stability as was found with lithium manganese spinels. The results revealed that the cycling stability of the aluminium doped oxides was not affected by the high temperatures.

Investigations on LiMn$_{0.5}$Ni$_{0.4}$Al$_{0.1}$O$_2$

The next material investigated in detail was LiMn$_{0.5}$Ni$_{0.4}$Al$_{0.1}$O$_2$. On the one hand, we expected this oxide to show a slightly higher specific charge, due to the lower content of the redox inactive aluminium. On the other hand, the problem was to find out if this lower amount of aluminium would still be large enough to achieve a similar cycling stability as obtained with LiMn$_{0.5}$Ni$_{0.3}$Al$_{0.2}$O$_2$.

Fig. 12.18 shows the cycling stability of LiMn$_{0.5}$Ni$_{0.4}$Al$_{0.1}$O$_2$ prepared at different temperatures. This oxide, compared to the previous one (LiMn$_{0.5}$Ni$_{0.3}$Al$_{0.2}$O$_2$), presented quite a strong dependence on the calcination temperature. While the specific charge of the two samples prepared at 800 and 850 °C remained practically constant for 5 cycles, the specific charge of the sample prepared at 750 °C almost immediately dropped of about 15 % after 5 cycles. The highest specific charge was obtained with the sample
calcined at 800 °C, which proved once more to be the optimal synthesis temperature. This specific charge of 140 Ah/kg is about 10% higher than the one obtained for LiMn$_{0.5}$Ni$_{0.3}$Al$_{0.2}$O$_2$. This result was expected due to the lower content of the redox inactive aluminium.

![Figure 12.18: Specific charge for discharge of LiMn$_{0.5}$Ni$_{0.4}$Al$_{0.1}$O$_2$ prepared at different temperatures. Data were obtained galvanostatically between 2.5 and 4.4 V vs. Li/Li$^+$ at 10 mA/g. The electrolyte used was 1 M LiPF$_6$ in EC:DMC 1:1 (w/w).](image)

In order to decide if the lower amount of aluminium in the oxide is still high enough to achieve the same cycling stability as in LiMn$_{0.5}$Ni$_{0.3}$Al$_{0.2}$O$_2$, long time experiments were performed with the samples prepared at 800 and 850 °C. Fig 12.19 shows the results of this long time experiment. The cycling performance of both oxides is excellent. For the one prepared at 850 °C a specific charge of about 125 Ah/kg was achieved after 180 cycles, without any loss. On the contrary, a slight increase from 117 Ah/kg during the first cycle to 125 Ah/kg during the 180$^{th}$ cycle was observed. The oxide prepared at 800 °C showed a similar performance with an initial specific charge of 141 Ah/kg which remained practically constant for more than 60 cycles. This specific charge of about 140 Ah/kg seems to be high enough to make this electrode material a real candidate for substituting LiCoO$_2$ in Li-ion batteries.
Figure 12.19: Cycling stability of two LiMn$_{0.5}$Ni$_{0.4}$Al$_{0.1}$O$_2$ oxides prepared at 800 and 850 °C. Data were obtained galvanostatically between 2.5 and 4.4 V vs. Li/Li$^+$ at 10 mA/g. The electrolyte used was 1 M LiPF$_6$ in EC:DMC 1:1 (w/w).

Figure 12.20: Discharge curves for the 1st, 10th and 60th cycle of LiMn$_{0.5}$Ni$_{0.4}$Al$_{0.1}$O$_2$ prepared at 800 °C. The electrolyte used was 1 M LiPF$_6$ in EC:DMC 1:1 (w/w).
This outstanding reversibility upon cycling is also shown in Fig. 12.20, where the discharge curves of LiMn$_{0.5}$Ni$_{0.4}$Al$_{0.1}$O$_2$ prepared at 800 °C for the 1$^{\text{st}}$, 10$^{\text{th}}$ and 60$^{\text{th}}$ cycle are displayed. As in the sample with 20 % aluminium, the lithium ions are inserted into the layers of the structure mainly between 3.7 and 4.3 V vs. Li/Li$^+$. The absence of any additional plateau formation during cycling indicated that even this oxide with only 10 % aluminum in the structure did not undergo structural change. This fact confirmed once more the advantage of stabilising the layered structure by aluminium. Fig. 12.21 shows the evolution of the specific charge for discharge of the LiMn$_{0.5}$Ni$_{0.4}$Al$_{0.1}$O$_2$ oxide prepared at 800 °C, both at room temperature and at 55 °C. As one can see, the cycling stability at 55 °C is as good as the one measured at room temperature. The initial specific charge achieved at 55 °C was 155 Ah/kg and remained constant for 50 cycles. Again, the higher amount obtained at 55 °C is due to a faster kinetics.

One of the reasons why we decided to take aluminium as doping element (see section 6.3.1) was its effect on the insertion potential of some oxides [85]. In earlier studies, it was calculated that LiAlO$_2$ has a theoretical insertion potential of ~ 5 V vs. Li/Li$^+$ and so it was suggested that the solid solution of LiAlO$_2$ with other lithiated transition metal oxides may increase the insertion potential of lithium ions. This effect was verified for LiCo$_{1-x}$Al$_x$O$_2$ [86] and for LiNi$_{1-x}$Al$_x$O$_2$ [107].

The question was whether this phenomenon would also appear in our doped mixed lithium manganese nickel oxide. Fig. 12.22 shows a comparison of the discharge curves obtained for the undoped oxide LiMn$_{0.5}$Ni$_{0.5}$O$_2$ and for the oxide doped with 10 % aluminium LiMn$_{0.5}$Ni$_{0.4}$Al$_{0.1}$O$_2$ (prepared at 800 °C). One can see that the doped oxide exhibits an insertion potential which is about 150 mV higher than the one obtained for the undoped oxide. As a result, this increase in the insertion potential would enhance the specific energy of the cell.

Summing up, the beneficial effect of aluminium was confirmed also in an oxide doped with only 10 % of the redox inactive aluminium. A specific charge of 140 Ah/kg for 60 cycles was demonstrated for LiMn$_{0.5}$Ni$_{0.4}$Al$_{0.1}$O$_2$ prepared at 800 °C. Measurements at 55 °C gave a specific charge of 155 Ah/kg for more than 50 cycles.
without any significant loss. Moreover, the predicted positive effect of aluminium on the insertion potential was confirmed.

![Graph showing specific charge for discharge of LiMn_{0.5}Ni_{0.4}Al_{0.1}O_2 (prepared at 800 °C) at room temperature and at 55 °C. Data were obtained galvanostatically between 2.5 and 4.4 V vs. Li/Li⁺ at 10 mA/g. The electrolyte used was 1 M LiPF₆ in EC:DMC 1:1 (w/w).](image1)

**Figure 12.21:** Specific charge for discharge of LiMn_{0.5}Ni_{0.4}Al_{0.1}O_2 (prepared at 800 °C) at room temperature and at 55 °C. Data were obtained galvanostatically between 2.5 and 4.4 V vs. Li/Li⁺ at 10 mA/g. The electrolyte used was 1 M LiPF₆ in EC:DMC 1:1 (w/w).

![Graph showing comparison of the discharge curves of the undoped oxide (LiMn_{0.5}Ni_{0.5}O_2) and of the oxide doped with 10 % aluminium (LiMn_{0.5}Ni_{0.4}Al_{0.1}O_2) prepared at 800 °C. The electrolyte used was 1 M LiPF₆ in EC:DMC 1:1 (w/w).](image2)

**Figure 12.22:** Comparison of the discharge curves of the undoped oxide (LiMn_{0.5}Ni_{0.5}O_2) and of the oxide doped with 10 % aluminium (LiMn_{0.5}Ni_{0.4}Al_{0.1}O_2) prepared at 800 °C. The electrolyte used was 1 M LiPF₆ in EC:DMC 1:1 (w/w).
12.5.3.2 Doping by borate groups

As explained above, boron, in form of BO$_3$ groups, was also expected to have a beneficial effect on the structural stability of the oxide upon lithium insertion and de-insertion. Three different oxides with different amounts of boron doping (5, 25 and 50-mole% to the sum of Mn and Ni) were prepared and characterised. Fig. 12.23 shows the cycling performance of the three oxides with the different boron content.

![Figure 12.23: Specific charge for discharge of boron doped LiMn$_{0.5}$Ni$_{0.5}$O$_2$ (prepared at 800 °C) with different boron content. Data were obtained galvanostatically between 2.5 and 4.4 V vs. Li/Li$^+$ at 10 mA/g. The electrolyte used was 1 M LiPF$_6$ in EC:DMC 1:1 (w/w).]

As one can see, a doping amount of 5% is already sufficient to stabilise the oxide in a significant way. A comparison with the cycling behaviour of the undoped oxide (Fig. 12.2) clearly shows the positive effect of boron. For the first cycle a specific charge of 122 Ah/kg was obtained, which raised to a value of 125 Ah/kg after 10 cycles. Unfortunately, it was not possible to locate the borate-groups exactly and to figure out how they act. What we could observe here was only the enhancement in the cycling stability, but this was our final goal. The figure also shows that a too high amount of boron reduced the cycling stability again. A possible reason for this could be that the
layers were somehow blocked so that the diffusion of the lithium ions in the insertion and de-insertion process was hindered. This suggestion is supported by the fact that by increasing the boron content the specific charge dropped significantly.

Fig. 12.24 shows the discharge curves for the three boron doped oxides. One can see that there is a big difference in the average discharge potential of the three oxides. While the oxide doped with 5 % boron inserted lithium ions mainly between 3.7 and 4.3 V vs. Li/Li⁺, the other two oxides inserted lithium ions between 3.7 and 3.9 V vs. Li/Li⁺. Up to a potential of 3.7 V vs. Li/Li⁺ the shape of the curve for the oxide with 50 % boron doping is very similar to the one obtained for the oxide with 25 %. From this point on the discharge curve of the former dropped suddenly, indicating that no more lithium ions were inserted. This effect could be attributed to the fact that the layers were somehow blocked by unidentified boron compounds.

Figure 12.24: Discharge curves (1st cycle) of boron doped LiMn₀.₅Ni₀.₅O₂ prepared at 800 °C. The electrolyte used was 1 M LiPF₆ in EC:DMC 1:1 (w/w).

Summing up, it can be said that also the doping with boron groups gave satisfying results. For LiMn₀.₅Ni₀.₅O₂ doped with 5 % H₃BO₃ a constant specific charge of 125 Ah/kg was obtained for the first 10 cycles.
12.5.3.3 Treatment by LiBH₄

As mentioned above, the idea was basically to remove protons by reaction with H⁺, to introduce Li⁺ instead and at the same time boron. First of all, the possible effects of this treatment on the structure of the oxide were investigated. Fig. 12.25 shows the XRD patterns of the oxide LiMn₀.₅Ni₀.₅O₂ treated with LiBH₄ (1:1 molar ratio). The patterns could be indexed in the space group R₃m, the same as the one of the oxides doped with aluminium (cell constants: a = 2.86 Å, c = 14.21 Å). **Thus, the boron-doped structure remains a layered one, too.**

![Figure 12.25: XRD patterns of the oxide LiMn₀.₅Ni₀.₅O₂ treated with LiBH₄ (1:1 molar ratio).](image)

Fig. 12.26 shows the cyclic voltammogram of the 1ˢᵗ, 10ʰ and 20ʰ cycle of LiMn₀.₅Ni₀.₅O₂ treated with LiBH₄. Once again a reversible lithium insertion and de-insertion process occurred between about 3.2 and 4.4 V vs. Li/Li⁺. In Fig. 12.27 we see that lithium ions were mainly inserted between 3.7 and 4.4 V vs. Li/Li⁺.
Figure 12.26: Cyclic voltammogram (1st, 10th and 20th cycle) of LiMn$_{0.5}$Ni$_{0.5}$O$_2$ treated with LiBH$_4$ (molar ratio 1:1) at 50 μV/s in 1 M LiPF$_6$ EC:DMC 1:1 (w/w).

Figure 12.27: Discharge curves of LiMn$_{0.5}$Ni$_{0.5}$O$_2$ treated with LiBH$_4$ (molar ratio 1:1). The electrolyte used was 1 M LiPF$_6$ in EC:DMC 1:1 (w/w).
Fig. 12.28 shows the cycling performance of LiMn_{0.5}Ni_{0.5}O_2 treated with LiBH_4. One clearly notices that the material has an excellent cycling stability with a low irreversible specific charge. Moreover, the irreversible specific charge obtained in the first cycle (~30%) has decreased compared to the untreated oxide (80%, see Fig. 12.2), indicating that protons were effectively removed. Yet, it must also be noted that we lost specific charge. This is probably due to the too high ratio oxide:LiBH_4 used in this experiment.

Figure 12.28: Cycling stability of LiMn_{0.5}Ni_{0.5}O_2 treated with LiBH_4 (molar ratio 1:1). Data were obtained galvanostatically between 2.5 and 4.4 V vs. Li/Li^+ at 10 mA/g. The electrolyte used was 1 M LiPF_6 in EC:DMC 1:1 (w/w).

To conclude, we demonstrated that also the treatment of the LiMn_{0.5}Ni_{0.5}O_2 oxide with LiBH_4 gave a material with enhanced electrochemical cycling performance.
13.1 Introduction

As already discussed in section 3.2.2, carbons are mostly used in the negative electrode of the Li-ion battery. The most desirable candidate among the carbon materials is graphite, due to its good lithium intercalation properties, such as low working potential (< 300 mV vs. Li/Li⁺), high reversible specific charge and good electronic conductivity. Moreover, graphite is expected to lose little charge in film forming and other parasitic reactions during the first charge/discharge cycle. The initial lithium intercalation and de-intercalation behaviour is studied routinely as a first step in evaluating carbons. The reversible lithium storage capacity depends strongly on the degree of crystallinity, which is controlled by precursor materials and heat treatment. The irreversible specific charge arises from the reaction of the electrolyte on the carbon surface and is strongly dependent on the electrolyte as well as on the carbon.

![Graphite crystal structure](image)

**Figure 13.1:** Left: crystal structure of hexagonal graphite. Right: view perpendicular to the basal plane of hexagonal graphite. Prismatic surfaces can be divided into arm-chair and zig-zag faces.
The usual structure of graphite is hexagonal (Fig. 13.1) with the layers stacked with a ABAB sequence. Another form of graphite is the rhombohedral one with a stacking sequence of the type ABCABC.

13.2 Graphite intercalation compounds

Due to the weak van der Waals interlayer forces in graphite, graphite intercalation compounds (GICs) may be formed by the insertion of layers of guest species between the layers of the graphite host material. In the so-called donor GICs, electrons are transferred from the donor intercalated species into the graphite layers, thereby raising the Fermi level $E_F$ in the graphitic electronic states, and increasing the mobile electron concentration, while leaving the intercalate layer positively charged [108]. The lithium intercalation into graphite proceeds according to equation (13.1):

$$xLi^+ + xe^- + C_n \leftrightarrow Li_xC_n$$  \hspace{1cm} (13.1)

For graphitic materials with a high degree of crystallinity a maximum amount of one lithium atom per six carbon atoms can be obtained under usual reaction conditions ($x \leq 1$ in $Li_xC_6$). The lithium ions are intercalated only at the prismatic surfaces and not at the basal planes, unless defects in the structure are present. The lithium intercalation produces a shift of the graphene layers from ABAB to AA. Figure 13.2 shows the structure of $LiC_6$. The volume increase due to the lithium intercalation was found to be 10.3 % [109].

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**Figure 13.2:** Crystal structure of $LiC_6$. 
The intercalated layers form an ordered superlattice structure, interleaved with the graphene layers through a phenomenon called staging. A GIC of stage $n$ has isolated intercalated layers separated from one another by $n$ graphene layers. This phenomenon can be easily observed during the electrochemical reduction (charge) of graphite in lithium containing electrolytes. Figure 13.3 shows schematically the potential-composition curve for the reduction of graphite.

As one can see from the picture, the second stage is split into two: $n = \text{II}$ ($x = 0.5$ in $\text{Li}_x\text{C}_6$) and $n = \text{II L}$ ($x = 0.33$ in $\text{Li}_x\text{C}_6$). Stage II L corresponds to a liquid-like stage II phase with a lower concentration of lithium between the planes $[110]$. The plateaux (where the potential remains constant) indicate coexistence of two phases.

If one wants to obtain the typical lithium intercalation compounds ($\text{LiC}_{18}$, $\text{LiC}_{12}$ and $\text{LiC}_6$; for crystal data see Tab. 13-1 and 13-2) the lithium ions have to be intercalated as 'naked' ions. However, the ions in the electrolyte are solvated and intercalation of such solvated lithium ions into graphite is possible. This solvated intercalation is detrimental to the graphite since it is accompanied by an exfoliation (volume increase $\sim 150 \%$) of
the graphite matrix. The solvated intercalation compounds are thermodynamically favourable with respect to the binary compounds, i.e. their formation takes place at potentials which are more positive than those for the formation of the binary compounds. The tendency to intercalate solvated lithium ions is strongly dependent on the electrolyte chosen. For example propylene carbonate (PC) based electrolytes turned out to be unsuitable for the graphite electrode. On the other hand, ethylene carbonate (EC) based electrolytes are suitable because they prevent the formation of the solvated intercalation. The reason for this different behaviour resides in the fact that EC decomposes (is reduced) much faster than PC. These decomposition compounds build a protective film on the graphite surface. This film is then permeable to naked lithium ions only, so the solvated intercalation is suppressed. Due to the high viscosity of EC based electrolytes, mixtures with other solvents, such as dimethyl carbonate (DMC), ethyl methyl carbonate (EMC), diethyl carbonate (DEC) and others are used [16,17].

<table>
<thead>
<tr>
<th>Table 13-1: Space group and crystal data of graphite and GICs [111].</th>
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<tr>
<td>Space group</td>
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<td>--------------</td>
</tr>
<tr>
<td>Graphite</td>
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<tr>
<td>LiC_{18}</td>
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<tr>
<td>LiC_{12}</td>
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<tr>
<td>LiC_{6}</td>
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<table>
<thead>
<tr>
<th>Table 13-2: 2θ values of the first peak of graphite and GICs.</th>
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<tbody>
<tr>
<td>Peak</td>
</tr>
<tr>
<td>------------------</td>
</tr>
<tr>
<td>Graphite (002)</td>
</tr>
<tr>
<td>LiC_{18} (003)</td>
</tr>
<tr>
<td>LiC_{12} (002)</td>
</tr>
<tr>
<td>LiC_{6} (001)</td>
</tr>
</tbody>
</table>
Figure 13.4 shows the experimental galvanostatic curve for the first reduction (charge) process. The staging phenomenon discussed above is clearly visible. Another aspect to observe is that the charge consumed during the first charging step exceeds the specific charge theoretically calculated for LiC₆ (372 Ah/kg). During the following discharge the charge recovery is about 90 % and for the subsequent cycles it is close to 100 %. This “charge loss” (irreversible specific charge) during the first cycle is attributed to the formation of the protective film discussed above.

Interestingly enough, there are remarkable differences between the electrochemical behaviour of the pure hexagonal graphite and the graphite enriched with rhombohedral units. It was found that, in some electrolytes, the former is very sensitive to exfoliation while the latter does not show exfoliation during the first electrochemical reduction [112]. A clear correlation was found between the irreversible specific charge and the amount of the rhombohedral phase content in commercial graphites [113]. It was also observed that graphites with at least 30 % of rhombohedral phase do not exhibit exfoliation even if electrolytes with 80 % PC are used [114]. However, the presence of the rhombohedral phase is not enough to prevent exfoliation. As a matter of fact, graphite with a rhombohedral phase content of 30 % annealed at 1000 °C still showed
exfoliation. A possible explanation could lie in the correlation of the content of crystal defects and the irreversible charge due to exfoliation. The rhombohedral phase is created by mechanical treatment, which implies that a lot of defects are created. These defects, which are thought to hinder the solvated intercalation, disappear after heat-treatment above 1000 °C [114].

Figure 13.5 shows the expanded view of the XRD patterns of an hexagonal graphite (a special sample obtained from Timcal), a graphite with 30-40 % rhombohedral phase content (Timcal SLM44) and the hexagonal one milled for 2 hours in a ball mill.

![XRD patterns](image)

**Figure 13.5**: expanded view of the XRD patterns of a hexagonal graphite (a special sample obtained from Timcal), a graphite with 30-40 % rhombohedral phase content (Timcal SLM44) and the hexagonal one milled for 2 hours in a ball mill.

From the figure it can be seen that a grinding time of 2 hours is sufficient to build up the rhombohedral phase from the pure hexagonal graphite. As a matter of fact, the peak at ~43.3° (which is characteristic of rhombohedral graphite) arises in the sample milled for two hours. Electrochemical experiments on these three graphites (hexagonal, hexagonal milled for two hours and the one with 30-40 % rhombohedral phase content) were
performed and compared. The electrolyte used for these experiments was 1 M LiPF6 in EC:DMC 1:1 (w/w). The irreversible specific charge of the pure hexagonal graphite was 60 %, while for the sample milled for two hours this specific charge could be decreased to 30 %. However, this irreversible loss is still too high compared to the one obtained for the best graphite materials used in Li-ion batteries (about 8-9 %).

To conclude we can say that the milling process had a beneficial effect as it reduced the irreversible specific charge of hexagonal graphite. However, this irreversible loss was still too high, which was probably due to the increase in the specific surface area caused by the milling process, as confirmed by BET measurements.

### 13.3 Reaction of graphite with intermetallic phases

The stabilisation of graphite is still an important part of the joint battery project at PSI and ETHZ. The idea was to bring anions (Sn⁴⁻) between the graphite sheets trying to stabilise graphite integrity towards intercalation and de-intercalation and so as to enhance its cycling performance. As the intercalation of electropositive metals is well known, graphite was let react with a highly reducing Zintl phase, i.e. Li₂¹Sn₅.

**Synthesis of Li₂¹Sn₅** [115]

Stoichiometric amounts of lithium and tin were heated in a sealed niobium ampoule at 800 °C with a heat rate of 100 °C/h. The product was single phase, as confirmed by XRD.

**Reaction of Li₂¹Sn₅ with graphite**

The graphite used for the reaction was TIMREX SFG6. The reactions were performed at 850 °C under inert gas conditions in a sealed niobium ampoule with a heat rate of 50 °C/h. After reaching the end temperature the samples were quenched at room temperature. Several samples with different Li:C ratios were prepared according to the following equation:

$$\frac{1}{21} Li_{21}Sn_5 + xC \rightarrow \text{intercal. graphite}$$

(13.2)
with $x = 1, 3, 6, 12$. For the sample with $x = 12$ the (002) peak of graphite at $26.6^\circ$ shifted towards a smaller $2\theta$ angle ($26.2^\circ$). This means that an expansion of the layers occurred (from $d=3.356 \, \text{Å}$ to $3.400 \, \text{Å}$). In the samples with $x = 3$ and $x = 6$ no shift of the (002) peak was observed. The XRD pattern of the sample with $x = 1$ is more complex. Reflections attributed to the compound Li$_2$C$_2$, which is thought to be electrochemically inactive, were found. All other diffraction peaks were attributed to graphite and Li$_x$Sn$_y$ compounds. In all the reactions that were performed the patterns of Li$_{21}$Sn$_5$ completely vanished. To conclude, we can say that a reaction occurred between graphite and Li$_{21}$Sn$_5$, but it seems that an intercalation took place only in the sample with $x = 12$.

![Graph showing electrochemical performance](image)

**Figure 13.6:** Electrochemical performance of the samples with (a) $x = 12$ and (b) $x = 1$. The electrolyte used was 1 M LiClO$_4$ in EC:DMC 1:1 (w/w).

*Electrochemical measurements*

Figure 13.6 shows the electrochemical performance of the samples with $x = 1$ and $x = 12$. Although the two samples present a satisfactory cycling stability, the value of the specific charge lies considerably below 360 Ah/kg, which is the today standard for graphite electrodes. Thus, further experiments on this system were stopped.
13.4 In-situ X-ray diffraction experiments on graphite electrodes

As described above, graphite forms several phases with lithium. These different phases can easily be detected using XRD diffraction. The aim of these experiments was to check the influence of the electrolyte composition on the electrochemical intercalation of lithium into graphite during the first charge process. All the electrolytes were based on ethylene carbonate (EC) for the reasons discussed in section 13.2.

13.4.1 Experimental

Electrode preparation and cell assembling

Synthetic graphite powder SLM44 (Timcal) was used as the carbon material. A slurry of the graphite powder and a solution of polyvinylidene fluoride (PVDF 10 % w/w) dissolved in 1-methyl-2-pyrrolidinone were mixed and coated on a 25 μm thick copper foil using the doctor blade method. A 34 mm diameter disc was then stamped out of the sheet. The prepared electrodes were dried under vacuum at 120 °C for 16 hours and transferred into a glove box. The cell assembling was made under argon atmosphere. Metallic lithium was used as counter electrode. The electrolytes used were: 1 M LiPF₆ in EC:DMC (1:1), 1 M LiClO₄ in EC:DMC (1:1), 1 M LiPF₆ in EC:EMC (1:1) and 1 M LiN(SO₂CF₃)₂ in EC:EMC (1:1) (w/w).

Electrochemical measurements

The cell was cycled galvanostatically at a constant specific current of 10 mA/gcarbon between 1.5 and 0.005 V vs. Li/Li⁺. The XRD patterns were recorded at the following potentials : open circuit voltage, 800, 250, 190, 100, 5 and again 250 mV vs. Li/Li⁺ in order to verify the reversibility of the lithium intercalation (see Fig. 13.7). For each electrolyte used two sets of measurements were performed.

Since the XRD probes the bulk of the particles and the potential is determined by the lithium concentration at the surface, before taking the XRD pattern at the desired potential, we waited until the current decreased to a value of about 1 mA/gcarbon, allowing the electrode to nearby reach the equilibrium. If the cell is not in equilibrium, the presence of lithium concentration gradients will give broad X-ray peaks. The
presence of such effects may result in an incorrect correlation between the cell voltage and the structural information.

Figure 13.7: Constant current charge curve (1st half-cycle) of the graphite SLM44 (Timcal) measured in 1M LiPF₆, EC:DMC 1:1 (w/w) showing at which potentials (mV vs. Li/Li⁺) the XRD patterns were recorded.

13.4.2 Results and discussion

The electrolyte 1 M LiPF₆ in EC:DMC 1:1 (w/w) was used as the reference electrolyte. The corresponding XRD patterns recorded at the different potentials and the summary of the XRD data are given in Fig. 13.8 and Tab. 13-3, respectively.
Figure 13.8: XRD patterns showing the (002) peak of graphite as measured potentials (in mV vs. Li/Li⁺), electrolyte 1 M LiPF₆ in EC:DMC 1:1 (w/w). The difference in the intensities is due to different scan times. The appearance of a peak at ~26.5° for all patterns is due to graphite particles which were obviously not contacted.
Table 13-3: Summary of the XRD data obtained for 1 M LiPF₆ in EC:DMC 1:1 (w/w)

<table>
<thead>
<tr>
<th>mV vs. Li/Li⁺</th>
<th>2Θ [°]</th>
<th>d [Å]</th>
<th>Layer distance increase [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>OCV</td>
<td>26.47</td>
<td>3.365</td>
<td>0.0</td>
</tr>
<tr>
<td>800</td>
<td>26.46</td>
<td>3.366</td>
<td>0.0</td>
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<td>26.23</td>
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</tr>
<tr>
<td>5</td>
<td>23.97</td>
<td>3.710</td>
<td>10.3</td>
</tr>
</tbody>
</table>

The formation of staged phases and transition to lower stages during Li-intercalation are clearly visible. The dominant peaks at the various potentials (mV vs. Li/Li⁺) were assigned as:

a) OCV: (002) peak of graphite;

b) 800 mV: (002) peak of graphite;

c) 250 mV: peak corresponding to a GIC with stage order n > IV (x < 0.16 in LiₓC₆);

d) 190 mV: peak corresponding to a GIC with stage order n = III (Li₀.2C₆);

e) 100 mV: peak corresponding to a GIC with stage order n = II (Li₀.5C₆);

f) 5 mV: (001) peak of LiC₆;

g) 250 mV (on discharge): peak corresponding to a GIC with stage order n > IV (x < 0.16 in LiₓC₆);

The pattern measured at 250 mV vs. Li/Li⁺ on discharge confirmed the full reversibility of the lithium intercalation.
Very similar results were obtained by Whitehead et al. [52], who used 1 M LiAsF$_6$ in EC:DEC 1:1 (w/w). In order to study the role played by the lithium salt and the solvent, three other experiments with the three electrolytes listed in the experimental part were carried out. Tab. 13-4 summarises the results.

**Table 13-4: Summary of the XRD data.**

<table>
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<td>LiPF$_6$</td>
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<tr>
<td>mV vs. Li/Li$^+$</td>
<td>2θ [°]</td>
<td>d [Å]</td>
<td>Layer distance increase [%]</td>
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<table>
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<tr>
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<tr>
<td></td>
<td>LiPF$_6$</td>
<td>LiN(SO$_2$CF$_3$)$_2$</td>
<td>LiPF$_6$</td>
<td>LiN(SO$_2$CF$_3$)$_2$</td>
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<tr>
<td>mV vs. Li/Li$^+$</td>
<td>2θ [°]</td>
<td>d [Å]</td>
<td>Layer distance increase [%]</td>
<td>2θ [°]</td>
<td>d [Å]</td>
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<td>3.710</td>
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Analysing the results obtained, it can be stated that all four electrolytes used (small variations of the values due to experimental errors taken into account) form the same graphite intercalation compound at the same potential. This may suggest that the size of the anion of the lithium salt plays only a minor role in the intercalation of lithium ions in graphite. The composition of the electrolyte solution (as far as EC is present) also seemed to have little, or no influence at all on the intercalation process.
Concluding remarks

The aim of this project was the synthesis and the electrochemical characterisation of new layered electroactive materials for the lithium-ion battery. We concentrated our attention on the synthesis of layered manganese oxides with the general formula LiMn$_{1-x}$M$_x$O$_2$, where M represents an appropriate doping element. In order to synthesise this compound, several synthesis routes were tried and very different results were obtained.

A few general remarks can be made. Firstly, we observed that layered doped lithium manganese oxides with a manganese content up to $x = 0.1$ in LiMn$_{1-x}$M$_x$O$_2$ could be obtained with almost all the synthesis routes tried. However, the electrochemical performance, especially the cycling behaviour of the oxides towards lithium extraction and re-insertion, was strongly dependent on the amount of manganese. As a matter of fact, all the samples with $x < 0.5$ showed a strong tendency to convert to the more stable spinel phase. This fact was correlated to the strong predisposition of Mn$^{III}$ to undergo Jahn-Teller distortion.

Amongst the several compounds prepared with different doping elements, the best electrochemical performance was obtained for mixed metal oxides of the type LiMn$_{1-x,y}$Ni$_x$Al$_y$O$_2$. In this family of oxides two compounds turned out to be very promising candidates for the active material in the positive electrode of lithium-ion batteries, namely LiMn$_{0.5}$Ni$_{0.3}$Al$_{0.2}$O$_2$ and LiMn$_{0.5}$Ni$_{0.4}$Al$_{0.1}$O$_2$.

Since both LiMn$_{0.5}$Ni$_{0.3}$Al$_{0.2}$O$_2$ and LiMn$_{0.5}$Ni$_{0.4}$Al$_{0.1}$O$_2$ showed an excellent behaviour, it would be interesting to study these mixed oxides further in order to optimise their composition and thus maximise the specific charge. To achieve this, a reduction of the amount of the redox inactive aluminium should be considered, but great attention has to
two or more of the methods which were found to improve the cycling stability of
LiMn_{0.5}Ni_{0.5}O_2 (i.e. doping by aluminium, doping by boric acid, and treatment by
LiBH_4) at the same time in order to see if their beneficial effects can be combined.

It is to be hoped that the results presented in this work will contribute to the
development of a new low cost and environmental friendly electrode material for
lithium-ion batteries.


Publications

Elektrodenmaterial für positive Elektroden wiederaufladbarer Lithium-Batterien.
Swiss Federal Institute of Intellectual Property, Bern, Switzerland.

Novel Cathode Materials for Lithium-Ion Batteries.

Advanced in situ methods for the characterization of practical electrodes in lithium-ion batteries.

Contributions to conferences

Oral presentation

Novel Mixed Metal Oxides for Positive Electrodes in Lithium-Ion Batteries.
50th International Society of Electrochemistry, Pavia, Italy (1999).

Posters

Novel Cathode Materials for Lithium-Ion Batteries.

Stable mixed metal oxides for the high-energy-density Li-ion-battery.
Curriculum Vitae

Marcello Coluccia

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Education

1978-1983: Primary school in Lamone-Cadempino (TI)
1983-1987: Secondary school in Savosa (TI)
1987-1991: Scientific high school in Canobbio (TI)
1991-1996: Graduate studies in chemical engineering at the Swiss Federal Institute of Technology (ETH) in Zurich
1997-2000: Ph.D. studies at the Institute of Inorganic Chemistry of the ETH Zurich, under the supervision of Prof. Dr. R. Nesper