Structural Changes in Lithium Battery Materials Induced by Aging or Usage

RICKARD ERIKSSON
Li-ion batteries have a huge potential for use in electrification of the transportation sector. The major challenge to be met is the limited energy storage capacity of the battery pack: both the amount of energy which can be stored within the space available in the vehicle (defining its range), and the aging of the individual battery cells (determining how long a whole pack can deliver sufficient energy and power to drive the vehicle). This thesis aims to increase our knowledge and understanding of structural changes induced by aging and usage of the Li-ion battery materials involved.

Aging processes have been studied in commercial-size Li-ion cells with two different chemistries. LiFePO$_4$/graphite cells were aged under different conditions, and thereafter examined at different points along the electrodes by post mortem characterisation using SEM, XPS, XRD and electrochemical characterization in half-cells. The results revealed large differences in degradation behaviour under different aging conditions and in different regions of the same cell. The aging of LiMn$_2$O$_4$-LiCoO$_2$/Li$_4$Ti$_5$O$_{12}$ cells was studied under two different aging conditions. Post mortem analysis revealed a high degree of Mn/Co mixing within individual particles of the LiMn$_2$O$_4$-LiCoO$_2$ composite electrode.

Structural changes induced by lithium insertion were studied in two negative electrode materials: Li$_{0.5}$Ni$_{0.25}$TiOPO$_4$ using in situ XRD, and Ni$_{0.5}$TiOPO$_4$ using EXAFS, XANES and HAXPES. It was shown that Li$_{0.5}$Ni$_{0.25}$TiOPO$_4$ lost most of its long-range-order during lithiation, and that both Ni and Ti were involved in the charge compensation mechanism during lithiation/delithiation of Ni$_{0.5}$TiOPO$_4$, with small clusters of metal-like Ni forming during delithiation.

Finally, in situ XRD studies were also made of the reaction pathways to form LiFeSO$_4$F from two sets of reactants: either FeSO$_4$·H$_2$O and LiF, or Li$_2$SO$_4$ and FeF$_2$. During the heat treatment, Li$_2$SO$_4$ and FeF$_2$ react to form FeSO$_4$·H$_2$O and LiF in a first step. In a second step LiFeSO$_4$F is formed. This underlines the importance of the structural similarities between LiFeSO$_4$F and FeSO$_4$·H$_2$O in the formation process of LiFeSO$_4$F.

**Keywords:** Li-ion batteries, XRD, EXAFS, HAXPES

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List of papers

This thesis is based on the following papers, which are referred to in the text by their Roman numerals.

I Analysis of aging of commercial composite metal oxide - $\text{Li}_4\text{Ti}_5\text{O}_{12}$ battery cells
Pontus Svens, Rickard Eriksson, Jörgen Hansson, Mårten Behm, Torbjörn Gustafsson, Göran Lindbergh
Journal of Power Sources 270, 131-141, 2014

II Non-uniform aging of cycled commercial LiFePO$_4$//graphite cylindrical cells revealed by post-mortem analysis
Matilda Klett, Rickard Eriksson, Jens Groot, Pontus Svens, Katarzyna Ciosek Högström, Rakel Wreland Lindström, Helena Berg, Torbjörn Gustafsson, Göran Lindbergh, Kristina Edström
Journal of Power Sources 257, 126-137, 2014

III Electrochemical lithium ion intercalation in $\text{Li}_{0.5}\text{Ni}_{0.25}\text{TiOPO}_4$ examined by in situ X-ray diffraction
Rickard Eriksson, Kenza Maher, Ismael Saadoune, Mohammed Mansori, Torbjörn Gustafsson, Kristina Edström

IV Electronic and structural changes in $\text{Ni}_{0.5}\text{TiOPO}_4$ Li-ion battery cells upon first lithiation and delithiation, studied by high-energy X-ray spectroscopies
Rickard Eriksson, Karima Lasri, Mihaela Gorgoi, Torbjörn Gustafsson, Kristina Edström, Daniel Brandell, Ismael Saadoune, Maria Hahlin
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V Formation of tavorite-type LiFeSO$_4$F followed by in situ X-ray diffraction
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Submitted to Inorganic Chemistry

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Comments on my contributions to the papers

Paper I  XRD measurements and analysis, took part in the writing.

Paper II  XRD measurements and analysis, took part in the writing.

Paper III  Planned and executed the experiments and analyzed the results, main author of the manuscript.

Paper IV  Planned and executed EXAFS experiments and analysis, took part in the NEXAFS evaluation. One of the main responsible for the manuscript.

Paper V  Planned and executed the experiments and analyzed the results. One of the main responsible for the manuscript.
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1. Introduction

Li-ion batteries dominate today’s market for portable electronics, and are the prime choice for energy storage in electric and hybrid electric vehicles. They are also highly relevant to large scale storage in support of renewable electrical energy production. There are many different electrode materials to choose from when constructing a Li-ion battery. This makes it possible to tune battery performance. An electrochemical cell can, for example, be designed to have either high energy density or high power capability. There is therefore no single type of Li-ion battery, but rather a whole family of battery concepts, each with its own special characteristics.

This thesis probes the atomic structures of the materials used in Li-ion batteries, and examines especially how these materials change during cell cycling - and how these changes influence the performance of the cells. The scope of the work can thus be summarized as follows: XRD was used to study the changes taking place in materials subjected to long-term cycling of commercial cells. *In situ* X-Ray Diffraction (XRD) has also been used to follow structural changes in new electrode materials during their lithiation and delithiation. Extended X-ray Absorption Fine Structure (EXAFS) and X-ray Photoelectron Spectroscopy (XPS) have also been used to further understand structural changes, and to follow how long-range-order is lost during cycling in specific battery materials. *In situ* XRD has further been used to evaluate the synthesis route in solution based synthesis of LiFeSO$_4$F.

1.1 Climate change and energy consumption

Predicted future climate change, with its increase in global temperature, rising sea levels, increased oceanic acidity etc., calls for a large scale transformation of the energy systems and how we use our energy resources today [1]. One of the major reasons for global warming is the widespread use of fossil fuels and the release of CO$_2$ that it produces [1]. The total amount of primary energy supplied to society worldwide in 2014 was about 13400 Mtoe (Million tons of oil equivalents), of which ca. 82 % originated from fossil sources (coal, peat, oil shale, oil and natural gas) [2]. Since the future amount of released CO$_2$ originating from fossil sources is unknown, the Intergovernmental Panel on Climate Change (IPCC) have developed a set of scenarios which vary in the amount of CO$_2$ (and other greenhouse gases) released [1]. These scenarios
predict the consequences for our global environment (sea-level rise, temperature increase, etc.) as a function of the total amount of greenhouse gases emitted. They can also be used to evaluate and find paths to avoid these consequences, which hopefully can guide us as consumers to make enlightened decisions on which energy to use and how best to consume it. The information from these scenarios can hopefully also guide our elected politicians to implement a framework of regulations and policies to successfully mediate a transition to a low- or zero-emission society.

1.1.1 Emissions from the transportation sector

Of the total primary energy supply, 18.7% is used for transportation, of which, 92.7% is from refined oil products, and a further 3.6% from natural gas [2]. Between 1990 and 2011, the energy consumption in the transport sector increased by almost 55%, thereby making it the fastest growing end-user sector, with 90% of it being consumed for road transportation [3]. Thus, the transport sector is both highly dependent on fossil fuels and accounts for an ever increasing part of the total energy usage. A technology shift to carbon-free transport would have a considerable effect on our total CO₂ emissions. However, such a technological shift is not trivial to achieve, even though we have technologies available for carbon-free propulsion: electric vehicles (EVs) for personal transport and electric rail transport for freight. EVs have a limited range, due to battery size and weight constrictions (low energy density compared to that of oil-based fuels), combined with uncertainties in battery lifetime. Electric-rail transport requires a greater investment in infrastructure than oil-fueled heavy-duty vehicles, and is therefore not a flexible enough alternative to road transport. In addition, both transportation systems are dependent on a supply of green primary energy to be truly emission-free.

When estimating future energy consumption in the transport sector, it is hard to separate passenger from freight transport, since they are not separated in the declaration of energy usage in the overall transportation system. Estimates must therefore be made on the basis of vehicle stocks, mileage and fuel-economies, or through the use of energy consumption questionnaires. The International Energy Agency (IEA) presents this data on a country-by-country basis, and they have so far been able to provide this separated information for 44 countries. These countries differ greatly, making it difficult to assess future trends resulting from different climate scenarios [3]. However, it is still clear that even incremental steps towards electrification of the road-based transport sector will substantially reduce CO₂ emissions, along with other pollutants such as NOₓ and particles [4].
1.1.2 The future of road-transportation systems

Several efforts have been made to simulate future trends in road transport [5–12]. Some have focused on private-cost or life-cost analysis of different vehicle and/or fuel systems [5, 6], and have demonstrated the continued cost efficiency of the internal combustion engine (ICEV). However, a complete system model must be used to fully capture trends in energy systems and their implications for the future. These system models must include the majority of energy sectors (transportation, electrical power generation, heat generation, industrial energy usage, etc.) to discover where carbon-based energy sources will continue to be used, and where they first will be replaced by other energy sources. Since energy production must be changed substantially if it is going to be carbon neutral, the models implement different combinations of energy production systems, such as: concentrated solar power (CSP), carbon capture and storage (CCS), increased nuclear power and/or different contributions from photovoltaic-, wind power, or other renewable sources [8–12]. These models can also implement different carbon trading systems or regulations.

To model the light-duty vehicle pool, different propulsion systems and energy carriers are incorporated into the models. These vehicle technologies are: electric vehicles (EVs), hybrid electric vehicles (HEVs) (with different liquid/gaseous fuels), plug-in hybrid electric vehicles (PHEVs), fuel cell cars (FCVs), and hydrogen fuel cell cars (HFCVs), as well as internal combustion engine vehicles (ICEVs) using different fuel alternatives (liquid biofuels, petrol, diesel) as well as advanced ICEVs, with improved internal combustion engine efficiencies. The general indications are that other sectors will be de-carbonized before the transport sector through the use of CCS, CFP, biofuel switching and increased nuclear power. The exclusion of some of these options will influence the availability of electrical power. HEVs are destined to be an important part of the future vehicle park, since they improve fuel efficiency in individual vehicles. The availability of cheap electricity (through CCS, and increased nuclear power) will result in an increasing share of EVs and PHEVs (along with HFCVs using hydrogen gas produced from coal with CCS). However, cheap electricity (from CCS) will also cause us to rely more on oil-based internal combustion engines, since early emission caps can be reached by CCS in large scale facilities.

Future fuels for the road-based freight transport are not as broadly debated, since the possibility of electrifying this part of the transportation sector cannot rely on batteries alone - their own weight would reduce the effective payload. Oil-based fuels are therefore expected to be the last to be replaced within road based freight transportation (and also within all types of air transport) [12]. However, small steps towards hybridization have already been taken for other heavy-duty vehicles (primarily buses); electric and hybrid electric buses are now on the market.
The main concerns/drawbacks associated with the electric power trains of today (in EVs, PHEVs or HEVs) are related to energy storage (the batteries used); specifically: the cost of battery systems, the unknown effect of usage and time on battery performance, and energy- and power-density limitations of the batteries. The best rechargeable battery system available today to supply high energy- and power-density is the Li-ion battery, despite the fact that cell cost is high and aging processes are not entirely understood, since this is still a fairly new and rapidly developing field. The studies described in *paper I* and *paper II* were conducted to further increase our understanding of aging processes in Li-ion batteries. The studies described in *paper III* and *paper IV* were made to extend our understanding of as yet uncommercialized electrode materials. Finally, a synthesis process for another comparatively new electrode material is described in *paper V*.

1.2 Aim of the thesis

The main aim of this thesis is to increase our knowledge and understanding of how the atomic structure of Li-ion battery materials is influenced by battery cycling. This is vital for evaluating the performance of materials used in commercial cells, and for understanding the degradation processes of materials in cells during real-world usage. *Post mortem* studies of commercial cells cycled with vehicle-like loads are one of the few methods available to measure material characteristics in used cells. However, the method is intrusive, since the cells must be cut open, but by doing so degradation can be studied in detail at cell level. Our understanding of electrode materials in working cells can be improved by combining these studies with material characterization for opened commercial or lab-scale cells. Changes in the structure of the electrode materials in Li-ion cells can be examined by exploiting synchrotron-based *in situ* X-ray diffraction techniques on a lab-scale. A further aim has been to use *in situ* X-ray diffraction to follow the synthesis of a new crystalline electrode material (LiFeSO₄F) to better understand the reaction pathway followed during its formation.
2. Methods

Several different methods and techniques have been utilized to analyze materials and structural changes during the work with this thesis. A brief description of the basis of the most important methods is given in this chapter. Detailed descriptions of each method can be found in specialized text books.

2.1 XRD – X-Ray Diffraction

Photons can interact with matter in many different ways. If the photon energy is in the X-ray range (1 - 100 keV) and the interaction is elastic (without energy transfer) and coherent (without time delay), the interaction is called X-ray diffraction or Bragg scattering [13]. A distribution of electrons (for example the electrons in an atom or a molecule) will interact with a photon wave to produce, a by interference modulated scattering pattern, called a diffraction pattern [13].

If multiple identical electron distributions are periodically placed in space (i.e., a crystal), the scattering from each of them will interact with that from the others. This periodicity can be described by a lattice and its periodicity will modulate the detection probability to become zero in wide parts of space due to destructive interference in all but a few directions. The allowed directions are fully determined by how the objects are placed in space and thus by the lattice [13]. However, further limitations of the intensities are introduced due to the symmetry of the electron density, where symmetry will disallow intensity in some of the, by the lattice allowed, directions. Thus, the symmetry of the electron density and the lattice, defines the allowed diffraction angles and the intensity in those points is defined by the distribution of electron density in the repetition unit [13].

Bragg’s law is a useful model to describe the relation between the allowed scattering angles ($2\theta$), the photon wavelength ($\lambda$) and an inter-planar distance ($d$) between parallel planes (constructed from the lattice points to represent the electron density repetitions length in the direction perpendicular to the planes), see equation 2.1.

$$2d \sin \theta = n\lambda \quad (2.1)$$

In single crystal diffraction, the diffraction pattern will be a function in three dimensions and the full record of this pattern can be used to solve the crystal structure. For a fully randomized mixture of many single crystals (an ideal
powder), the diffraction patterns will be reduced to only depend on one diffraction angle. More detailed information about X-ray diffraction can be found in several textbooks [13, 14].

The recorded diffraction peak from a sample will have an angular width (giving a peak width) due to the broadening from the instrument (slit widths, beam divergence, beam size on sample, wavelength variations of the incoming beam etc.). Additionally, the peaks can be broadened by the finite size of the crystallites (or by faults in the crystal - such as stacking faults or strain) [14]. The first measurement using the line broadening to estimate crystallite sizes was done by Scherrer in 1918 [15], who derived a formula to link the full width at half maximum (FWHM) to the side length of a cube which formed the crystallite model. Since then, both the way to measure the peak width and the constant used in relating broadening to crystallite size have been revised and reviewed [16, 17]. Some important notes can be made regarding peak broadening: it does not correlate with the particle size, but with the coherent domain length where long range order is preserved. Thus, a crystalline material that gradually loses the long range order, either due to crystallite disintegration or decreased long range order, will show a broadening of peaks and a decay of the peak intensity [16]. This is observed in the experiments in paper III.

All diffraction measurements carried out in this thesis were powder measurements. X-ray diffraction has primarily been used to follow changes occurring during Li-ion insertion into materials, after battery usage or to detect new phases formed during synthesis of an electrode material. Structure refinements using the Rietveld method have been employed to quantify the amount of different phases in a sample and to monitor small changes during lithium insertion/extraction. In paper II, the phase composition of partially delithiated electrodes was determined with the Rietveld method. In paper V the phase composition at different times during a synthesis of LiFeSO₄F was determined.

2.1.1 Structure refinements with the Rietveld method

The Rietveld method is a least squares method for structure refinement, where a structure model is fitted directly to the measured intensities of a recorded diffraction pattern [18]. An extensive description of the Rietveld method can be found elsewhere [19]. The method was first used on neutron diffraction data [18], but it has later been widely employed on X-ray diffraction data as well [20, 21]. The least squares procedure is minimizing the difference between the, for a specific model, calculated diffraction pattern and the measured diffraction pattern, using refinable parameters (atom positions, occupancies, thermal displacement parameters, etc.). Therefore the model and the initial value of the refinable parameters must at start be a good approximation of the measured material [19].
2.2 XAS – X-ray Absorption Spectroscopy

A photon with sufficient energy that interacts with an atom can transfer its energy to a bound electron in the atom so that the electron is excited. This is called X-ray absorption. X-ray Absorption Spectroscopy (XAS) measures the change in X-ray absorption in a sample as a function of the incoming photon energy. The work in this thesis has employed two X-ray absorption spectroscopy techniques: X-ray Absorption Near Edge Structure (XANES) and Extended X-ray Absorption Fine Structure (EXAFS).

An example of the magnitude of the linear attenuation coefficient for Ni, as a function of incoming photon energy, can be seen in figure 2.1a. The function can be described as a decreasing probability for absorption with increasing photon energy but with some sharp edges where the absorbance will drastically increase. In figure 2.1a, the K and L-edges are indicated. These sharp increases in absorbance appear when the photon energy is sufficient to excite electrons from a lower lying shell to the continuum (this energy is the binding energy of the electron). The K-edge is where electrons from the 1s orbital are excited and it is the only absorption edge not consisting of several closely spaced levels (e.g. L-edges are composed of L₁, L₂ and L₃ from the 2s, and 2p₁/₂ and 2p₃/₂ electron states, having different energies). For the theoretical case of a free single atom, these edges are sharp and distinct (as in figure 2.1a). For other atoms, the region around the edge and thereafter is modulated by the probability of the transitions of the bound electron to the exited state (or higher energy bound states in transitions appearing before the edge) and the density of these states. These modulations at the Ni K-edge are clearly visible in the measured absorption of a Ni metal sample, shown in figure 2.1b. The absorption edge features can be described with their relative position to the absorption edge. The features seen before the absorption edge are called pre-edge features. The techniques used to interpret the modulations in the edge region are called XANES (sometimes NEXAFS) and for the region above ~100 eV after the edge it is called EXAFS [22].

2.2.1 XANES – X-ray Absorption Near-Edge Structure

The XANES region of XAFS is in the immediate surroundings of the absorption edge: about ±50 eV from the edge. Below the edge there can be pre-peaks in the absorption as a result of transitions of the core electrons to bound unoccupied states within the atom/molecule. Changes in the intensities of these pre-peaks can be due to changes in the occupancy of the unoccupied states (changing of oxidation state of atoms) or changes in the local surroundings of the absorbing atom [24].

Right after the edge, the emitted electron is in an unbound state although with a limited kinetic energy. In this energy region the mean free path of the electron is long as it is at a minimum at about 30 eV [22]. For low energy
Figure 2.1. (a) Change in attenuation coefficient as a function of photon energy for nickel [23]. (b) K-edge absorption edge of nickel metal, showing the XANES and EXAFS regions.

Photoelectrons this leads to that the XANES region also contains the information of the EXAFS region but in a highly densified and difficult-to-evaluate manner.

In paper IV, XANES was used to couple the bulk changes in oxidation states of Ni and Ti to the results of surface sensitive measurements of oxidation states, done by HAXPES.
2.2.2 EXAFS – Extended X-ray Absorption Fine Structure

Extended X-ray Absorption Fine Structure (EXAFS) can be used to probe the local structure of materials. It is element specific since it uses the rippling features after an absorption edge, for the examination of the local structure surrounding the specific element.

The basic phenomenon creating the absorption ripples is the interference between the outgoing photoelectron wave and the same wave backscattered (one or several times) from the surrounding electron densities. The energy of the emitted electron can be described by equation 2.2, where the relation between the incoming photon energy ($h\nu$), the emitted electron energy ($E_e$) and the binding energy of the electron ($E_B$), is shown. As the important property of the emitted photoelectron is its wavelength, the EXAFS-ripples are discussed as a function of $k$ instead of the photon energy, see equation 2.3 where the mass of the electron is denoted $m_e$ [22].

$$E_e = h\nu - E_B$$  \hspace{2cm} (2.2)

$$k = \sqrt{\frac{2m_eE_e}{\hbar^2}}$$  \hspace{2cm} (2.3)

The self-interference of the photoelectron wave will be oscillating between constructive and destructive interference at the absorbing atom (as a function of $k$). This will modulate the total absorption after the edge. This oscillation will have a frequency in $k$-space corresponding to a certain inter atomic distance ($r$) between a defined set of atoms in real space.

The measured absorption $\mu(k)$ (as for example seen in the post-edge part in figure 2.1) is the atomic absorption $\mu_0(k)$ modulated by the changes induced by the local structure $\chi(k)$. This can be described with equation 2.4.

$$\chi(k) = \frac{\mu(k) - \mu_0(k)}{\mu_0(k)}$$  \hspace{2cm} (2.4)

In this relation $\mu_0(k)$, which is the absorption of the isolated atom at the same energy, is of significant importance. However, $\mu_0(k)$ is not possible to measure. Therefore it is approximated with a spline, a smoothly varying function in $k$, denoted $\mu_{\text{spline}}(k)$.

The extraction of the EXAFS-function ($\chi(k)$) is done in several steps [25]: energy calibration, pre-edge background subtraction, normalization, definition of $E_0$ and conversion into $k$-space, spline-fitting and extraction of $\chi(k)$. Thereafter $\chi(k)$ is often multiplied by $k$, $k^2$ or $k^3$ to counteract the dampening of the oscillations.

The EXAFS-function from a scattering atom $i$ can be modeled as seen in equation 2.5, where $\chi_i(k)$ is the sum of all scattering paths (scattering from surrounding atoms, and multiple scattering) [22].
\[ \chi_i(k) = \sum_j N_j S_0^2 F_j(k) e^{-2k^2\sigma_j^2} e^{-2R_j} e^{-2k^2\sigma_j} e^{-\frac{2k^2 R_j}{j}} \sin \left[ 2kR_j + \varphi_{ij}(k) \right] \] (2.5)

- \( N_j \) = degeneracy of path
- \( S_0^2 \) = amplitude reduction factor
- \( F_j(k) \) = backscattering amplitude of path
- \( R_j \) = half of the total path length
- \( \sigma_j \) = Debye-Waller factor, thermal and structural disorder
- \( \Lambda(k) \) = mean free path of photoelectron
- \( 2kR_j \) = phase-shift due to path length
- \( \varphi_{ij} \) = phase-shift due to central atom \( i \) and scattering atom \( j \)

A starting model is needed to be able to evaluate the EXAFS-function in terms of local structure. This model can be based on a crystalline structure or on a purpose built model structure of the surrounding of the absorber. This is needed as \( F_j(k), \Lambda(k) \) and \( \varphi_{ij} \) have to be calculated by \textit{ab initio} methods as they vary with the local structure. These calculations can be done with the FEFF-software [26]. The model can then be compared with the data and refined by changes in \( N_j/S_0^2, R_j, \sigma_j \) and the edge energy \( E_0 \).

The backscattering amplitude is a function of \( k \), and different atoms (different Z values) have different backscattering "envelopes" [25]. This means that the maximum backscattering amplitude occurs at different \( k \)-values for different elements. This is seen in figure 2.2 where the backscattering of the Ni-O interaction in cubic NiO and the amplitude of the Ni-Ni interaction in metallic Ni are plotted, as calculated with the FEFF6L software [26]. This can, by visual inspection of the \( \chi_i(k) \) function give clues regarding what element is involved in an unknown interaction. The physical reason for this difference in maximum amplitude, is that the scattering process is more likely to occur if the kinetic energy of the photoelectron is of the same magnitude as the orbital kinetic energy of the electron causing the scattering [25].

The photoelectron phase shift is, as seen in equation 2.5, not only dependent on the path length but is also changed by the scatterer and the exited state of the absorbing atom. The reason for this is that the kinetic energy of the electron increases in the vicinity of atoms due to the increased attraction between the electron and the nuclei. The wavelength of the photoelectron is thus changed in a small volume around the scatterer and the absorber [25].

In this thesis, EXAFS was used to probe the local structure around Ni in lithiated \( \text{Ni}_{0.5}\text{TiOPO}_4 \) (in \textbf{paper IV}).
2.3 XPS – X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy utilizes the photoelectric effect where an electron absorbs energy from an incoming photon (X-ray photon) and leaves the sample. The kinetic energy of the emitted electron can then be measured. By knowing the photon energy and the work function (which is the energy difference between the Fermi level and the vacuum level) the binding energy of the electron can be calculated [27]. This relation is described by equation 2.6 where \( E_b \) is the binding energy of the electron, \( h\nu \) is the energy of the incoming photon, \( E_k \) is the kinetic energy of the electron and \( \phi \) is the work function [27].

\[
E_b = h\nu - E_k - \phi
\]  \hspace{1cm} (2.6)

\[
I \propto I(\sigma, \rho, \Lambda, S)
\]  \hspace{1cm} (2.7)

The intensity of the peaks in a XPS spectrum can be described by equation 2.7, where \( \sigma \) is the cross section, \( \rho \) is the density of the corresponding element in the sampling volume, \( \Lambda \) is the mean free path of the electron in the sample, and \( S \) is the spectrometer function describing the electron-optical system [27].

The binding energy of a core electron will change as a function of the chemical surrounding of the element. This is known as the chemical shift [28]. As the valence electrons of the probed atom interact with the surrounding atoms the electron density on the atom will change and this will influence the binding energy of the core electrons as probed with core level XPS. A higher local electron density on the atom will decrease the binding energy of the core electrons and lower electron density will increase the binding energy. Thus, different chemical spices containing the same element can be identified and quantified with respect to each other. In this work we have used XPS as a
"fingerprinting tool" to identify different chemical species and to measure the relative amounts of those different species in our samples.

Two things are important to notice: firstly the mean free path of the electron depends on the kinetic energy, thus higher photon energy will emit detectable electrons from deeper within the sample. Secondly, the cross section depends on the energy of the photon, with a decreasing cross section as the energy increases. Hence, when using higher photon energy (denoted Hard X-ray Photoelectron Spectroscopy, HAXPES) the measurements will be more "bulk" sensitive but the intensity will generally be lower [29].

XPS/HAXPES is used to examine the solid electrolyte interphase (SEI) on aged graphite electrodes in paper II and on Ni$_{0.5}$TiOPO$_4$ electrodes in paper IV, where also the oxidation states of the Ni and Ti are examined.

2.4 EDX – Energy-Dispersive X-ray Spectroscopy

Energy Dispersive X-ray Spectroscopy (EDS/EDX) measures the number of emitted photons as a function of photon energy from a sample, where core holes have been created (often with high energy-electron bombardment as in a Scanning Electron Microscope (SEM)). The method records the X-ray decay of the exited states of the sample [30]. Since the electronic structures of the elements are different they have different X-ray emission lines. The limitation in energy resolution is one of the main drawbacks of this method. This has largest impact on the soft X-ray emission part of the spectra as the energy levels for light elements are less separated in eV than the K-levels of heavier elements [30].

EDX is used for element detection and is a quantitative method. To accurately determine element concentrations in unknown samples, flat samples that are composed of known mixtures of the investigated elements should be used as references [30]. Furthermore, the probe volume is dependent on the sample: here a mixture of low and high Z elements will give a lower low-Z-element contribution due to absorption of the emitted X-rays from these elements by the high-Z-elements. The electron beam interacts more strongly with high Z-elements and thus the probing depth will be lower for matrices or areas in a sample rich in elements with higher Z [30]. The lateral resolution in a SEM-EDS system is also quite poor as multiple scattering of the incoming electron deflects it away from the entry point. Thus both the spatial and depth probing volume are estimated to be in the range of 1-5 μm for metal-oxide samples (such as standard positive electrode materials for Li-ion batteries) [30]. EDX was used for element detection in paper I and II.
2.5 Electrochemical measurements

To monitor battery state of health (SOH) onboard vehicles during usage, non-intrusive methods are needed. These tests are often implemented in a battery system unit as test protocols. The test protocols assess the battery or electrochemical cell parameters by galvanostatic- or potentiostatic cycling in combination with Electrochemical Impedance Spectroscopy (EIS) and other (non-intrusive) methods. In this thesis, electrochemically based methods have been used to measure some standard cell parameters (capacity, discharge/charge curves) to later be able to couple them to results from post mortem material characterization of opened cells. In this section some of the methods used to evaluate galvanostatic discharge/charge curves will be summarized. These methods were used in paper I.

One fundamental concept when discussing cells is the state of charge (SOC). This is the amount of charge that a cell is able to deliver (during discharge) as compared to the capacity of the fully charged cell, i.e. the capacity left in the battery divided by the capacity of the fully charged battery.

A plot of $\Delta Q/\Delta V$ as a function of $V$ will show plateaus in the standard charge/discharge curve (a V(Q)-function) as sharp peaks. It will also show solid-solution lithium intercalation (sloping voltage plateaus) as peaks but these will be broader than the ones from the two phase reactions. This method of plotting data collected from galvanostatic cycling, is called Incremental Capacity Analysis (ICA) [31]. Since peaks in the ICA-plot can originate both from the negative and positive electrode material (or rather it is the difference in potential between them), this method is easiest to use on cells where one of the electrodes have a constant voltage for the full range of the cell capacity. Such cells are, for example, cells with one of the electrodes composed of: Li metal, LiFePO$_4$ or Li$_4$Ti$_5$O$_{12}$.

The change in the ICA-plot from an aged cell when compared to a measurement from the beginning-of-life, can be used to determine if the lost capacity is from: loss of active material, from changes in the cell chemistry, or from increased polarization of the cell leading to a situation where the voltage cut-off is reached before all lithium has been moved from one electrode to the other [31]. A loss of active material can be seen as a decrease in intensity of the peaks. Increased polarization will shift peaks closer to the potential cut offs.

Another way to plot standard galvanostatic discharge curves is as $\Delta V/\Delta Q$ vs. $Q$ [32]. This has the advantage that individual half-cell data (galvanostatic measurement of an electrode material combined into a working cell with a counter electrode of lithium metal) from the two electrode materials can be combined to match that of the full-cell data. This can reveal the reason to why a full-cell has lost capacity: either due to loss of active material on any or both of the electrodes, or if it is due to loss of lithium inventory [32–34]. This method is used in paper I.
The loss of active material on the negative or positive electrode and loss of cyclable lithium inventory can lead to an electrode miss-match between the electrode capacities. This miss-match is called electrode slippage and will reduce the usable capacity of the cell [35, 36].

For a longer summary of the different approaches to estimate SOH and other battery-pack or cell parameters for use in vehicle systems, see reference [37].
3. Lithium-ion batteries

The use of lithium in battery cells is attractive both as lithium metal has a high gravimetric capacity and a low redox potential (-3.04 vs. H+/H2). This means that batteries with voltages around 4 V can be made [38]. The first lithium batteries were primary cell using lithium metal. The development of secondary cells with lithium metal as negative electrode material was hampered by safety problems due to dendritic growth of lithium during charge, and the "rocking chair battery" was developed to reduce this risk [39]. These batteries use primarily intercalation or insertion materials for both the negative and the positive electrodes and in this way lithium plating can be avoided. Graphite has been one of the most commonly used negative electrode materials in Li-ion batteries as it intercalates lithium at a potential close to that of metallic lithium deposition (0.2 V vs. Li+/Li), giving a high potential to the cell [40]. Graphite was also combined with LiCoO2 as the positive electrode material in the first Li-ion battery introduced on the market in 1990 by Sony [41]. In this chapter the properties of the electrode materials used in batteries studied in this thesis will be described.

Between the positive and the negative electrode material an electrolyte is needed. The function of the electrolyte is to electronically isolate the electrodes from each other but to allow ionic exchange between them. The most common electrolytes in Li-ion batteries are mixtures of organic solvents, such as propylene carbonate (PC), ethylene carbonate (EC), diethyl carbonate (DEC) and others. In the solvent mixture a salt is dissolved, for example LiPF6 [42, 43]. The stability window of the organic solvents in the electrolyte is in the range of 1-4.5 V vs. Li+/Li [43]. When low potential anodes, as graphite, are used the stability of the cells are dependent on the formation of a stable electrolyte decomposition layer, called the solid electrolyte interphase (SEI) [44]. To circumvent the problem due to SEI formation other electrolytes might be used, such as polymer electrolytes or ionic liquids [42, 43, 45]. Otherwise, other negative electrode materials operating at higher voltages must be used and one such alternative is lithium titanate (Li4Ti5O12) [46]. However, this will give the whole cell a lower cell potential.

In this thesis several cell chemistries have been used; in paper I, the cell chemistry LiCoO2+LiMn2O4//Li4Ti5O12 was examined under different cycling conditions, in paper II, LiFePO4//graphite cells were examined under different cycling conditions, in papers III and IV, two negative electrode materials were examined, both of which can be described as Li2xNi0.5−xTiOP4, and in paper V, the synthesis of LiFeSO4F was studied.
3.1 Electrode materials

3.1.1 LiCoO₂ - Lithium cobalt oxide

LiCoO₂ was the first commercialized positive Li-ion battery electrode material and was brought to the market in 1990 by Sony. The structure of, and Li-intercalation into, this layered material have been extensively studied [47–49]. The reversible intercalation of Li in LiₓCoO₂ is only possible for lithium contents above above x=0.5 (below 4.05 V) giving a capacity of 130 mAh/g at a potential of 3.9 V.

Cycling of LiCoO₂ have been shown to lead to capacity loss due to Co dissolution [50]. Also structural degradation of the surface of the particles have been seen by electron diffraction [51] on cells stored at room temperature [52] and at elevated temperature [53]. Experiments on prismatic cells showed increased peak broadening (XRD) especially for the 003 peak and particularly for cells stored at higher SOC [54, 55]. Prolonged cycling [56, 57] and storage at elevated temperatures [58] showed a decreased intensity of the 003 peak.

The structural instability at high potentials have mainly been resolved by the introduction of Ni (the new electrode material called NCO) and also by doping with Al (called NCA) or Mn (NMC) [59]. But also surface coatings have made the material to deliver higher capacities [60]. With these modifications, the use of high potentials is the most influential parameter determining the rate of degradation [59]. When cells consisting of LCO//Li₄Ti₅O₁₂(LTO) were cycled with a load pattern mimicking EVs there are two regions of aging. The first region with a slow fade in total capacity was due to a slow loss of active material of the LTO. The second region, showing faster cell performance decay, was due to a fast loss of active LCO-material [61]. For mixed LCO+LiMn₂O₄/graphite cells, the capacity fade is increasing for storage over 50 °C and if stored at high SOC [62]. The high temperature aging was later attributed to SEI formation on the graphite for these cell chemistries [63], but a small loss of LCO-material was also found [64].

3.1.2 LiMn₂O₄ - Lithium manganese oxide

A wide range of materials of the composition LiₓMnₙOₙ can be used for Li intercalation and an extensive review on the early work on this system can be found elsewhere [65]. One of the most studied members of these materials is the lithium manganese spinel LiMn₂O₄ (LMO), which was used as the positive electrode material in one of the first published Li "rocking chair" batteries [38]. LMO can be used both for Li insertion at a potential 2.96 V vs. Li and for Li extraction with two potentials, at 4.0 V and 4.15 V. The most common application of this material in Li-ion batteries is as a cathode material, thus giving a battery with a working potential around 4 V.

The structure of LiMn₂O₄ is a cubic spinel [66], with a ccp-oxygen array with Mn occupying edge sharing octahedral sites and Li in tetrahedral sites.
with no face sharing with Mn. The structural changes during lithium extraction (solid solution at 4.0 V and a two phase transition at 4.15 V) have been studied by XRD [66–68] as well as with neutron diffraction [69].

The formation of Li$_2$Mn$_2$O$_4$ has been seen on particle surfaces from cells cycled between 4.2-3.5 V [70] and also in cells stored at elevated temperatures and SOC100 [53]. One of the major contributors to the instability of the Mn-spinel (LMO) in usage tests is the dissolution of Mn ions into the electrolyte [71]. This process is enhanced in electrolytes containing LiPF$_6$ [59], especially at high temperatures [63].

3.1.3 LiFePO$_4$ - Lithium iron phosphate

LiFePO$_4$ (LFP) is a well-studied positive electrode material with lithium extraction at a potential of 3.45 V and a capacity of 170 mAh/g. LiFePO$_4$ was first used as a positive electrode material by Padhi et al. [72]. The Li insertion/extraction takes place as a first order two-phase transformation, which has been extensively studied from a structural point of view when trying to understand the phase propagation through the crystallites in the material [73–79]. Both theoretical calculations [80, 81] and experimental results [82], have shown the Li-ion mobility to be an one-dimensional process along the b-axis in the material. To explain the high rate capabilities of the material, a solid solution range of the two end members was proposed to exist by Shrinivasan and Newman [83] and shown to exist both at elevated temperatures [84] and at room temperature [85, 86]. However, phase propagation and lithium insertion/extraction continues to be examined and discussed [78, 79]. Both phases, LiFePO$_4$ and FePO$_4$, crystallize in space group Pnma, where the FePO$_4$ has slightly shorter a and b cell-edges and a slightly increased c-axis compared to LiFePO$_4$ [87, 88].

Aging of LFP has mainly been studied in cells combining LFP with graphite. The measured properties that relate to LFP is Fe-dissolution [89] and electrolyte decomposition products [90, 91] on cycle-aged electrodes.

3.1.4 LiFeSO$_4$F - Lithium iron sulfate fluoride

LiFeSO$_4$F (LFSF) exists in two polymorphs; tavorite and triplite, both of which can be used as Li-ion insertion positive electrode materials. These materials, which combines the increased electronegativity of sulfate as compared to the phosphate used in LFP with an additional F ion, was identified to have a higher potential for Li extraction than LFP [92]. The problem with LiFeSO$_4$F is its low thermal decomposition temperature, but by reacting FeSO$_4$·H$_2$O with LiF in an ionic liquid, the tavorite polymorph could be synthesized at 300 °C [92]. This was explained to be possible due to the structural similarities of FeSO$_4$·H$_2$O and the end product, the crystal water was exchanged for
LiF through a topotactic reaction. LFSF was later synthesized using polymers [93] or tetraethylene glycol (TEG) as reaction medium at temperatures as low as 220 °C could be used [94]. The *tavorite*-polymorph has a deintercalation voltage of 3.6 V [92] and a capacity of 151 mAh/g. The surface chemistry of *tavorite*-LiFeSO₄F synthesized in TEG was studied and the capacity and rate performances were improved [95] and an intermediate Li₅FeSO₄F-*tavorite* structure was identified with *in situ* XRD and also by chemical delithiation of the pristine material [96].

3.1.5 Graphite

Graphite is a commercially used negative electrode material for Li-ion batteries and intercalate a maximum of one Li per six C atoms with a theoretical capacity of 372 mAh/g. Graphite intercalates most of the Li at a potential just above that of Li-metal deposition [40]. The staging of the Li intercalation into graphite was studied with XRD and showed a gradual intercalation of Li into graphite via a number of different stages with voltage plateaus starting at 0.21 V down to 0.085 V vs. Li metal [44].

When discussing aging of graphite electrodes the most influential part is the solid electrolyte interphase (SEI) that forms between the graphite and the electrolyte [40]. Passivation layers formed from the decomposition of organic solvents was first seen on alkali metals [97]. The SEI is formed before the first lithiation of graphite in Li-ion batteries at a potential around 0.8 V vs. Li⁺/Li which thereafter protects the electrolyte from further decomposition [40]. The properties of the SEI, its composition, formation and dissolution during usage etc. have been extensively studied [98–101].

Aging studies on graphite-containing cells have shown that the graphite side of the cell is the major reason for cell aging both for cells aged by different cycling procedures and for cells stored at elevated temperatures [63, 64, 89, 102–108]. Results from cells stored at different SOC and at different temperatures show that both high temperatures and high SOC increase the aging, with high temperature having a larger impact on performance than that of SOC. Cycling studies show that the main reasons for cell degradation is the loss of lithium inventory (mainly due to SEI reformation on the graphite) [89, 102, 104] and loss of negative electrode material [89, 103, 104]. Both high temperature and high cell potentials during cycling lead to increased aging [104].

3.1.6 Li₄Ti₅O₁₂ - Lithium titanate

The lithium-titanium-oxygen system contains many compounds that can be used as electrode materials for Li-ion batteries [109, 110]. Li₄Ti₅O₁₂ (LTO) is one of them, which has a spinel structure, and it has been explored as negative electrode material for Li-ion batteries since the early 1980’s [111]. LTO can
insert one Li per formula unit resulting in a theoretical capacity of 175 mAh/g and it has a flat insertion plateau at 1.55 V vs. Li+/Li, where a two phase transition takes place during lithiation [46]. This transition is from the spinel structure to a rock salt type Li7Ti5O12 material [112–114].

During Li insertion into LTO the cell-edge length does not change and this zero-strain property [114] of the material makes it well suited as a Li insertion material as no changes in particle size will physically mill the composite electrode. The high potential vs. Li+/Li makes this a high voltage material above the formation of the SEI. This reduces the loss of Li and the problems with the SEI formation/reformation processes are avoided.

Aging studies have shown LTO to be a stable electrode material and cells with LTO negative electrodes are primarily aged due to the positive electrode degradation [61, 115]. However, when LMO/LTO-cells with a LiPF6 containing electrolyte are stored at high temperature, gas evolution from electrolyte decomposition at the LTO surface has been observed and the LTO loses capacity [116].

3.1.7 Ni0.5TiOPO4 - Nickel titanium oxyphosphate

Ni0.5TiOPO4 is built up of corner sharing TiO6-octahedra (grey in figure 3.1) zigzagging in the c-direction. The corners between these octahedra are occupied by the non-phosphate oxygen atoms and the zigzag structure is stabilized by the connections of neighboring pairs of Ti-octahedra through a common phosphate ion (purple) [117]. The two other oxygens in the phosphate ion connect to other parallel zigzags of TiO6-octahedra. The Ni atoms (green) are also octahedrally coordinated by oxygen - face-sharing with two Ti-octahedra from different zigzags. This gives a highly interconnected Ni-Ti-O-PO4-structure in the bc-plane. These parallel structures are interconnected through Ti-PO4 interactions. Ni0.5TiOPO4 can be synthesised by solid state reaction [117, 118] or by the co-precipitation synthesis method [119].

Ni0.5TiOPO4 was first used in a lithium secondary battery by Belharouak et al. in 2005 [120] with the material synthesized through solid state synthesis. First lithiation (discharge to 0.5 V) gave a capacity of 415 mAh/g while the following charge/discharge cycles had a capacity of 284 mAh/g (corresponding to 2 Li per formula unit). XANES measurements on the Ti and Ni K-edges showed changes on the Ti-edge, indicating a Ti4+ to Ti3+ transition during lithiation but with no visible changes at the Ni K-edge [120]. In situ XRD during first discharge showed the appearance of a new phase at the same time as the pristine material lost most of the structural long range order [121, 122]. This new phase could, however, not be identified from the XRD measurements. Experiments of cut-off voltages showed that a higher cut-off (1.1 V) resulted in the same electrochemical behavior after a couple of cycles as the 0.5 V had after 1 cycle [123].
3.1.8 Li_{0.5}Ni_{0.25}TiOPO_{4} - Lithium nickel titanium oxyphosphate

The structure of Li_{0.5}Ni_{0.25}TiOPO_{4}, shown in figure 3.2, is fairly similar to Ni_{0.5}TiOPO_{4} containing the same zigzagging corner sharing TiO_{6} octahedra stabilized by sharing PO_{4}-ions in the c-direction. Also the Ni atoms are located so that they share faces with TiO_{6} of different parallel zigzags at the same site as in Ni_{0.5}TiOPO_{4} but now in Li_{0.5}Ni_{0.25}TiOPO_{4} the site is only occupied to 50%. The material has a reversible capacity of 200 mAh/g when cycled between 3.0 and 0.5 V [124]. It has also been studied by RIXS and XAS to follow the electronic changes on Ti, Ni and O, where their electronic states were found to change simultaneous during first discharge [125].

![Figure 3.1. Structure of Ni_{0.5}TiOPO_{4} viewed down the a,b and c-axis [117].](image)

![Figure 3.2. Structure of Li_{0.5}Ni_{0.25}TiOPO_{4}, based on [126]. Note that the Ni-sites (green) are only half occupied.](image)
4. Studies on commercial cells

Long-time cycling of Li-ion cells, optimized for use in electric and hybrid-electric vehicles, is greatly influencing the aging processes of the cells, and at a detail level this is not yet well understood. There are few studies that combine long time cycling with post mortem examinations of Li-ion battery cells. In this thesis, two sets of commercial cells have been evaluated with similar approaches. The first set is described in paper I and was a comparison of full SOC-swing cycling and calendar ageing of a prismatic power optimized Li-ion cell (3.1 Ah capacity) consisting of a mixed positive electrode with LiCoO$_2$ (LCO) and LiMn$_2$O$_4$ (LMO) and a negative electrode of Li$_4$Ti$_5$O$_{12}$ (LTO). The second set of experiments is described in paper II, where power optimized cylindrical Li-ion cells (2.3 Ah) consisting of LiFePO$_4$ (LFP) and graphite chemistry, were studied.

4.1 Short overview of published aging studies

As stated in the introduction (chapter 1) one of the main concerns for the use of Li-ion batteries in HEVs or EVs is the aging of cells. This can lead to a loss of cell capacity, and hence a reduced driving-range for a vehicle using batteries. However, it might also be the loss of power-capability during short periods of high energy consumption (i.e. acceleration). To monitor the degradation, methods such as ICA and $\Delta V/\Delta Q$-plots can be used (see section 2.5), but to understand the underlying chemical changes causing the aging, chemical analysis of aged cells must be undertaken.

The aging properties are dependent on the materials used in the cell: both the electrode material as described in section 3, but also on the electrolyte used. Several different degradation processes occur in the cells; loss of cyclable lithium, loss of active material (due to cracking of particles or due to loss of electrical contact caused by volume change of particles), surface film build-ups and modifications, current collector corrosion and change in the composite electrode porosity, etc. [127, 128].

For aging studies of materials and how they change, small laboratory cells (pouch cells, coin cells, or swagelok cells) have often been used. Post mortem analysis of the electrode materials in these small cells have provided some experimental results that have been used to explain cell-performance decay in larger cells. Most studies, however, focus on the full cell performance measured by non-intrusive methods, ICA, $\Delta V/\Delta Q$-plots and EIS, to find the
sources of lost capacity and lost power. This is especially true for the evaluation of larger, prismatic or cylindrical cells, composed of long spirally wound electrodes.

In post mortem studies of large commercial cells, there is the possibility to examine any number of points on the electrodes such as: the middle of the electrode or at the edge of it. Published results from cells where many different positions on the electrodes have been examined are, however, rare [89]. Post mortem characterization of only one sample point are more common [63, 64, 90]. Liu et al. [89] sampled the unwound electrodes from LFP/graphite cells at outer, middle, and inner parts of the jelly-roll. When assembling half-cells (Swagelok cells) with electrode material harvested from the different points of the large-cell electrodes, they found no loss of active material in any of these points [89]. This was in contrast to their measurements on the whole cylindrical cell, using an in situ cell with a reference electrode, that showed loss of the active negative electrode material [89]. Kassem et al. [90] used half-cells (coin cells) with electrode material harvested from LFP/graphite cells, and found a loss of graphite and reduced rate capabilities of the anode after storage at 60 ° and with cells at SOC100. They also reported that the graphite was fully delithiated at the discharged state of the whole cell (as also seen by non-intrusive tests of commercial cells [89, 103–105]). Guan et al. [64] found residual capacity (i.e. not fully delithiated graphite at cell discharge) on the negative electrode side when assembling half cells (coin cells) of both negative and positive electrodes in their study of LCO/graphite cells. Small scale cells of LiFePO4 were also found to have a spatial distribution of SOC within the cell [129]. This was measured with μXRD to examine the fractions of FePO4/LiFePO4 at different positions in the cell [129].

To summarize the methods used for evaluation of cell performance: non-intrusive techniques are important to develop as they are the ones possible to use onboard vehicles. The non-homogeneity detected by post mortem studies at different locations inside large cells have not yet been discussed in terms of how they will affect the results from non-intrusive measurements. It is not enough to evaluate non-homogeneous degradation based on post mortem studies of small cells which do not experience gradients in temperature or current loading etc. as is the case for large cells. Therefore post mortem studies of large scales using multiple sampling points are important, as they can detect and describe the non-homogeneous degradation, also in terms of the parameters extracted from onboard measurements.

In paper I, post mortem analysis was combined with half-cell studies of harvested material from aged LCO+LMO/LTO cells showing that changes in the positive electrode material was the major source of capacity fade. In paper II, the inhomogeneities within LFP/graphite cylindrical cells are shown and evaluated for cells cycled with different load patterns.
4.2 LiMn$_2$O$_4$-LiCoO$_2$/Li$_4$Ti$_5$O$_{12}$ cell – Paper I

One Li-ion cell was charged/discharged with constant current (6.8 A) in the full potential range (2.8 V to 1.5 V) at 55 °C and a second cell was calendar aged at room temperature for the same length of time. The cycling was stopped after 9 months, which corresponded to 9201 full cycles, and the cells were stored for 30 months. Thereafter capacity vs. voltage profiles and electrochemical impedance were measured (all at 25 °C) and the cells were then disassembled, rebuilt to half-cells (with lithium foils as counter and reference electrodes, glass fiber separator, 1 M LiPF$_6$ EC:DEC 1:1 (Merck) electrolyte). Some material was also harvested for SEM/EDX and XRD analyses. Only one sample position on the unwound electrode was used. The calendar aged cell was opened at SOC ~0 % and the cycle aged at SOC ~50 %.

The capacity change during the aging process was negligible for the calendar aged cell and substantial for the cycle aged cell. The capacity of the cycle aged cell, when measured at low currents, was 29 % lower than the initial capacity.

4.2.1 SEM/EDX

SEM micrographs of the positive and negative electrodes after the different aging conditions showed only small differences. EDX maps of the positive electrodes of the two differently aged cells are shown in figure 4.1a (calendar aged cell) and in 4.1b (the cycle aged). For the calendar aged cell, figure 4.1a, a mixture of particles where each particle is either LiCoO$_2$ or LiMn$_2$O$_4$ is seen. For the cycle aged cell, figure 4.1b, the metal atom distribution in the electrode show that at least one of Mn or Co is moving and depositing on the particles of the other material. In figures 4.1a and b, two points in each figure indicate where the EDX spectra, shown in figures 4.1c and d, were measured. It can be noted that all four measuring points shown in figures 4.1c and d have contributions of both Mn and Co.

EDX of the negative electrode show deposition of Mn on the LTO for the cycle aged cell but not for the calendar aged one, see figure 4.2. No Co was seen on the LTO indicating that the element moving/redepositing on the positive electrode is Mn.
Figure 4.1. (a,b) Element mapping of the positive electrode, green color indicating cobalt dominated position and magenta showing manganese domination. (c) EDX spectra from points indicated by 1 and 2 in figure 4.1a. (d) EDX spectra from points indicated by 1 and 2 in figure 4.1b. Reprinted from paper I with permission from the publisher.

Figure 4.2. The EDX spectra of the negative electrode of both the calendar aged and cycle aged cells. The Mn peak in the insert shows the deposition of Mn on the negative electrode material for the cycle aged cell. Reprinted from paper I with permission from the publisher.
4.2.2 XRD

The results of the XRD measurements are plotted in figure 4.3. The peak widths for the cycle aged cell were broader than for the calendar aged cell. The peaks from LiMn$_2$O$_4$ were broader than the peaks originating from LiCoO$_2$. The broadening indicates an increased amount of defects in the material or a reduced domain size (particle cracking).

![Diffraction patterns showing the peak broadening of the cycle aged cell compared to that for the calendar aged. This broadening is more pronounced for LiMn$_2$O$_4$.](image)

Figure 4.3. Diffraction patterns showing the peak broadening of the cycle aged cell compared to that for the calendar aged. This broadening is more pronounced for LiMn$_2$O$_4$.

4.2.3 Incremental capacity analysis and differential voltage analysis

Incremental capacity measurements are shown in figure 4.4: full cell measurements of both cells in (a); cycle aged full cell at different cycling rates in (b); positive electrodes from both cells in (c); and negative electrodes from both cells in (d). In figure 4.4a one distinct peak (at 2.35 V) and two smaller peaks (at 2.45 and 2.6 V) are observed. The 2.35 V peak is the two phase region in the delithiation of LiCoO$_2$ (at 3.93 V vs. Li$^+/Li$) and the other two originate from the two peaks observed when delithiating LiMn$_2$O$_4$ (at 4.0 V and 4.15 V vs. Li$^+/Li$). The full cell data (figure 4.4a) show that the LiCoO$_2$ was the most affected by the cycle aging, as the peak at 2.35 V shows the largest change.
The capacity mismatch between the electrodes showed that both full cells were found to be limited at low potential by the metal oxide positive electrode material and at the high potential it was limited by the negative electrode material. Thus in none of the cells, the electrode materials are utilized to their full capacity, due to the loss of lithium inventory.

Figure 4.4. (a) dQ/dV-plot for calendar aged (C/20) and cycle aged (C/100) cells. (b) Cycled aged cell at different currents. (c) Positive electrode material vs. lithium at C/100. (d) Negative electrode material vs. lithium at C/100. Reprinted from paper I with permission from the publisher.

4.2.4 Conclusions of Paper I

Comparison of two ageing situations showed that calendar aging does not significantly influence the performance of a LCO-LMO/LTO cell. Constant current cycling, however, mainly age the cell by loss of cyclable Li and loss of positive active material. Both these processes are reducing the available capacity of the cell. This loss of active material on the positive side of the cell (the LCO/LMO electrode) is in agreement with previous results for LCO, LMO and LTO cells, where the metal oxides lost capacity (active material) at a higher rate than the LTO [61, 115]. There is also a significant impedance rise in the cell, limiting the power that the cell was able to deliver. The reason for this could be the formation of the different surface layers known to be formed
on LCO [51, 52] and LMO [53], but could also be due to the Mn dissolution and redeposition of Mn on both electrodes. 

Mn was found on the negative electrode material after constant current ageing (as have been previously reported for LMO [71]) and redepositing of Mn on the LiCoO₂ particles was seen on the positive electrode side. This suggests that Mn might be intercalated into the LCO structure, disturbing the two phase region of lithium intercalation at 3.9 V, reducing the capacity at this potential as seen in the cycle aged cell.

When examined by XRD, the LMO showed broader peaks for the cycle aged cell than for the calendar aged, indicating an increased disorder in the material or reduced particle size. The XRD results showed the largest change for LMO, in line with the severe Mn dissolution seen by EDX. However, this is in contrast to the capacity measurements that showed a larger change in the capacity originating from the LCO, when comparing the cycle aged cell to the calendar aged.

### 4.3 LiFePO₄/Graphite cell – Paper II

In paper II, cylindrical cells (2.3 Ah) cycled with two different loads were examined together with a cell that was calendar aged. The cells were cycled with a hybrid electric vehicle cycle (HEVC), a constant current cycle (CCC) or stored without cycling (CAL). The HEVC was a load pattern to represent cell usage as for a battery in a vehicle application, the CCC was a constant current charge-discharge between fixed cut-off potentials. The CAL cell was stored at room temperature. At the end of life the cells were opened and several parts of each electrode from all cells were examined with different characterization methods to investigate how the cells had aged. Samples were collected from several positions of the jelly roll. Sample positions are illustrated in figure 4.5. The results show a clear difference between the different usage patterns but also variations in material utilisation and SEI formation through the cell jelly roll. The aging was seen as an increase in impedance and capacity losses of primarily the graphite electrodes. This also influenced the degree of lithiation of the LiFePO₄, as measured by XRD on the cells disassembled in discharged state. The differences in aging within each cell are likely connected to the temperature variations and the current distributions within the cells.
4.3.1 SEM

SEM micrographs of midpoint and edge samples for all cells are shown in figure 4.6. The SEM results can be summarized as follows: the LiFePO$_4$-electrode had a uniform appearance for all samples. The graphite from the CAL-aged cell has a uniform appearance at all sample positions. The midpoint sample of the CCC graphite has a thick coating covering the entire graphite electrode leaving no graphite flakes visible. The edge sample of the CCC graphite show a more granulated structure compared to the structure of the graphite from the CAL-aged cell. The midpoint sample from the HEV cell has the same appearance as the CAL cell edge sample. The edge sample from the HEV cell shows a granulated graphite like the one seen in the CCC-edge sample.

Figure 4.5. Schematic picture of an opened cell indicating the different sample points.

Figure 4.6. SEM micrographs of electrodes from commercial cells aged differently and from two sample positions of the negative electrode material (graphite) and one position from the positive (LiFePO$_4$). (a,b,c) Cell cycled with a load mimicking a hybrid electric vehicle load. (d,e,f) Cell cycled with constant current full SOC-swing load. (g,h,i) Calendar aged cell. Reprinted with permission from the publisher.
4.3.2 EDX and XPS

To evaluate the graphite samples, EDX and XPS were used. Fe was detected by EDX on the CCC and HEVC midpoint samples, and originates most probably from iron dissolution at the positive electrode. XPS measurements of Fe 2p$_{3/2}$ detected Fe only in the CCC samples. These differences in iron measurements might be due to different probing depths for the two methods.

XPS results can be seen in figure 4.7 (HAXPES) and figure 4.8 (in house XPS). Figure 4.7 shows the spectra collected for C 1s, O 1s, P 2p and F 1s from the midpoint sample position for all three cells. The results in figure 4.7 show that the SEI on the CCC and CAL are the most different. The HEV cell has C 1s and O 1s spectra resembling the CCC sample and P 2p spectra more like the CAL cell. In figure 4.8 the intensities of selected LiF, CO$_3$ and P-O/P=O peaks are shown for the CCC and the HEV cell, measured at both the skin middle and the midpoint sample positions. The in house XPS measurements in figure 4.8 show that the difference between different sample points of the same battery is as large as those created by the different cycling conditions.

The differences between the cells can, as seen from the HAXPES/XPS measurements, be summarized as: the CCC cell has more LiF and CO$_3$ species than the HEV cell, whereas the HEV cell has a larger P-O/P=O content. The differences between the skin and the material further into the electrode coil are that the contribution from CO$_3$ is higher in the midpoint samples whereas LiF and P-O/P=O are higher in the skin region.
Figure 4.7. C 1s O 1s P 2p F 1s spectra of midpoint sample position of the graphite electrode measured with HAXPES. The photon energy was 2300 eV. Reprinted from paper II with permission from the publisher.

Figure 4.8. Relative intensities of some peaks from the F 1s, O 1s and P 2p spectra for skin-middle and midpoint samples. The photon energy was 1486.6 eV (Al Kα radiation). Reprinted from paper II with permission from the publisher.
4.3.3 XRD

XRD was used to probe the crystalline composition of the positive electrode, *i.e.* the relative amounts of LiFePO$_4$ and FePO$_4$ in the electrode. The state of charge of the electrode can be seen as the degree of lithiation in the electrode. From XRD and subsequent structure refinements with the Rietveld method the phase fractions (in weight percentage) can be determined and then expressed as the degree of lithiation of the cathode. Since the cells were discharged prior to disassembly an ideal LFP/graphite cell would have a uniformly 100% lithiated positive electrode showing no FePO$_4$ in the diffraction pattern. In figure 4.9a, an indicative part of the diffraction patterns are shown (to the left) and a map of percentage of LiFePO$_4$ at 6 different sample points is shown for all cells. The cell with the most uniform distribution of LiFePO$_4$ was the CAL cell. This cell had a lithiation degree varying between 83-93%. The CCC cell had a lower degree of lithiation and also a less homogenous distribution of LiFePO$_4$ where the edge part of the electrode jelly-roll had a higher degree of lithiation. The HEV cell had both the sample points with the highest degree of lithiation but also parts with very low lithiation showing a very non-uniform distribution of the lithium throughout the electrode.
Figure 4.9. XRD measurements of the LiFePO$_4$ electrode at various points of the electrode jelly-rolls showing the inhomogeneity of the utilization of the electrode roll (all standard deviations as calculated in the structure refinements were less than 0.5 %). (a) Calendar aged cell showing a uniform discharged state with high lithiation degree. (b) The CCC showing high content of FePO$_4$ indicating high lithium loss or the incapability to fully discharge the cell. (c) HEVC showing high variations in the capability to fully discharge the cell, indicating highly localized ageing and large discrepancies in utilization capacity between different parts of the cell. Reprinted from paper II with permission from the publisher.
4.3.4 Electrode capacity at disassembly

From all parts of the batteries small samples (discs with 18 mm diameter) were harvested from the electrodes and assembled into half-cells (with a Li foil as counter electrode). By charging the electrodes they were delithiated and the amount of lithium that can be drawn from the electrodes is a measure (like the XRD) on how well the discharge process worked prior to the disassembly. Cycling of the harvested electrode samples gave information on the amount of active material that was still able to deliver capacity in different parts of the battery. In figure 4.10, the measurements on both positive and negative electrode materials are put together to visualize the usable capacity of the battery (indicated by pink in the graphs), seeing that a slippage between the electrodes results in lower usable capacity than the separate electrodes would suggest. This slippage is attributed to the loss of lithium inventory. This loss of lithium is most prominent for the CCC midpoint sample as seen by the narrow pink region in figure 4.10, highlighting the limited utilization of the electrodes. In this cell, less than half of the cathode material and only 65% of the anode material is used during the full-cell cycling. This point was also the one with thick deposits as seen by SEM, and low lithiation degree of the LFP as seen by XRD. This low usable capacity can be a result of SEI reformation during cycling consuming the available lithium.

4.3.5 Conclusions of Paper II

Whole-cell analysis showed calendar aging to be less detrimental compared to two different cycling conditions: as previously seen by others [89, 102]. Of the two cycling loads, constant current resulted in the fastest decay in cell performance. Further, the spatial distribution of electrode degradation was found to be substantially different between the three cells examined. This spatial difference was seen in terms of different parts of the same cell showing different capacities and impedances. This is in line with the results of the small cell studies of Liu et al. [129], which showed spatial distribution in the degree of lithiation in LFP pouch cells. This uneven aging is believed to be a result of temperature differences within the cylindrical cell, but is also influenced by usage pattern. A better understanding of this spatial distribution in the observed degradation can lead to better models for cell utilization and thus to a better understanding on how different load patterns will age a cell.
Figure 4.10. Electrode slippage determined from lithiation measurements of the negative and positive electrode material. Indicated in pink are the usable windows for cycling after the different ageing conditions. The long vertical dashed line is the point where the cells were opened, after they had been fully discharged. Reprinted from paper II with permission from the publisher.
5. Studies on $\text{Li}_x\text{Ni}_{0.5-x/2}\text{TiOPO}_4$ material – Paper III and IV

Graphite is the most commonly used negative electrode material for commercial Li-ion batteries. It has a theoretical capacity of 372 mAh/g and operates at a low potential (0.2 V) close to that of $\text{Li}^+$/Li which gives battery cells delivering high voltages when combined with a standard positive electrode material. This low potential of lithium intercalation into graphite is also the major drawback of graphite as it decomposes the organic solvents in the standard liquid electrolytes (see section 3.1.5). To circumvent this problem, either other negative electrode materials operating above the SEI formation at 0.8 V [100] must be used or the electrolyte changed to a polymer [130] or an ionic liquid [131] based system. The suggestion to change the electrolyte is interesting but shall not be discussed further in this thesis.

Lithium titanate (LTO) reversibly inserts lithium at potentials above the SEI formation and it has been extensively studied. LTO shows high power capabilities with limited volume expansion in the material during lithium insertion and is highly interesting for batteries used for hybridization of heavy duty vehicles. LTO is the most well known high potential negative electrode material and despite the many benefits of LTO, there is a need to find alternatives; these materials should have capacities beyond the 175 mAh/g that LTO delivers.

Elements that can alloy with lithium can be used as alternatives to graphite and LTO (e.g., Si and Sn) or conversion materials such as metal oxides reacting with lithium to form metal and lithium oxide e.g., NiO and CoO [132–134]. They normally operate above 1 V and thus above the SEI formation potential [134]. The main problems with conversion materials are the large non-reversible capacity of the first cycle and the large potential hysteresis between charge and discharge [134].

In this thesis, two negative electrode materials both of the general composition $\text{Li}_x\text{Ni}_{0.5-x/2}\text{TiOPO}_4$ have been studied. They are materials that combine both conversion and insertion characteristics, making them interesting as model materials for self-assembling nanoconversion materials, framed into a lithium insertion matrix. $\text{Li}_{0.5}\text{Ni}_{0.25}\text{TiOPO}_4$ (studied in paper III) has a stable capacity of 200 mAh/g when cycled between 3.0 and 0.5 V vs. $\text{Li}^+$/Li and a voltage plateau at about 1.6 V giving a capacity of about 100 mAh/g [124]. The structure degradation during the first full cycle of this material was studied in paper III. $\text{Ni}_{0.5}\text{TiOPO}_4$ (studied in paper IV) has a reversible capacity of 260 mAh/g [123], but exhibits a more sloping potential profile between 3.0
and 0.5 V vs. Li+/Li. The loss of long range order in this material during cycling has been studied by XRD [121–123], and therefore the short range order around Ni was examined by EXAFS in paper IV. This was also combined with HAXPES and XANES measurements to evaluate the participation of Ti and Ni during lithium insertion and to study the SEI formed on the material.

5.1 Li$_{0.5}$Ni$_{0.25}$TiOPO$_4$ - XRD studies – Paper III

In paper III, Li$_{0.5}$Ni$_{0.25}$TiOPO$_4$ was investigated with in situ XRD, to examine if the clear voltage plateaus seen during the first cycle of lithiation are due to crystalline-to-crystalline transitions.

The cycling performance of the in situ cell for the experiment is shown in figure 5.1. The results in figure 5.1 show a high polarization of the cell and also that the capacity is lower than expected from previous studies; only 250 mAh/g for the first discharge. There was also instability in the potential during the experiment. There are several reasons for the observed difference when comparing to previous reports. Firstly, the powder particles in this study were not coated with carbon, as in earlier papers [124], and this together with the higher current used for the experiment can be a possible explanation for the large polarization. Secondly, the temperature inside the measuring room at the beamline is known to vary periodically by a few degrees. This gives rise to small fluctuations in the potential most clearly seen in the discharge curve during the experiment.

Diffraction patterns collected at different times during this first cycle (discharge and charge) are shown in figure 5.2. The results show that during the first lithiation of the pristine material (called phase A) two phases appear consecutively and they are denoted phase B and C.

The appearance of B (at 50 mAh/g) is preceded by a solid solution behaviour with insertion of lithium into the pristine phase with primarily an increase in the a-cell parameter, while the b- and c-cell parameters are mostly unaffected. This is observed as a difference in peak positions, by comparing the peaks 200, 211, -211 that are moving as a function of lithiation with the more fixed peaks with indices 012 and 022. The set of peaks for the B phase could be indexed with a unit cell, see table 5.1. After the appearance of phase B there is a two phase region consisting of A and B until 200 mAh/g has been reached where a third set of peaks emerges, this might indicate a second phase transition at the end of the lithiation. However, the peaks are very broad in this new set indicated by C.

During the consecutive delithiation (charge) of the electrode material no changes are seen in the diffraction pattern until close to the end of charge. For the fully charged sample, the peaks from the original phase emerges although they are weak and broad when compared to the diffraction pattern from the pristine material. During charge the intermediate phase B is not detected.
Table 5.1. Cell parameters for phases identified or indexed in the in situ experiment seen in figure 5.2. Phase A is the starting material Li_{0.5}Ni_{0.25}TiPO_4, the peaks labelled "B" in figure 5.2 can be indexed by a monoclinic unit cell with the cell parameters found in this table.

<table>
<thead>
<tr>
<th>Time(h)</th>
<th>Phase</th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>beta</th>
<th>Bragg R</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>A</td>
<td>6.397(2)</td>
<td>7.259(4)</td>
<td>7.366(3)</td>
<td>90.31(8)</td>
<td>13.4</td>
</tr>
<tr>
<td>6</td>
<td>A</td>
<td>6.413(3)</td>
<td>7.287(6)</td>
<td>7.393(4)</td>
<td>90.41(11)</td>
<td>51.1</td>
</tr>
<tr>
<td>6</td>
<td>B</td>
<td>9.085(4)</td>
<td>8.414(5)</td>
<td>6.886(5)</td>
<td>99.85(4)</td>
<td></td>
</tr>
<tr>
<td>end</td>
<td>A</td>
<td>6.392(18)</td>
<td>7.275(40)</td>
<td>7.423(21)</td>
<td>90.79(93)</td>
<td>52.4</td>
</tr>
</tbody>
</table>

5.1.1 Describing the changing structure

The reduction of Ti (seen by Hollmark et al. [125]), during the first plateau at 1.43 V, would lead to an increased bond length between the Ti and the surrounding O. Since the structure is highly interconnected between PO_4-units and TiO_6-octahedra and this especially is the case in the bc-plane an increase in bond length between Ti-O would mainly affect the a-direction, as is also seen in figure 5.2.

The reduction of Ni in the structure would also lead to an increased Ni-O bond length, but since the Ni-octahedra are not as highly interconnected with each other as the Ti-octahedra are, the unit cell volume would be more isotropic. Later during the lithiation, Hollmark et al. [125] observed a change in the Ni oxidation state and this might then lead to the reduced crystallinity seen at end of discharge in figure 5.2.

The difference in crystallinity between the pristine material and the charged sample (after one full cycle) is also in line with the model that the reduction of Ni is the main reason to the reduced crystallinity, as the Ni never return to the fully oxidized 2+ state [125].

The structural change during charge does not proceed through the intermediate B-phase seen on discharge. The B-phases seem thus to be stabilized by the Ni ions and when those are not present as Ni^{2+} the B-phase is not formed.
Figure 5.1. Voltage profiles for the in situ XRD experiment with constant current discharge and charge.

Figure 5.2. Diffraction patterns from various times of the in situ XRD experiment.
5.2 \textit{Ni}_{0.5}\textit{TiOPO}_4 - examining the collapsing structure -
\textit{Paper IV}

In \textit{paper IV}, the lithiation and delithiation of \textit{Ni}_{0.5}\textit{TiOPO}_4 were examined during the first 1.5 cycles with HAXPES, XANES and EXAFS. By examining cells stopped at different potentials during the first 1.5 cycle a clearer view of the charge compensation mechanism and structural changes could be achieved. The different samples were stopped as indicated by the numbers in the curves in figure 5.3 and they are also referred to with their degree of lithiation denoted $x$ in Li$_x$Ni$_{0.5}$TiOPO$_4$. HAXPES results showed that both the Ni$^{2+}$ and the Ti$^{4+}$ are reduced during the first lithiation. At the end of the following delithiation Ti has returned to Ti$^{4+}$, while Ni is a mixture of Ni$^{2+}$ and Ni$^{0}$. Additionally, XANES results show that the electronic structure of P does change reversibly during lithiation and EXAFS results showed the formation of small Ni clusters during lithiation.

![Figure 5.3. Discharge-charge curve for Ni$_{0.5}$TiOPO$_4$ vs. Li$^+$/Li showing where the cells were stopped for examination by HAXPES, XANES and EXAFS.](image)

5.2.1 HAXPES – Electrode material

HAXPES measurements can provide information on the oxidation state of the elements in the active material. XPS is a surface technique but HAXPES, with a higher energy of the incoming X-rays, has a larger probing depth and our results show that material underneath the SEI can be characterized. Thus, the oxidation state of the metals in the active materials can be determined using HAXPES. In figure 5.4, HAXPES measurements of Ni 2p$_{3/2}$, Ti 2p, and C 1s are shown. These spectra are calibrated to the C-C/carbon black peak in the C 1s spectra at 284.3 eV. A summary of the oxidation states for Ni and Ti is
shown in table 5.2. HAXPES measurements show the non-reversibility of Ni and also that the changes in oxidation state of Ni and Ti only sums up to 75% of the charge delivered to the cell, and that the extra capacity is found below 1.5 V.

For all the measured energy levels the results from the pristine sample are rather different compared to the results from the lithiated samples. In the Ni 2p3/2 and Ti 2p spectra, there are states at higher binding energies than expected for Ni2+ and Ti4+. For the Ni it could be due to oxygen deficiencies around the Ni, but this was not verified. The higher energy peak in the Ni 2p3/2 spectra return upon full delithiation but with lower relative intensity. However, the observed states at higher binding energies for Ti 2p are only seen in the pristine sample.

The HAXPES measurements of the first lithiation show that the reduction of Ni2+ and Ti4+ are not clearly sequential but rather takes place in parallel. During the first discharge, the Ni is reduced to a metallic state and the Ti changes to a mixture of 4+, 3+ and 2+. These changes are summarized in table 5.2.

The delithiation of the material shows that the Ni does not return to a 2+ state only. In the fully charged sample there is a mixture of Ni2+ and Ni0. The Ti is oxidized back to Ti4+ at the end of charge.

**Figure 5.4.** HAXPES results for Ni 2p3/2, Ti 2p and C 1s for the different sample points. The photon energy was 2300 eV.
Table 5.2. Extracted fractions of the distribution of different oxidation states for Ni and Ti for the different samples. The column sum is the total change in number of electrons as calculated from the start of charge or discharge.

<table>
<thead>
<tr>
<th>x = Li</th>
<th>Ni^{2+}</th>
<th>Ni^{0}</th>
<th>Ti^{4+}</th>
<th>Ti^{3+}</th>
<th>Ti^{2+}</th>
<th>Ti-average</th>
<th>Sum</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.00</td>
<td>0.00</td>
<td>1.00</td>
<td>0.00</td>
<td>0.00</td>
<td>4.00</td>
<td>0.00</td>
</tr>
<tr>
<td>0.5</td>
<td>0.82</td>
<td>0.18</td>
<td></td>
<td></td>
<td></td>
<td>0.18</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>0.62</td>
<td>0.38</td>
<td>0.42</td>
<td>0.58</td>
<td>0.00</td>
<td>3.42</td>
<td>0.96</td>
</tr>
<tr>
<td>2</td>
<td>0.12</td>
<td>0.88</td>
<td>0.38</td>
<td>0.54</td>
<td>0.08</td>
<td>3.3</td>
<td>1.58</td>
</tr>
<tr>
<td>3.5</td>
<td>0.00</td>
<td>1.00</td>
<td>0.26</td>
<td>0.56</td>
<td>0.19</td>
<td>3.1</td>
<td>1.9</td>
</tr>
<tr>
<td>1</td>
<td>0.11</td>
<td>0.89</td>
<td>0.46</td>
<td>0.42</td>
<td>0.13</td>
<td>3.36</td>
<td>0.37</td>
</tr>
<tr>
<td>2</td>
<td>0.64</td>
<td>0.36</td>
<td>0.87</td>
<td>0.13</td>
<td>0.00</td>
<td>3.87</td>
<td>1.41</td>
</tr>
<tr>
<td>1</td>
<td>0.12</td>
<td>0.88</td>
<td>0.45</td>
<td>0.41</td>
<td>0.14</td>
<td>3.31</td>
<td>1.08</td>
</tr>
<tr>
<td>2</td>
<td>0.04</td>
<td>0.96</td>
<td>0.26</td>
<td>0.50</td>
<td>0.23</td>
<td>3</td>
<td>1.47</td>
</tr>
</tbody>
</table>

5.2.2 EXAFS

EXAFS-functions and their Fourier transforms are shown in figure 5.5. The pristine material shows multiple waves with different frequencies in $\chi$-space (as expected for the pristine material) but in the fully lithiated sample there is only one frequency present. The major change in the EXAFS-function is seen between the x=1.5 to x=2, where the single frequency for the fully discharged sample has started to dominate the high $k$-region. At low $k$, it is still modulated by other frequencies.

The frequency and the envelope of the EXAFS-signal in the fully discharged sample suggest that the single interaction may be Ni or Ti atoms surrounding the central Ni atoms. To evaluate if this could be a Ni-Ni interaction, a structural model of metallic Ni was fitted to the EXAFS measurements and then to the measured sample. The fit can be seen in figure 5.6. The created model also included a Hedin-Lundqvist potential to make the model fit the Ni metal measurements with a coordination number of 12. This model was then fitted to data from the fully discharged sample. The results of the fittings are seen in table 5.3, showing a similar inter atomic distance but a lower coordination number for the electrode material than for the Ni metal. This is interpreted as formation of metallic-like Ni clusters during the lithiation. In these clusters the atomic distances are close to those in Ni metal but any ordering within these clusters are non-existent as no multiple scattering is seen in the EXAFS measurements. The coordination number is also much lower, less than half of that for the crystalline metal.
Table 5.3. Values from the fit of Ni metal model (first coordination shell), when fitted to the reference metal data and to the fully discharged data.

<table>
<thead>
<tr>
<th></th>
<th>Ni metal</th>
<th>Fully discharged sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>R-window:</td>
<td>1.14 - 2.85</td>
<td>1.16 - 2.83</td>
</tr>
<tr>
<td>k-window:</td>
<td>3.33 - 15.47</td>
<td>3.14 - 12.04</td>
</tr>
<tr>
<td>E₀ (eV):</td>
<td>8330.899</td>
<td>8331.777</td>
</tr>
<tr>
<td>R-factor:</td>
<td>3.19</td>
<td>5.15</td>
</tr>
<tr>
<td>Energy shift (eV):</td>
<td>7.3 ± 0.3</td>
<td>1.4 ± 0.7</td>
</tr>
<tr>
<td>Path degeneracy:</td>
<td>12.0 ± 0.3</td>
<td>5.4 ± 0.3</td>
</tr>
<tr>
<td>Path length (Å):</td>
<td>2.483 ± 0.001</td>
<td>2.399 ± 0.004</td>
</tr>
<tr>
<td>Debye-Waller (Å²):</td>
<td>0.0062 ± 0.0001</td>
<td>0.0121 ± 0.0004</td>
</tr>
</tbody>
</table>

5.2.3 Finding the full picture

From the combined results of HAXPES, EXAFS and XANES the lithiation process during the first discharge of Ni₀.₅TiOPO₄ was shown to involve: reduction of Ni²⁺ to Ni⁰ where Ni⁰ form small non-crystalline clusters. Reduction of Ti⁴⁺ to Ti₃⁺ and Ti²⁺. There is also a SEI formed below 1 V, and a shift in HAXPES peaks from SEI components relative to the peaks from the bulk material, Ni and Ti, at lower potentials. The following delithiation/lithiation cycle show that Ni⁰ is not oxidized back to Ni²⁺ at fully delithiated state but that the reduction of the Ti ions is fully reversible. Furthermore, our measurements show that approximately 25% of the sustained capacity after the first lithiation could not be explained by redox processes involving the metals in the material as measured with HAXPES. The Li 1s spectra from the HAXPES measurements did not contain any signal of Li₂O, and this indicates that Li₂O is not formed during lithiation.
Figure 5.5. EXAFS-functions for Ni measurements are shown to the left, as a function of degree of lithiation and to the right the Fourier transforms of the EXAFS-functions are depicted. This shows the transition from the original phase with NiO₆-coordination around the Ni to the metal-like distance between Ni-Ni found in the fully lithiated sample.
Figure 5.6. Model (dotted line) fitted to the EXAFS measurement from the fully discharged sample (solid line) showing both the Fourier transform (bottom) and the filtered fitting space (top).
6. LiFeSO₄F synthesis examined by _in situ_ XRD – _Paper V_

To produce battery electrode materials in a more sustainable way, the synthesis conditions as precursor material, temperature and pressure can be fine-tuned to reduce energy consumption and emissions. One way to better understand the synthesis of crystalline material is to use _in situ_ XRD. In _paper V_ the synthesis of LiFeSO₄F, _tavorite_-type, was examined to determine if the synthesis is necessarily a topotactic reaction starting from the structurally similar FeSO₄ · H₂O and LiF or if it is possible to synthesize through a non-topotactic reaction starting from Li₂SO₄ and FeF₂. The formation mechanism of _tavorite_-LiFeSO₄F has been under discussion, as the first publications [92] synthesized _tavorite_-LiFeSO₄F through a topotactic reaction starting from FeSO₄ · H₂O. But _tavorite_-type LiFeSO₄F has also been synthesised from Li₂SO₄ and FeF₂ [135]. It was later shown that FeSO₄ · H₂O and LiF were formed during the synthesis when starting from Li₂SO₄ and FeF₂ before the formation of LiFeSO₄F [136].

_In paper V_ this was investigated by _in situ_ X-ray diffraction. The starting materials were mixed in tetraethylene glycol (TEG) and inserted into a reaction cell and heated to the reaction temperature 230 °C. The reaction was then possible to follow in a straightforward way and the results show that the topotactic pathway is the one followed for the formation of _tavorite_-type LiFeSO₄F using both sets of reactants.

### 6.1 Starting from FeSO₄ · H₂O and LiF

Starting from FeSO₄ · H₂O and LiF, and heating the mixture to 230 °C and then keeping the mixture at this temperature for 3 h and 30 min lead to that no structural change could be observed. The temperature was then increased in two steps, first to 260 °C and then held for 1 h and 20 min. Then the temperature was increased to 280 °C where it was held until the end of the experiment, where almost 100 % of the product was formed. The diffraction patterns are shown in figure 6.1a and the refined phase fractions together with the temperature variations are shown in figure 6.1b.

Structure refinements were done to extract weight fractions of the different phases in the sample at different steps in the synthesis. The first collected diffraction pattern showed 80.8 % FeSO₄ · H₂O and 19.2 % LiF. The end-of-experiment diffraction pattern showed a composition of 92 % LiFeSO₄F, 2.3 % FeSO₄ · H₂O and 5.7 % LiF.
Figure 6.1. In situ XRD experiments of the synthesis of LiFeSO$_4$F from FeSO$_4$·H$_2$O and LiF. (a) Diffraction patterns collected during the experiment. (b) Phase fractions as determined by structure refinements with the Rietveld method showing the formation of LiFeSO$_4$F as a function of time. Plotted are also the temperature changes during the experiment.
6.2 Starting from Li$_2$SO$_4$ and FeF$_2$

Two experiments were done starting with Li$_2$SO$_4$ and FeF$_2$. The first had a water contaminated reactant: the main impurity being Li$_2$SO$_4$·H$_2$O. The results from that experiment are shown in figure 6.2. To reduce the amount of contaminant, an additional experiment was carried out starting from dried Li$_2$SO$_4$. The main contaminant in that experiment was Fe$_2$F$_5$·2H$_2$O, and the result from this experiment is shown in figure 6.3.

In the experiment containing the Li$_2$SO$_4$·H$_2$O impurity there was a varying pressure in the reaction vessel due to gas leakage: the pressure variations are plotted in figure 6.2b together with phase fractions. The diffraction patterns are shown in figure 6.2a. The small diffraction peak at 2\(\theta\) ~10 degrees is from Fe$_2$F$_5$·2H$_2$O and was not included in the structural refinements. During the initial heat ramp to 230 \(\degree C\), the impurity Li$_2$SO$_4$·H$_2$O dehydrates, starting at ~145 \(\degree C\), about 20 minutes into the experiment, and shortly thereafter followed by dehydration of Fe$_2$F$_5$·2H$_2$O. After that there was formation of LiF and FeSO$_4$·H$_2$O. This is probably a recrystallization process forming the intermediate precursors for the formation of LiFeSO$_4$F. Further into the experiment (at ~3 h), the formation of LiFeSO$_4$F starts and at the end of experiments only LiFeSO$_4$F, LiF and the excess of Li$_2$SO$_4$ are present.

A second experiment was performed with dried Li$_2$SO$_4$ to eliminate the Li$_2$SO$_4$·H$_2$O contaminant to examine where the water to form FeSO$_4$·H$_2$O comes from. Thus, the starting composition in this experiment was 69 % of Li$_2$SO$_4$ and 29 % FeF$_2$, and with small amounts of Fe$_2$F$_5$·2H$_2$O (about 2 %). The diffraction patterns collected during this experiment are shown in figure 6.3. The result shows that the Li$_2$SO$_4$ and FeF$_2$ convert to FeSO$_4$·H$_2$O and LiF during the initial heating (as in the previous experiment) thus showing that the hydrate contamination is not the only source of water in this experiment. It is the water introduced by the hygroscopic TEG (containing ~1100 ppm H$_2$O as determined by a Karl Fisher titration) that makes the formation of FeSO$_4$·H$_2$O possible. To induce the formation of LiFeSO$_4$F the pressure and temperature was changed in the reaction cell: at 7 h the pressure was reduced to 10 bar and then increased to 28 bar at 8.33 h without any difference in the diffraction pattern. The temperature was increased first to 250 \(\degree C\), 8.75 h into the experiment and then to 270 \(\degree C\), 9.5 h into the experiment without any change in the diffraction pattern.

6.2.1 Conclusions of Paper V

The reaction to form tavorite-type LiFeSO$_4$F at low temperatures in TEG-medium is through FeSO$_4$·H$_2$O and LiF even when starting from Li$_2$SO$_4$ and Fe$_2$F.

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Figure 6.2. (a) Diffraction patterns for the synthesis of LiFeSO₄F starting from Li₂SO₄ and FeF₂ showing the immediate formation of LiF and FeSO₄·H₂O during the initial heatup and the following formation of LiFeSO₄F starting after 3.5 h. (b) Phase fractions of all phases present during the experiment, as calculated by structural refinements using the Rietveld method.
Figure 6.3. Diffraction patterns for the synthesis of LiFeSO₄F starting from Li₂SO₄ and FeF₃ but without contamination of Li₂SO₄·H₂O showing the formation of LiF and FeSO₄·H₂O, formed with the water in the TEG solvent.
7. Conclusions

Aging in two sets of commercial cells was studied by *post mortem* analysis. The main conclusion is that cells can, when aged by cycling, undergo non-uniform degradation in the cell electrodes. The degradation was found to be non-uniform, as different parts of the cell had higher local capacity or better high-rate performances. This non-uniform degradation was found to be dependent on usage pattern, implying that different test procedures (pulses or slow charge/discharge) could well utilize different parts of the cell. Non-uniform usage of aged cells could also blur results obtained from commonly used methods to measure cell performance such as $\Delta V/\Delta Q$ or ICA. Though not addressed in this thesis, cell design will also greatly affect this non-uniform degradation: good design can minimize temperature and current gradients within the cell.

Further, the decrease in long-range order occurring during the first lithiation step in Li$_{0.5}$Ni$_{0.25}$TiOPO$_4$ was studied: the remaining long-range order was found to result from the Ti-O-PO$_4$ network. HAXPES and EXAFS were used to further examine the role of Ti and Ni in the redox processes during lithiation by measuring the changes in the electronic structure for Ti and Ni, as well as changes in the local structure around Ni. Ni clusters of metal-like Ni are found to form, and Ti in the fully lithiated sample is a combination of Ti$^{4+}$, Ti$^{3+}$ and Ti$^{2+}$.

XRD was also used to examine the formation of *tavorite*-type LiFeSO$_4$F. The *tavorite*-type LiFeSO$_4$F structure forms from the reaction of LiF with FeSO$_4$·H$_2$O. FeF$_2$ and Li$_2$SO$_4$ are found to react to form LiF and FeSO$_4$·H$_2$O, from which LiFeSO$_4$F is formed. This also demonstrates an elegant and straightforward way of using X-ray diffraction to follow a synthesis, which is otherwise very laborious to study using *ex situ* methods.
7.1 Suggestions for further studies

More post mortem studies should be made of batteries cycled under different conditions to further evaluate the non-uniformity of aging and its influence on full cell performance. Calculations of temperature and current distributions within large cells could also provide useful information as to why this non-uniform degradation takes place. Both prismatic and cylindrical cells should be used in these studies to assess whether there is a difference in their aging under the same load pattern.

Long-time cycling of Li$_x$Ni$_{0.5-x}$TiOPO$_4$-materials should be performed to examine if the changes observed in the local structure around Ni and in the oxidation state of Ni and Ti also are seen after many cycles. It would be interesting in general to discover whether a starting material can be made in such way that it generates an well-composed material that it can exploit the multiple benefits of conversion, insertion and alloying materials in new negative electrodes for Li-ion (and Na-ion) batteries.

In situ XRD experiments should also be performed at different temperatures and pressures to further examine the formation of LiFeSO$_4$F in a TEG medium. In situ X-ray diffraction is a relatively new tool for studying the synthesis of crystalline compounds (as electrode materials), and has the potential for becoming an important technique for the scientific community.
8. Populärvetenskaplig sammanfattning

Den samlade mänsklighetens inverkan på våra globala levnadsvillkor har faststälts av internationella klimatpanelen i ett antal publicerade rapporter som tydligt kopplar de av oss utsläptta volymerna av växthusgaser till den ökande temperaturen på jorden. Av dessa växthusgaser är koldioxid den mest betydande då den produceras i stor mängd vid förbränning av fossila bränslen som kol, olja, torv och naturgas. Ungefär 82 % av den energi som vi förbrukar kommer från fossila bränslen och om kraftiga framtida temperaturökningar ska förhindras måste denna andel av fossila bränslen kraftigt reduceras inom en snar framtid.

Energianvändning inom transportsektorn

En av de stora sektorerna för energianvändning i vårt samhälle är transporter, denna sektor står för ungefär 19 % av vår totala energikonsumtion. Av dessa kommer ca 96 % från fossila bränslen, främst raffinerade oljeprodukter, såsom diesel, bensin och flygfotogen. För att minska transportsektorns koldioxidutsläpp krävs en förändrad fordonssflotta som förlitar sig på förnybara bränslen såsom väggas, el eller biobränslen från förnybara källor. Elfordon eller fordon med partiell eldrift (s.k. hybridfordon) finns redan på marknaden idag och det är redan fullt möjligt att byta ut stora delar av den lätta trafiken (personbilar och lättastillverkningar) till fordon med el- eller elhybriddrift. Li-jonbatterier som har utomordentligt bra energitäthet, jämfört med andra uppladdningsbara batterisystem, dominerar idag helt marknaden för portabel elektronik såsom mobiltelefoner, bärbara datorer och surfplattor. Denna batterityp har även stor potential för att användas i elfordon. Li-jonbatteriernas höga energiinnehåll gör att de är det bästa alternativet vi idag har för energilagring i elfordon och elhybriddfordon. Det stora problemet är att dagens batterier ger sådana fordon en begränsad räckvidd (i jämförelse med diesel och bensin) och att batteriernas åldringsprocess (hur länge batteriet håller för användning) inte är helt förstådd.

Litiumjonbatterier

Ett Li-jonbatteri består av två elektrodmaterial vilka är separerade av en separator indränkt i en flyttande elektrolyt. Under användning, uppladdning, transporteras litiumjoner mellan de två elektrodmaterialen via elektrolyten.
Under batteriets uppladdning transporteras litiumjonerna i ena riktningen och vid urladdning transporteras de tillbaka. I det första kommersialiserade Li-jonbatteriet bestod elektroderna av grafit respektive av litiumkoboltoxid. Sedan dess har många nya elektrodmaterial utvecklats och kommersialiserats för att övervinna de tillkortakommanden som litiumkoboltoxiden har: begränsad kapacitet och instabilitet vid höga temperaturer och höga laddningsspänningar. De alternativ till litiumkoboltoxid som har studerats i den här avhandlingen är litiumjärfosfat och litiummanganoxid. Även grafitsidan i batteriet har problem, dessa är främst kopplade till att elektrolyten bryts ner av den låga potential som används för att litium ska transportereras in i grafiten. De restprodukter som bildas på graffitytan av den nedbrutna elektrolyten hindrar fortsatt nedbrytning men detta lager är tunt och viss nedbrytning fortsätter även efter att detta skyddslager bildats. Istället för graf kan material som tar in litiumjoner vid högre potentialer användas, ett sådant alternativt material är litiumtitanat.

Metoder för att studera batterimaterial

För att kunna utvärdera batterimaterial behövs både upp- urladdningstester under lång tid samt tekniker för att studera de ingående materialen i detalj. De metoder som är viktigast för arbetet i den här avhandlingen är: röntgendiffraktion, som kan användas för att följa de strukturförändringar som sker i kristallina material. Fotoelektronspektroskopi, som kan användas för att studera de extremt viktiga ytskikten som finns mellan elektrolyt och elektrodmaterial. Röntgenabsorptionsspektroskopi, som kan användas för att följa strukturförändringar i närmiljön runt atomer i kristallina och icke-kristallina material.

Resultat

I de två första artiklarna i denna avhandling undersöktes två olika batterikemier och deras åldring när batterier används med olika belastningscykler. I artikel I användes batterier bestående av litiumkoboltoxid blandat med litiummanganoxid och en motelektrod av litiumtitanat. I artikel II användes batterier bestående av litiumjärfosfat samt grafit. Båda dessa studier visar en stor skillnad för hur batterier åldras beroende på hur de används. I artikel II visas även genom post mortem studier av öppnade batterier att nedbrytningen som leder till åldring är olika i olika delar av batterier och att det är en skillnad på elektrodmaterial som varit i ytterkanten av cellen jämfört med material från de centrala delarna i ett batteri.

I de följande två artiklarna, artikel III och IV, undersöktes material som potentiellt kan ersätta grafit. Båda dessa snarlika material som undersöks består av liitumnickeltitanoxyfosfat med olika koncentrationer av litium och nickel. I artikel III användes röntgendiffraktion för att följa den partiella ned-
brytningen av den atomära strukturen som sker i dessa material när de tar upp litiumjoner. Resultaten visar att viss struktur hålls kvar av ett titanofosfatnätverk. I artikel IV studerades vad som händer vid litiumupptag i dessa material med röntgenabsorptionsspektroskop, där den lokala strukturen i omgivningen kring nickel undersöktes, samt med elektronspektroskop för att detaljstudera elektronupptaget i materialet. Resultaten visar att nickel bildar små metallliknande kluster insprängda i materialen samt att både nickel och titan tar upp elektroner samtidigt som litiumjoner går in i materialet.

I artikel V studerades syntesvägen för att producera ett annat nytt elektrode material, som även detta kan användas istället för litumkoboltoxid. Denna studie gjordes med röntgendiffraction där syntesen från två olika reaktantkombinationer (litiumfluorid och järnsulfatomohydrazt samt järnfluorid och litiumsulfat) studerades. Resultaten bekräftade att båda dessa reaktantkombinationer reagerar och bildar litiumjärnsulfatfluorid men att den senare kombinationen först ombildas till litiumfluorid och järnsulfat-monohydrat innan litiumjärnsulfatfluoriden bildas. Detta typ av experiment är ett av de första i sitt slag och visar att i framtiden kan ny kunskap om hur kristallina ämnen bildas studeras på ett tidsekononiskt och tillförlitligt sätt.
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