Redox Reactions in Li-ion Battery Cycling and in Cu Corrosion Studied by Soft X-ray Spectroscopy

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Abstract

The topic of this thesis is redox reactions in two technologically important contexts: firstly, in Li-ion battery electrodes during cycling, and secondly, in copper corrosion in oxygen-free ground water containing sulfide. In an attempt to expand the understanding of the charge uptake process in battery electrodes and the chemical reactions on copper surfaces upon sulfide exposure, soft X-ray spectroscopy has been used to study the electronic structure of these systems.

To ascertain the changes in electron density at different atomic sites in a battery electrode material, both X-ray absorption spectroscopy (XAS) and resonant inelastic X-ray scattering (RIXS) have been applied to different electrode materials. This thesis explains in detail the assembling procedure, cycling, and in situ sample preparation of the battery materials. Furthermore, two different designs used in in situ experiments for study of batteries during cycling are also discussed.

The main result from the Li-ion battery materials is the justification to abandon the view of valences as integers. This is true for all battery electrodes examined in this thesis. Generally, oxygen plays a more important role in the charge uptake than commonly assumed, but also the transition metals and other species apart from expected behavior. In LiMnPO₄, even the notion of Li⁺ as strictly Li⁺ must be questioned.

Copper is intended to act as a corrosion barrier in a nuclear waste repository. In the corrosion experiments presented in this thesis, different copper oxides were exposed to the conditions present at the planned repository site, with exception for the concentration of sulfide, which was greatly increased.

The conclusion from these experiments is that sulfide effectively reduces Cu(II) oxide to Cu(I) compounds and possibly forms a compound containing both oxygen and sulfur. Also, the thickness and inhomogeneity of the copper oxide surface layers are of great importance for the corrosion mechanisms, including passivation.

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to Malin and Freya
List of Papers

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


II H. M. Hollmark, Maher, K, Saadoune, I., T. Gustafsson, K. Edström, L. -C. Duda, Resonant inelastic X-ray scattering and X-ray absorption spectroscopy on the negative electrode material Li_{0.5}Ni_{0.25}TiOPO_4 in a Li-ion battery, Phys. Chem. Chem. Phys., 2011, 13(14), 6544-6551.

III H. M. Hollmark, T. Gustafsson, K. Edström, L. -C. Duda, Resonant inelastic X-ray scattering and X-ray absorption spectroscopy on the cathode materials LiMnPO_4 and LiMn_{0.9}Fe_{0.1}PO_4 - a comparative study, Submitted to: Phys. Chem. Chem. Phys., March 8, 2011.


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1. Why Spectroscopy?

When studying the matter that surrounds us, one of the most powerful methods at hand is irradiating a sample we wish to know more about with electromagnetic radiation. Different wavelengths, or rather, a spectrum of wavelengths, of this radiation will tell us different stories about our sample.

In a dictionary (in this case Merriam-Webster) you find this definition of the word *spectrum*:

A continuum of color formed when a beam of white light is dispersed (as by passage through a prism) so that its component wavelengths are arranged in order.

alongside this alternative definition:

Any of various continua that resemble a color spectrum in consisting of an ordered arrangement by a particular characteristic (as frequency or energy).

This illustrates just how broad a concept spectroscopy is. In this thesis, though, I will only refer to a spectrum in the sense of dispersion of electromagnetic radiation, as in the former of the two definitions.

So, back to the use of radiation to study matter: we can for instance use the radiation from a laser common in many optical research laboratories, namely the helium-neon (HeNe) laser. Such a laser usually has a wavelength of 632.8 nm which allows us to, for instance, detect vibrational changes in molecules during chemical reactions by analyzing the vibrational modes of a molecule before and after the reaction. This kind of experimental technique, where you study the molecular bonds by measuring the difference in wavelengths between the incident and the reflected radiation, is called Raman spectroscopy after the Indian physicist S. Raman.

Nonetheless, if you wish to study the electronic structure of the valence band rather than vibrations in the molecular bonds in your sample, the wavelength of the HeNe laser will be too long. Electromagnetic radiation with wavelengths shorter than visible light can interact with deeper electronic levels in the atom. Appropriately, a light source that can be tuned to specific wavelengths in the X-ray region can be used to probe electronic transitions in your sample. X-rays are of great importance since they interact with those electrons in the studied material that are active in chemical bonds and reactions.
X-rays in the energy region 50-1500 eV are called soft X-rays and are situated in an energy region just below hard X-rays, the kind of X-rays most of us have experienced at the dentist. Soft X-rays cannot, as opposed to hard X-rays, travel straight through your teeth but is instead easily absorbed even in air. Hence all experiments with soft X-rays must be performed in vacuum.

Furthermore, in order to be able to study processes that are very unlikely to occur, i.e. have very small cross-sections, you will have to use an X-ray light source with high intensity, i.e. high flux density, such as a synchrotron accelerator. A comparison of the photon flux from an X-ray tube (Mo target) with beamline U41-PGM at the Berliner Elektronen Speicherring SYnkrotron (BESSY, a 3rd generation synchrotron) shows that the X-ray tube has a photon flux of about $10^4$ photons per second, while U41-PGM generates a photon flux of between $10^{12}$ and $10^{13}$ photons per second, depending on at which energy the monochromator is set.

A common HeNe laboratory laser (1 mW) has a high photon flux of $1.27 \cdot 10^{18}$ photons/(s·cm$^2$), but unfortunately there are no lasers with variable wavelength that can operate in the X-ray region. That is likely to change with the development of the free electron lasers (FEL), which however requires as huge facilities as synchrotrons and are at least as expensive. Thus, synchrotron facilities have been built around the world and still new and more powerful ones are on the way.

This thesis presents the method of probing a few materials with the help of soft X-ray spectroscopy. The materials are of high interest since they may prove important in future energy storage devices and in corrosion prevention. The first material category studied might be the next generation battery material, the second category involves the safety concerning of nuclear waste storage and the third is a catalyst that may provide a method to split water molecules through electrolysis.

The following chapter serves as an introduction to the interactions of interest and chapter 3 the methods at hand for observing them. Chapter 4 describes the materials studied and results from the experiments are presented in chapter 5. In chapter 6, I present my conclusions and future outlook and a brief summary in Swedish is included in chapter 8.
2. Light-Matter Interaction

Since our synchrotron light source allows us to probe electronic transitions in matter we need to understand more in detail what happens during the interaction between light and matter. First of all, we must understand the principles telling us how to find a specific electronic transition, i.e. where in the material the transition takes place. The following first out of three sections in this chapter will very briefly present some basic concepts for the quantum mechanical background to orbital notation and calculations. The subsequent two sections will describe the processes that take place in the interaction between light and matter.

2.1 Atoms and orbitals

There are mathematical expressions that tell you where in an atom a certain electron is most likely to be found. These expressions are called wave functions and are denoted $\psi(r,t)$. The probability to find an electron at any given point $(r,t)$ is proportional to $\psi^2$ at that point. The wave function for an electron describes its atomic orbital and it was Erwin Schrödinger who first came up with a solution for the equation for a single electron atom (i.e. hydrogen) in 1926. The equation, in non-relativistic mechanics, has the following form:

$$i\hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m} \left( \frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} \right) + V \psi \tag{2.1}$$

If the kinetic and potential energy terms are expressed with the Hamiltonian operator, $\hat{H}$, we get

$$i\hbar \frac{\partial \psi}{\partial t} = \hat{H} \psi \tag{2.2}$$

Furthermore, if we assume that we can separate the Schrödinger equation into a time-independent part and a time-dependent part, we can arrive with individual expressions for these parts. The time-independent equation then takes the form:

$$i\hbar \frac{\partial \psi}{\partial r} = \hat{H} \psi(r) = E \psi(r) \tag{2.3}$$
When equation 2.3 is solved, $E$ denotes the eigenvalues that characterize the energy states of the system, described by the principal ($n$), angular momentum ($l$) and spin ($s$) quantum numbers. These numbers can be viewed as coordinates defining the characteristics of orbitals, such as size, shape and orientation. The nomenclature and value ranges for the quantum numbers are shown in table 2.1.

The Pauli exclusion principle states that no two electrons in an atom can have identical sets of quantum numbers. This is a result of particles having half-integer spin (e.g. electrons) and these must have antisymmetric wave functions, forcing the wave function to vanish if two electrons are in the same state. In other words, the Pauli exclusion principle states that no more than two electrons can occupy any given orbital, and that two electrons occupying the same orbital must have paired spins (meaning one spin up and one spin down).

This is the basis for the Aufbau principle, which tells you how to place electrons in the orbitals when you “build” your atom. Place the two first electrons (with opposite spins) in the unoccupied orbital with the lowest energy, i.e. the $1s$ ($n = 1, l = 0$) orbital. The second pair goes into the $2s$ ($n = 2, l = 0$) orbital. The range of lowest to highest energy orbital for transition metals is as follows:

$$1s < 2s < 2p < 3s < 3p < 4s < 3d$$  \hspace{1cm} (2.4)

Note in the order above, that $4s$ comes before the $3d$ orbital. This is because the solution to the Schrödinger equation describes a H atom, indicating that there is only one electron in the system and hence there are no electron-electron repulsion effects. If those effects are taken into account, a slight rearrangement of the energies for the orbitals is made. This is done by comparing different states’ term symbols, such as

$$S^{+1}L_J$$

in which all spins ($s$) combine to produce $S$, all orbital angular momenta ($l$) couple to produce $L$, and spin and orbital terms combine to produce a total angular momentum $J$. Hund’s rule then states that:

1. The term with maximum $S + 1$ has lowest energy
2. For a given $S + 1$, the term with the largest value of $L$ has lowest energy
3. For atoms with less than half-filled shells, the term with the lowest value of $J$ has lowest energy

In light atoms (where the atom number $Z \leq 30$, which is the case for $3d$ transition metals), the energy levels of atomic electrons are affected by the interaction between the orbital angular momentum and the spin angular momentum of the electron. This is the so-called spin-orbit coupling and is manifested in $J = L + S$. Since the angular momentum, $l$, for a $2p$ electron is 1 and
the spin, $s$, is $\pm 1/2$ (cf. table 2.1) the possible $j$ are $j = l + s = 1 + 1/2 = 3/2$ or $j = 1 - 1/2 = 1/2$. This is the LS, or Russel-Saunders, coupling and is responsible for a splitting of the soft X-ray absorption spectra for transition metals. The lower energy level is referred to as $2p_{3/2}$ or $L_{III}$ and the higher as $2p_{1/2}$ or $L_{II}$.

The angular quantum number, $l$, describes the shape of the orbital. For $l = 0$, the shape of the orbital can best be described as a sphere and for $l = 1$ the shape is more like a dumbbell. As $l$ increases, the shapes of the orbitals become more and more complex. For the 3$d$ subshell there exist five different orientations of the orbitals. These are labeled $3d_{xy}, 3d_{xz}, 3d_{yz}, 3d_{x^2-y^2}$ and $3d_{z^2}$. Four of the five functions describing these orbitals result in the same orbital shape but with different spatial alignment. The fifth function ($3d_{z^2}$) has a different shape. In Fig. 2.1, the shapes of the 3$d$ subshell atomic orbitals in a one-electron atom are shown. Pictures like these are helpful when studying materials, but are not to be considered as “truth”. They are only simplified models based on mathematical solutions (spherical harmonics) to the Schrödinger equation for hydrogen-like atoms.

![Figure 2.1: Shapes of the 3d subshell orbitals in a one-electron atom.](image)

### 2.2 The excitation process

We are now ready to move on to what happens when light interacts with the electrons in an atom. Laser allows electrons from the valence band to move up
Table 2.1: Table showing the spectroscopic notation of quantum numbers \( n, l \) and \( s \).

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<th>( n )</th>
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<td>( s )</td>
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</table>

Table showing the spectroscopic notation of quantum numbers \( n, l \) and \( s \).

To the conduction band, while X-rays instead have sufficient energy to interact with the core level electrons and excite them to the valence band. In Fig. 2.2 the principle of the excitation processes with X-rays compared to visible light is shown. The figure shows two atomic species, A and B, in a material. The valence band electrons for both atoms A and B have overlapping wave functions, which lead to hybridization and the formation of an occupied energy band. Similarly, the unoccupied orbitals form the (normally empty) conduction band, and the conduction electrons are even more free to move around in the material. As depicted schematically, the core levels are much more defined in energy than the valence and conduction bands and, in addition, they are local in the sense that the electrons are bound to one specific atom. In essence, the larger space a certain orbital occupies, the more likely it is to overlap with another orbital.

\[ \Delta E \]

\[ \Delta E_{\text{c,A}} \]

\[ \Delta E_{\text{c,B}} \]

Figure 2.2: Excitation processes by X-ray and visible light for atoms A and B. Energy differences are denoted by \( \Delta E \). The index \( c \) indicates core level, \( vb \) indicates valence band and \( cb \) indicates conduction band.

Fig. 2.3 shows the energy diagram of a metal, which means that there is no band gap between the valence band and the conduction band, instead there is a band overlap between the valence and conduction bands. The Fermi level is situated in this overlap region. Naturally, an excited electron has to find an empty spot in the unoccupied parts of the bands, i.e. above the Fermi level.
The $x$ axis in Fig. 2.3 is the number of states per interval of energy at each energy level that are available to be occupied, i.e. the density of states (DOS), and the $y$ axis is the energy.

![Figure 2.3: Absorption process resulting in a) an excitation process, and b) a photoionization process.](image)

Irradiating an atom with X-rays can either cause core electrons, i.e. electrons occupying levels closest to the atom nucleus, to be excited to a higher energy level or to be completely removed from the atom, leaving it ionized with a vacancy in one of the core orbitals. This interaction between light and matter is a process governed by atomic physics and selection rules only allow certain band transitions for the electrons. The matrix elements describing the dipole transition between two states can due to symmetry reasons become zero. In these cases the transition is said to be forbidden and it is possible from studying the dipole transitions to construct selection rules. I will here cut to the chase and conclude that dipole transitions are allowed if:

- $\Delta m_s = 0$
- $\Delta m_l = 0, \pm 1$
- $\Delta l = \pm 1$
- no restrictions for quantum number $n$

where $m_s$ is the spin projection quantum number and $m_l$ the magnetic momentum quantum number.

When the incoming photons have a certain energy, $\hbar \omega_a$, which is just enough to lift an electron to an unoccupied (and allowed by the selection rules) state with higher energy, the atom will be excited (Figure 2.3a). If the energy of the incoming photons is sufficient, $\hbar \omega_b$, the electron completely leaves the system as in Fig. 2.3b, in an ionization process.
As mentioned, the higher the energy of the incoming photons, the deeper in the electronic structure of the atom they interact. Therefore, X-rays can excite core electrons in the orbitals closest to the atom nucleus, while laser radiation excites the outermost valence band electrons. Thus, by using X-rays to probe the core states we acquire element-specific information and are able to resolve the structure of the valence band. This is of great interest since valence electrons are active in chemical reactions and react strongly to changes in the surroundings.

2.3 The de-excitation process

An atom in the excited state is not stable, and shortly after the excitation process it has to dispose of the extra acquired energy. Depending on whether the atom was in an excited or ionized state there are two possible decay processes as shown in Fig. 2.4.

Fig. 2.4a) illustrates one way for an excited atom to dispose of extra energy: an electron from the valence band falls down to occupy the hole at the core level. The process is accompanied by the release of another electron, also from the valence band. This electron receives all the remaining extra energy the unstable atom must dispose of and leaves the system. It is called Auger electron [1] after the physicist Pierre Auger (even though the discovery was first published by Lise Meitner in 1922 [2]).

The unstable atom can also decay via an electron filling the void in the core level, but this is accompanied by the release of a photon which gets the excess
energy from the excitation process (Figure 2.4b). This decay process is also called fluorescence.
3. Soft X-ray Spectroscopy and Transition Metals

Different X-ray energies will make different dipole transitions possible in the atom and a discrimination between soft and hard X-rays is made. Hard X-rays are for instance responsible for absorption at the 3d transition metal K-edge, which means that the 1s core electron may be promoted into the 4p levels as well as into the 3d levels. The latter is in fact not a dipole transition, but this transition is allowed through a weak quadrupole transition, which may exist in hard X-ray spectroscopy. The energies for these edges are in the range 4 to 9 keV. Soft X-rays are, when it comes to 3d transition metals, responsible for L-edge absorption, meaning 2p – 3d electronic transitions, and the energies range from 0.3 to 1 keV. This thesis will deal with soft X-rays, which interact with core electrons, but not as deep in energy as hard X-rays. This allows you to view core orbitals with a more complex structure than deeper lying orbitals, displayed in absorption spectra as multiplet structures.

My work has been devoted to soft X-ray spectroscopy on different transition metal materials. A transition metal is according to the IUPAC definition [3] an element whose atom has an incomplete d subshell, or which can give rise to cations with an incomplete d subshell. I have solely studied 3d transition metal compounds, which are elements 21 through 30 in the periodic table. The elements are: Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, and Zn. These elements are rather common in modern technology and can be found in anything from steel constructions to electronics. I have mainly focused on two cases where soft X-ray spectroscopy might be able to shed some light on questions; mechanisms in the charge uptake in Li-ion batteries and Cu corrosion in nuclear waste storage canisters. In this chapter I will try to explain some of the reasons why 3d transition metals have such a rich palette of properties and the methods we use to look at these properties, while the following chapter will go into detail concerning battery materials and nuclear waste storage.

3.1 Density of states and transition metals

The reason for my focus on the 3d orbitals stems from the fact that 3d electrons are the outermost electrons in transition metals and are thus the ones involved in interaction with the environment. All 3d transition metals are prone to form oxides, and these oxides are all solids under normal pressure and tem-
perature conditions. When a 3\textit{d} transition metal forms an oxide, it “shares” some electrons with an O atom. In the IUPAC definition [3] of oxidation state, O has an oxidation state of -2 when it is present in most compounds (exceptions to this is that O has an oxidation state of -1 in peroxides, e.g. H\textsubscript{2}O\textsubscript{2}). In this oxidation state definition, when O is assumed to acquire oxidation state -2, it fills up its 2\textit{p} atomic orbitals which is favorable according to the octet rule. This rule of thumb states that atoms tend to combine in such a way that they each have eight electrons in their valence shells. A consequence of this is, that if you know the exact composition of a binary oxide you can calculate the oxidation state of the 3\textit{d} transition metal, since the oxide needs to conserve charge neutrality. This simple model works rather well and is the basis for what is called crystal field (CF) theory. CF theory describes how the atomic orbitals of the transition metal ions change in accordance with their surroundings, and I will now briefly go through some important concepts of this theory that is of importance in soft X-ray spectroscopy.

For a transition metal oxide such as NiO, which adopts the rock salt structure with octahedral Ni\textsuperscript{2+} and O\textsuperscript{2−} sites, the five \textit{d} orbitals divide into two sets. The sets are named \textit{e\textsubscript{g}} and \textit{t\textsubscript{2g}}, and the orbitals fall into either set depending on its reducibility in the octahedral symmetry point group (\textit{O\textsubscript{h}}). This means that 3\textit{d}_{\text{xy}}, 3\textit{d}_{\text{xz}}, and 3\textit{d}_{\text{yz}} belong to set \textit{t\textsubscript{2g}} and 3\textit{d}_{\text{x}^2-\text{y}^2} and 3\textit{d}_{\text{z}^2} belong to set \textit{e\textsubscript{g}}.

There is an energy difference between \textit{e\textsubscript{g}} and \textit{t\textsubscript{2g}} orbitals, and this difference is called CF splitting. A schematic presentation of the CF splitting is shown in Fig. 3.1.

\begin{figure}[h]
\centering
\includegraphics[width=0.3\textwidth]{figure3.1.png}
\caption{Orbital energies split up into the two orbital sets \textit{e\textsubscript{g}} and \textit{t\textsubscript{2g}}.}
\end{figure}

The electrons in a 3\textit{d} transition metal occupy the \textit{e\textsubscript{g}} and \textit{t\textsubscript{2g}} orbitals in accordance with the Pauli exclusion principle. For an isolated 3\textit{d} transition metal ion in its ground state the electrons also follow Hund’s rule, which sorts the electronic states energy-wise.

In my research as an experimentalist I have tried to compare the experimental data with theoretical crystal field simulations of different environments for 3\textit{d} orbitals for transition metals. The calculations are done by varying the cubic-crystal-field parameters defining the environments. When comparing the experimental to the theoretical data, one must take into consideration that calculations do not only simulate spectroscopic data with perfect resolution,
but also that there exist intrinsic broadening mechanisms, such as lifetime effects, vibrations and hybridization that are not taken into account in the calculations. Thus, comparing calculations and experimental data is something of a detective work, where experience and routine is just as important as knowing the physical mechanisms behind the experiment.

Another theoretical concept worth knowing a little about is band theory. A basic approach in this theory is to look at the electrons as a gas moving in a periodic potential of a crystal lattice. This is a model that works rather well for metallic materials in describing the behavior of the conduction electrons. It is not, however, a useful model if we want to describe the $d$ electrons in transition metal compounds, since the $d$ electrons are more tightly bound to the atom.

The $e_g$ and $t_{2g}$ orbitals can in a molecule be of bonding or anti-bonding nature depending on whether the wave functions in the molecule constructively or destructively interfere. This is best explained by studying a simple case such as two H atoms placed close enough together to have overlapping wave functions, as shown in Fig. 3.2.

![Figure 3.2: Electron density around two H atoms (a and b) in different bonding scenarios.](image)

As mentioned above, the probability density for finding an electron at a certain place is given by $\psi^2$. If the the wave functions constructively interfere we will get (1s orbitals in this case): $(\psi(r) + \psi(r + \Delta r))^2$. This gives some extra electron density in the area between the H nuclei, meaning we have a bond. In the destructive case ($(\psi(r) - \psi(r + \Delta r))^2$) the same calculation will result in a decrease in electron density between the H nuclei, compared to a non-bonding scenario where there is no interaction between the atoms. In an H$_2$ molecule there are no non-bonding orbitals, so the non-bonding scenario is here merely a thought experiment. In other cases, for instance when one of two atoms forming a molecular bond has several more electrons than the other (e.g. F in HF), non-bonding orbitals exist.

A bond that is symmetric along the bond axis, as is the case for the H–H bond, is denoted $\sigma$, and an anti-symmetric one is denoted $\pi$. The addition of a superscripted asterisk (*) after the bond type symbol indicates anti-bonding.
From Fig. 3.2 we can conclude that different bonding types have different number of electrons participating in the bond and therefore have different energy. The overlap of the orbitals also affect the energy of the bond, and in the $\sigma$ symmetry the orbital overlap is larger than in $\pi$ symmetry. The energy for the different bond types are shown schematically in Fig. 3.3. A summation of all states at a certain energy in the figure adds up to the DOS at that energy, which is approximately what we acquire experimentally from our XAS and RIXS measurements.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{energy_diagram.png}
\caption{Energies for the symmetric bond, $\sigma$, and anti-symmetric bond, $\pi$, and their respective anti-bonding versions.}
\end{figure}

### 3.2 X-ray Absorption Spectroscopy - XAS

So how does X-ray absorption spectroscopy (XAS) work? It is a technique where the energy deposition from incident X-rays makes core electrons move to unoccupied higher energy valence orbitals. Sweeping the incident X-ray energy around the energy expected for a certain electronic transition in a specific atom allows you to study the density of unoccupied states by measuring the absorption coefficient, which is proportional to the number of core holes produced in an infinitesimally thin layer that the X-rays penetrate. This information is obtained indirectly by measuring the resulting core hole decay after that particular transition. The decay process, in turn, results in either Auger and scattered low energy (secondary) electrons or fluorescence (cf. Fig. 2.4).

Emitted secondary electrons can be detected as current drawn from the sample and the number of electrons is proportional to the absorption intensity. Naturally, if more electrons are lifted from the core level to the unoccupied
valence states, a larger current will be recorded from the sample yielding a higher absorption intensity. This technique to record XAS is called total electron yield (TEY). Alternatively, the absorption intensity may be recorded as a function of fluorescent light escaping the sample, in the case of fluorescent decay processes. This technique to record XAS is called total fluorescence yield (TFY). Analogous to the current in TEY, the fluorescence leaving the sample is proportional to the absorption intensity.

Plotting the absorption intensity as a function of energy of the incoming light provides you with an absorption spectrum, such as can be seen in Fig. 5.4. Since the absorption spectra for most elements do not overlap on the energy scale, you receive element-specific information from XAS. Furthermore, the spectrum from a XAS measurement will give you a linear combination of all individual sites, a fact that needs to be taken into account if you have elements positioned at different sites and with different neighboring elements in your sample.

The intensity ($I_{abs}$) of an X-ray absorption process can theoretically be described by Fermi’s Golden rule [4]:

$$I_{abs}(\omega) \propto |\langle \Phi_f | \hat{e} \cdot \mathbf{r} | \Phi_i \rangle|^2 \delta_{E_f - E_i - \hbar \omega}$$

(3.1)

where $\Phi_i$ and $\Phi_f$ are the initial and final states operated on by the dipole matrix element $\hat{e} \cdot \mathbf{r}$. The term $\delta_{E_f - E_i - \hbar \omega}$ maintains energy conservation, with $E_i$ the energy of the initial state for the electron, $E_f$ the energy of the final state for the electron, and $\hbar \omega$ the energy of the incoming photon matching the energy gap between $E_f$ and $E_i$.

For hard X-rays, it is possible to measure absorption by a more straightforward method than what is necessary for soft X-rays, namely by transmission. If you know the thickness of the sample, $x$, then the intensity, $I_{trans}$, of the transmitted X-ray beam is:

$$I_{trans} = I_i \cdot e^{-\mu x}$$

(3.2)

where $I_i$ is the intensity of the incoming X-ray beam and $\mu$ is the absorption coefficient. Eq. 3.2 is commonly called Beer-Lambert law. Transmission experiments using soft X-rays would, due to the short absorption length, require thin film samples.

There are several acronyms for XAS spectroscopy meaning the exact same thing, two common being XANES (X-ray Absorption Near Edge Structure) and NEXAFS (Near Edge X-ray Absorption Fine Structure). Another combination of letters, also a member of the XAS family, is EXAFS (Extended X-Ray Absorption Fine Structure). EXAFS is when you treat the structures just above (i.e. in energy) your absorption edge. The structure in this region is affected by backscattered photoelectrons that interact with electrons in the surrounding non-excited atoms. These interactions show up like ripples in the
XAS spectra above the absorption edge. Through Fourier analysis of your data you may be able to extract information on the coordination environment around the excited atoms.

3.3 Resonant Inelastic X-ray Scattering - RIXS

While XAS allows you to characterize the unoccupied part of the valence band, resonant inelastic X-ray scattering (RIXS) will help you to detect the properties of the occupied part of the valence band. In non-resonant emission, or in the absence of a monochromator, you irradiate your sample with energies well above the absorption threshold of the atom you study. In this kind of spectroscopy, information from chemical shifts for different atomic species in the material drowns in the flood of emissions from all states in the valence band. Typically the bandwidth of the valence band is several times larger than the chemical shifts. You should instead make use of the monochromator’s ability to select a certain energy. The idea is as follows: when the empty core state, produced by the absorption process (see Fig. 2.3a), is filled by an electron from an occupied state, a photon will be emitted. If you tune the incoming radiation so that it matches one of the atomic X-ray transitions of the system, the absorption and emission processes can begin to resonate. The spectroscopy method that utilizes this effect is thus called resonant inelastic X-ray scattering (RIXS).

The intensity ($I_{RIXS}$) of a RIXS process can theoretically be described by a modified Kramers-Heisenberg formula [4, 5]:

$$I_{RIXS}(\omega, \omega') \propto \sum_f \left| \sum_{im} \frac{\langle \Phi_f | \hat{e}' \cdot \mathbf{r} | \Phi_{im} \rangle \langle \Phi_{im} | \hat{e} \cdot \mathbf{r} | \Phi_i \rangle}{E_i + \omega - E_{im} - i\Gamma_{im}} \right|^2 \delta_{E_f + h\omega' - E_i - h\omega}$$  \hspace{1cm} (3.3)

In equation 3.3, $\Phi_i$, $\Phi_{im}$ and $\Phi_f$ are the initial, intermediate, and final states operated on by the dipole matrix element $\hat{e} \cdot \mathbf{r}$ and $\hat{e}' \cdot \mathbf{r}$. The prime (’) notation indicates connection to the emission part of the process. $\omega$ is the angular frequency of the photons, $E$ is the energy for a certain state, and $\Gamma_{im}$ represents the core-hole lifetime in the intermediate state. Note that the denominator would, without the $\Gamma_{im}$, become $= 0$ when the energy of the incoming photon matches the absorption transition from $E_i$ to $E_{im}$. This would cause the intensity, $I_{RIXS}$, to be infinite, but with the core-hole lifetime term the denominator is $\neq 0$ and the intermediate state avoids the infinite intensity. The $\delta$ function serves the same purpose as in equation 3.1.

The acronym RXES stands for Resonant X-ray Emission Spectroscopy and is basically the same thing as RIXS but some are of the opinion that you should compare loss features at different excitation energies in order to call it RIXS. RIXS is a powerful spectroscopic method partly due to its element- and
orbital-specificity. This means that you can single out specific atomic transitions for a certain element in a material, and you can even discriminate between different chemical surroundings at different sites for that element.

There are several paths through which an excited electron can decay when using RIXS. Fig. 3.4 shows a schematic illustration of the possible RIXS processes, specifically, in this case, the $2p \rightarrow 3d \rightarrow 2p$ RIXS process in Cu. For spectroscopic methods that are able to distinguish between the different excitations, you might be able to retrieve information about the local environment around a certain element in a material.

Figure 3.4: Schematic presentation of the RIXS process for Cu, involving elastic emission, crystal field excitation and charge transfer excitations for a $2p \rightarrow 3d \rightarrow 2p$ RIXS process in Cu.

In the above example, Cu is assumed to be oxidized as CuO, meaning that two of its outer shell electrons have large overlap with O atoms. The ground state for metallic Cu is $[\text{Ar}]3d^{10}4s^1$, and when two electrons are absent the ground state for the Cu(I) oxide is $[\text{Ar}]3d^9$. The absorption process in Fig. 3.4 starts in the lower left corner, in the ground state for Cu. An incoming photon with a matching energy can excite a $2p$ electron to the empty $3d$ state. Since this is an excited state the atom must now release the extra energy, and it can do so in different ways. The first and most obvious way is that the electron simply decays to the same state it was excited from while emitting a photon of the same energy as the incident photon energy. A peak in a RIXS spectrum from this emission is called elastic scattering.

If instead a different $3d$ electron, from a state of slightly lower energy, falls back, it will emit a photon of slightly lower energy. This kind of process is
called crystal field excitation or $d - d$ excitation. Both elastic emission and crystal field excitation are local processes occurring around a certain atom in the material. There are also a non-local excitation process in which an electron from a neighboring O atom fills the empty seat in the $2p$ band. This is called charge transfer excitation. The notation $\mathcal{L}$ in the case of a charge transfer, indicates that a ligand electron is part of the electronic configuration. There is also a possibility for the atom to release the extra energy by filling the core hole with one electron and emitting another electron. This is the Auger process, and since there is no emitted photon it is not registered by X-ray spectrometers. Luckily, the other emission processes discussed above, i.e. elastic emission, crystal field excitation and charge transfer excitation, tend to emit photons with energies separated with a few electron volts, and can therefore often be resolved using modern soft X-ray spectrometers.

An important characteristic of RIXS is that it involves several possible paths for the process to follow (cf. Fig. 3.4). The assumption that it is a two-step process of excitation followed by de-excitation, is incorrect for cases when multiple intermediate states interfere. Instead, RIXS can be regarded as a one step process where the various excitation – de-excitation paths interfere in the scattering process [6].

3.4 The grazing incidence spectrometer

So how is the emitted light in XAS and RIXS processes detected and registered? A spectrometer can be used to measure the intensity of the emitted photons. Its independent variable is the energy of the incident photons, measured in electron volts (eV). The spectrometer I have used in my research is a laboratory-built grazing incidence Rowland type spectrometer [7]. Fig. 3.5 is a photograph of the spectrometer “resting” in its home at the Ångström Laboratory in Uppsala. The crucial parts inside the measuring chamber, detector house, and detector arm cannot be seen from the outside.

All experiments using soft X-ray spectroscopy has to be managed in high vacuum (HV); the spectrometer was typically operating in the low $10^{-8}$ mbar region during my experiments. The vacuum is a necessity since soft X-rays are easily absorbed in air. There is a transmission peak at 400 eV for X-rays traveling through air at 1000 mbar, often referred to as the “water window”, but even at this transmission peak energy only 6 % of the X-rays are transmitted through 1 cm of air.

The Rowland spectrometer built in our group has three crucial components: an entrance slit, a diffraction grating, and a detector. It works much like an ordinary camera, except for the replacement of the lens for a grating. The entrance slit is what defines the source (i.e. the object in ordinary photography) and is consequently what we want to be in focus on the detector. The entrance slit is necessary to reduce the size of the beam entering the spec-
Figure 3.5: The laboratory-built gracing incidence spectrometer mounted on its portable vacuum chamber endstation.

trometer, since in most cases the spot size produced by the beamline is too large. Unfortunately, by placing the entrance slit between the sample and the grating you lose many of the photons emitted from the sample. This makes the count rate on your detector lower and, thus, the measuring time longer in order to get reasonable statistics. It would therefore be preferable to have a
highly focused beam exiting the beamline, making it possible to open up the entrance slit without compromising the focus or resolution on the detector.

In between the entrance slit and the detector is the grating. It is a diffraction grating, which is an optical component with a periodic structure, in this case, with lines. Diffraction gratings are made so that they either transmit or reflect incoming light at different angles depending on the wavelength of the incoming light. The early gratings (before 1888) were simply grooves made as even as possible on a reflective surface, which is a design that works. However, most of the light will diffract in the zeroth order, i.e. the angle of reflected or transmitted light, $\theta_r$, will be the same as that of the incident light, $\theta_i$, which for spectroscopic purposes is quite useless, since there will be no discrimination between emitted photons of different energies. Lord Rayleigh showed that it is theoretically possible to squeeze much more of the diffracted light into the non-zeroth orders [8] and consequently, in the beginning of the last century, gratings with controlled groove-shapes were available. These gratings are said to be blazed and Fig. 3.6 shows a schematic illustration of how a blazed reflection grating diffracts incoming photons of different energies at different angles.

![Section of a blazed reflection grating showing three different orders of diffraction.](image)

The diffraction from a grating is governed by the grating equation (Eq. 3.4), which is valid both for transmission and reflection, and reads:

$$d(sin\theta_r - sin\theta_i) = m\lambda$$  \hspace{1cm} (3.4)

where $d$ is the spacing between the grooves, $\theta_i$ and $\theta_r$ are the angles of the incoming and reflected radiation (in respect to the grating normal), $m$ specify the order of the various principal maxima, and $\lambda$ is the wavelength of the radiation. The zeroth order mentioned above, means that $m = 0$, and under this criteria the grating acts as a mirror and reflection angles $\theta_r = \theta_i$. 

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To have a grazing incidence on the grating is important since soft X-rays are easily absorbed in the matter, and hence also in the grating. At more grazing angles, though, more of the incoming light is reflected from the grating. The grazing angle for the grating used in my experiments is 88.1° in respect to the normal to the grating. To further improve the specular reflectivity the grating is gold plated. When comparing different gratings one important aspect is the groove density, 1/d (mm⁻¹), and the groove density is 1200 for the grating I have used.

The detector is naturally also a very important part of the spectrometer. The one currently mounted on our spectrometer consists of several parts: a retarding plate, micro- (or multi-) channel plates (MCP’s), a fluorescent powder coated screen (in this case a Eu-doped yttrium oxide) and a charge-coupled device (CCD) camera. The detector works as follows (cf. the schematic presentation in Fig. 3.7): incoming photons hit the top MCP (coated with CsI) and are absorbed, which results in electron emission. The MCP material is highly resistive and is perforated with tiny channels. Each MCP is kept in a strong electric field and acts as an electron multiplier. It produces, from the impact of the initial electron, a cascade of electrons that propagates through each channel, through which the original signal is amplified by several orders of magnitude, depending on the electric field strength. Following the stack of five MCPs, the electrons hit the fluorescent powder in which they are absorbed, resulting in visible fluorescence. These emitted photons are registered by the detector and the RIXS count rate will normally scale with the absorption cross section at the chosen excitation energy.

Figure 3.7: A schematic view through an X-ray detector.
The electron cascade that bursts out from the bottom of the last MCP in the stack spreads out on its way toward the fluorescent powder coated screen. This might at first seem as a disadvantage, from a resolution point of view, but the CCD software executes a center of gravity calculation for every electron hit on the screen. This means that a larger spot size on the CCD renders a better center of gravity calculation. Since the fluorescent powder grain size is smaller than the spot size, the MCP channel size and density are the limiting parameters for achieving good resolution. Narrow, closely spaced channels will enable discrimination between photons of close energies. Notable in this technique is the fact that the low yield from emission processes, which produces a quite low count rate on the detector, makes it possible to treat every hit individually. The MCPs currently used in the detector offer a resolution of about 30 μm. Spatial resolution is further achieved by recording images of the fluorescent powder coated screen with the CCD camera at 14 frames per second.

As mentioned above, I have used a Rowland type spectrometer, which means that it has a certain geometry involving the spatial placement of the three integral parts, i.e. the entrance slit, the grating, and the detector. This geometry is a circle (Rowland circle) and Fig. 3.8 shows the principles of the design. The Rowland criteria states [9] that if a spherical grating with radius \(2R\) is illuminated by a point source, both the source and focus are situated on a circle of radius \(R\).

![Rowland Circle](image)

*Figure 3.8: The Rowland circle design, in which the radius of the grating is \(2R\) and the radius of the Rowland circle is \(R\).*

In Fig. 3.8, light coming through the entrance slit with a certain wavelength will have a focus somewhere on the Rowland circle. Since the detector has a
certain width, it covers an interval of wavelengths. However, the flat detector is placed in a tangential plane to the Rowland circle, resulting in a fulfillment of the Rowland criteria [9] only at one specific wavelength. This is not a huge setback since by centering the detector with respect to the incoming photons you will only attain a moderate deviation from the Rowland circle. A bigger source for errors is astigmatism, an effect which is severe at grazing incidence and renders skewed lines on the detector. The fact that we see lines on the detector is caused by the grating’s inability to focus both in the sagittal and transverse planes at one point in space. The sagittal plane is in this case the vertical plane running through the mid-line of the Rowland circle, whereas the transverse plane is the horizontal equivalent.

Figure 3.9: A typical image from the detector. In this case from RIXS measurements at the Ni L-edge on a LiNi0.65Co0.25Mn0.1O2 battery electrode.

An example of a typical detector image is shown in Fig. 3.9. This particular image is from RIXS measurements on the battery electrode material LixNi0.65Co0.25Mn0.1O2 at the Ni L-edge. RIXS measurements are usually presented as 2D graphs with the energy dispersive direction on the x-axis and intensity (in arbitrary units) on the z-axis. When converting these 2D figures to a xy-plot with energy on the x-axis and intensity on the y-axis you add the slices along a curvature, adjusted to account for the skewed (curved) lines.
4. Materials

The previous chapter presented methods for examining electronic transitions in atoms with the help of soft X-ray spectroscopy. The present chapter will describe the materials I have investigated and in which the various electron densities at different atomic sites are important in order to understand the processes occurring in the respective materials. These materials are all of high interest since they may prove important for future alternative energy storage devices, namely, next generation batteries, nuclear waste repository material and a catalyst involved in a method to split water molecules through electrolysis for energy production.

4.1 Battery materials

There are two major types of batteries: primary, i.e. non-rechargeable, and secondary, i.e. rechargeable, batteries. I have only done research on Li battery materials that are intended for use in secondary batteries.

An incredible rate of development has taken place in electronics, often depicted by Moore’s law which states that memory capacity doubles every 18 months. Compared to these advances, the development in battery technology has been modest. A common, modern type Li-ion battery can store about 180 Wh/kg, and this is only five times as much as can be stored in an old fashioned lead-acid battery. This is however not evidence of limited research devoted to battery technology. On the contrary, since the introduction of Li battery (and nowadays Li-ion battery) technology there has been extensive research and development of these energy storage devices. Today, Li-ion batteries are found in a wide range of products - from mobile phones to electrical cars - and their importance for society is incontrovertible.

Several factors are important for progress in battery technology research: an improved energy storage capacity is crucial, but other factors may be essentially equally important. For instance, the rate at which the battery can be cycled is important since different applications for the battery may demand specific current outputs. The rate at which a battery can be cycled is commonly represented as C/x, where x is the number of hours every cycle, C, demands.

Another important quality for a battery is safety. Since most batteries use flammable materials there is always a risk for fire or explosion. Also, con-
Structuring a battery that contains as little hazardous material as possible is imperative, especially since it is impossible to control where all batteries end up after they are disposed.

Li is today produced by mining and if for example, in the future, all vehicles use batteries as energy source, a substantial amount of all Li resources would need to be employed. Luckily there are vast amounts of Li in the oceans, and sea water Li could easily be extracted from brines.

A schematic presentation of the technology behind a standard Li-ion battery is shown in Fig. 4.1. It consists of two electrodes, anode and cathode, separated by an electrolyte. The two electrodes have different potentials, dictated by the reactions occurring at their respective interfaces with the electrolyte. When a connection exists between the negative and positive poles on the battery, an electron current runs through the connection due to the voltage difference between the electrodes. This forces Li-ions, hosted in the graphite anode as LiC₆, to migrate through the electrolyte and into the cathode, in this case LiₓCoO₂, and thus conserving charge neutrality for the battery cell. The process of Li-ion migration into a material is referred to as lithiation or intercalation, and in a Li-ion battery this is the process that takes place in the cathode during discharge of the battery. The electrolyte separating the two electrodes has ideally very low conductivity for electrons but allows high mobility for the Li-ions.

![Figure 4.1: A schematic illustration of a LiCoO₂ battery.](image)

The reactions occurring during discharge of the battery cell in Fig. 4.1 can for the positive electrode be written as:

\[
\text{LiCoO}_2 \rightleftharpoons \text{Li}_{1-x}\text{CoO}_2 + x\text{Li}^+ + xe^- \quad (4.1)
\]

and for the negative electrode as:

\[
x\text{Li}^+ + xe^- + 6\text{C} \rightleftharpoons \text{Li}_x\text{C}_6 \quad (4.2)
\]
4.1.1 Battery assembly and cycling

The battery cells used in my research are assembled at an in house facility at Uppsala University. The active electrode materials come from two different research groups; ECME, University Cadi Ayyad, Marrakech, Morocco and High Power Lithium HPL SA, Ecole Polytechnique Fédérale de Lausanne, Switzerland.

Once you have your active material (powder) you should find your battery slurry recipe. The battery electrodes I have used in my research are made from a mixture (i.e. slurry) containing mostly active material, but also carbon powder, binder, and solvents. The carbon powder improves conductivity and the binder holds the electrode material together. The mixture is applied onto an aluminum foil and dried for 6 h at 80°C to remove solvents. Circular electrodes are cut from the aluminum foil and transferred into an Ar-filled glove box (< 1ppm H₂O and O₂) and dried in vacuum at 120°C overnight to remove water from the electrode material. A photograph of the glove box is shown in Fig. 4.2b.

A battery cell is then assembled in an plastic-covered aluminum pouch cell [10], as shown in Fig. 4.3, inside the glove-box and with Li metal foil as counter electrode. The aluminum pouch is made from a plastic covered aluminum foil otherwise used as packaging material for coffee beans. This aluminum foil is easily foil-welded along the edges to create the pouch. At one edge of the pouch, a Ni metal foil strip is inserted as a connector to the Li counter electrode in the battery. Next to it, an Al metal foil strip is inserted.
as a connector to the cathode electrode. Before foil-welding that edge a soft plastic strip is placed between the connectors and the pouch, making the seal air-tight. A Li salt, LiPF₆, dissolved in a mixture of ethylene carbonate and diethylcarbonate, EC:DEC (2:1 by volume), is used as electrolyte. A separator is used to keep the electrodes apart and to prevent the cell to fail due to short circuit.

![Image of a plastic-covered aluminum pouch cell battery](image)

*Figure 4.3: A plastic-covered aluminum pouch cell battery. On top of the battery the two connectors protrude. The slightly tilted square shape inside the pouch is the separator and the somewhat smaller round shape is the electrode.*

Electrochemical cycling was performed to test the batteries. This entails charging and discharging the batteries using a multipotentiostat, which is an instrument that records currents and voltages with high accuracy. Fig. 4.2a is a photograph of one of the multipotentiostat test stations available at the Advanced battery center at Ångström laboratory in Uppsala. It is a device designed to, for instance, keep the current through an electrochemical cell constant, disregarding changes in the load itself. This is made possible by the potentiostat’s extremely high internal resistance.

It is important to cycle the batteries at a slow enough rate, thus making certain that the chemical redox reactions have time to complete. When you cycle the batteries, you can expose them to the situation they would experience if they were in use in a device of some sort. There are numerous properties of a battery that is of interest to test. Among them, the most important are the specific capacity (in mAh/g) and how well the battery maintains its specific capacity after consecutive cycles. During the lithiation (intercalation), the cells
can be stopped at different degrees of lithiation. A typical result from a cycling procedure is shown in Fig. 4.4.

![Figure 4.4: Results from cycling of a Li$_x$Ni$_{0.25}$TiOPO$_4$ battery electrode using a BioLogic VMP multipotentiostat.](image)

There are several noticeable features in a cycling curve as the one seen in Fig. 4.4. At the starting point (C$_0$) the battery is fully charged, in this case meaning that $x$ in Li$_x$Ni$_{0.25}$TiOPO$_4$ is 0.5. When Li-ions first start to intercalate the structure, there is a voltage drop which is quickly followed by a plateau build-up at approximately 1.5 V, indicating that a chemical reaction is taking place in the cell. In the region around $x=1.4$ to 1.5 another considerably smaller drop in potential takes place, again followed by a plateau. This is an indication of a different chemical reaction taking over. As soon as all constituents in these chemical reactions are consumed the voltage starts to decrease, as can be seen in the region above $x=1.8$. Beyond this point, i.e. in a potential region below 1.0 V, the electrolyte is not stable anymore, resulting in interfaces building up on the electrode surface and other unwanted side reactions. In this particular example this potential region is purposely infringed in order to investigate the behavior of the electronic structure for Ti, Ni, and O in this region.

After the electrochemical cycling of the batteries they are transferred into an Ar-filled glove box, where they are kept for approximately 24 h before opening the pouch cell. The electrodes are then put onto a sample holder and packeted in an air-tight container for transport to the synchrotron facility.
Since the oxidation states of the transition metal atoms are of great importance for the performance of electrode materials, I have paid attention to this when analyzing spectroscopic data, both in XAS and RIXS measurements.

In situ experiments

A long term goal of my graduate studies, was to perform in situ soft X-ray measurements of the intercalation process. To reach this goal, several difficult problems had to be solved. Firstly, it requires keeping a working battery in vacuum in the main chamber of the spectrometer. Secondly, there must be a small window on the battery, enabling X-rays to enter as well as escape the battery cell. Finally, it must be possible to connect leads to the battery from outside the main chamber, in order to connect a potentiostat.

The first attempts to achieve all this was by building a battery inside a liquid cell. Fig. 4.5 shows a cutaway drawing of this cell.

Figure 4.5: A cutaway drawing of the liquid cell.

The body of the cell is made from polyetheretherketone (PEEK), which is a vacuum-compatible, strong, chemical- and heat-resistant thermoplastic. There are rubber gaskets between the PEEK body and the front and back of the cell, keeping it air- and liquid-tight. The window is a commercial 1x1 mm Si$_3$N$_4$ window with a thickness of 100 nm. Attached to the top of the cell are a couple of tubes with fine diameter, making it possible to flow electrolyte in and out of the cell. The liquid cell is assembled in a glove box much like the battery
pouch cells discussed above, and transported to a synchrotron facility in an Ar-filled container. The first attempts at building a battery in the cell was by sputtering WO$_3$ onto the Si$_3$N$_4$ window as cathode and using Li metal foil as anode electrode.

Despite numerous attempts at performing in situ soft X-ray measurements of the intercalation process with the presented liquid cell setup, there are still no good in situ data. This is due to several obstacles, the main one being the unfavorable dimensions of the battery. Not only is the area of the cathode electrode small (10 mm$^2$), but the distance to the anode is large (5 mm). This results in very small currents to control with the potentiostat, typically in the region of a few hundred nA when working with the sputtered WO$_3$ films. Such small currents are extremely difficult to control at a synchrotron facility, with its excess of interfering electric fields. A second obstacle that needs to be maneuvered around, is the volatility of the electrolyte, making it difficult to keep the cell completely filled during experiments. The vaporization of the electrolyte can potentially be accounted for by adding more electrolyte, from outside the measuring chamber, via the tubes. This is a delicate procedure, since if you increase the pressure inside the cell, the Si$_3$N$_4$ window is likely to break.

It has also become apparent that material damage from the X-ray beam, often referred to as beam damage, plays a much more important role when liquid electrolyte is in contact with the electrode material. This fact was revealed when another in situ design was tested. This time a pouch cell of the type discussed above was used, but with the addition of a Si$_3$N$_4$ window glued directly onto the battery. To overcome the fact that the X-rays would only see the aluminum foil backside of the electrode we used an aluminum mesh as a substrate for the electrode material. By analyzing the coated mesh in a microscope following irradiation, a dark coating had formed on both the mesh and the Si$_3$N$_4$ window, indicating that the electrolyte had been present also on the backside of the electrode. This is naturally a disadvantage, since we do not want to study the electrolyte, instead we need a free path for the X-rays to be able to penetrate the electrode material.

**Ex situ experiments**

In parallel to the in situ experiments, I performed measurements on several battery materials ex situ. In this thesis I present studies on a few possible candidates for next generation battery materials, such as:

- LiNi$_{0.65}$Co$_{0.25}$Mn$_{0.1}$O$_2$ (paper I)
- Li$_{0.5}$Ni$_{0.25}$TiOPO$_4$ (paper II)
- LiMnPO$_4$ (paper III)
- LiMn$_{0.9}$Fe$_{0.1}$PO$_4$ (paper III)
4.1.2 LiNi$_{0.65}$Co$_{0.25}$Mn$_{0.1}$O$_2$

Presently, LiCoO$_2$ [11, 12, 13, 14, 15] is among the most common (if not the most common) cathode material in commercial batteries. LiCoO$_2$ is a crystal structure with layers of octahedra formed by the Co and O atoms. Fig. 4.6a shows an example of such a structure.

For LiCoO$_2$ the main drawbacks are the high cost of cobalt, its toxicity, and its instability at high potentials. Pure LiNiO$_2$ [16, 17, 18] has also been considered, but here the serious drawbacks include safety issues and the difficulty to synthesize without unwanted extra-nickel [19, 20] ending up in the Li plane in the structure, inhibiting Li diffusion. Therefore attention has been directed toward LiNi$_{1-y}$Co$_y$O$_2$, in which the cobalt will support the synthesis of the material. Moreover, it is known that with increased Co content in the solid solution the structure will show more of a 2D character, which is desirable [21, 22]. Additionally, the substitution of Mn for Ni and Co in LiNi$_{1-y}$Co$_y$O$_2$ will improve the electrical conductivity of the material and the stability of the structure.

This material has a 3% Li/Ni disorder in the structure and it has shown an hexagonal volume change of only 3%, when Li is removed. It has good mechanical stability and a discharge capacity of 150 mAh/g in the voltage range 2.5-4.5 V. Substitution of Mn$^{4+}$ for Ni$^{3+}$ and Co$^{3+}$ leads to a presence of both Ni$^{2+}$ and Ni$^{3+}$ which makes the electron hopping easier [23]. We show that the combination of XAS and RIXS is a powerful tool to extract details [24, 25, 26, 27] about the chemical and symmetry-dependent electronic structure of this material as a function of delithiation degree, as achieved in a real functioning battery.

Open questions concern the interplay of charge uptake between the metal ions among themselves, as well as between, the metal ions and the O-ions. For instance, it is not clear whether Co-ions actively participate in the lithiation process [23] and to what extent Ni participates in the charge uptake.

4.1.3 Li$_{0.5}$Ni$_{0.25}$TiOPO$_4$

So far, LiFePO$_4$ has been the main candidate when it comes to LiMPO$_4$ (M = Fe, Mn, and Co) systems [28, 29, 30, 31, 32]. In an attempt to overcome the drawbacks of the LiFePO$_4$ material as high voltage materials for Li-ion battery electrodes, such as poor electrical conductivity and slow kinetics of Li-ion diffusion, carbon coating and decreasing particle size has been employed. LiMnPO$_4$, LiCoPO$_4$, and LiNiPO$_4$ has also attracted interest lately, but they all suffer from the same drawbacks as LiFePO$_4$. Another attempt to improve the existing candidates has been by creating solid solutions between different olivine structured LiMPO$_4$ systems [33]. Lately, Li$_{0.5}$Ni$_{0.25}$TiOPO$_4$ has been suggested as a future candidate since it has a low cycling potential ($\approx$1.7 V) and a good capacity retention during cycling [34]. In Fig. 4.6b the structure of this material is shown.
Open questions are the same as for LiNiO.65Co0.25Mn0.1O2, namely the interplay of charge uptake between the metal ions among themselves, as well as between, the metal ions and the O-ions. For instance, it would be of great interest to clarify if Ni or Ti changes its valence first, or if they both change valence simultaneously during discharge. In the material LiO.5NiO.25TiOPO4 we have Ni2+ and Ti4+. It is today believed that during the insertion of 1.5 Li-ions in the LiO.5NiO.25TiOPO4 structure the valence numbers change from Ni2+ to Ni and Ti4+ to Ti3+ [34]. The calculated theoretical capacity of LiO.5NiO.25TiOPO4 is 225 mAh/g, but since the material shows an experimental capacity of about 300 mAh/g for the first discharge, it is speculated that a formation of a solid electrolyte interface (SEI) also contributes to the experimental capacity of the material during the first discharge [34]. Further, it is claimed that Ti4+/Ti3+ is the main active redox couple and that Ni2+/Ni accompanies at a later stage in the discharge curve.

4.1.4 LiMnPO4 and LiMn0.9Fe0.1PO4

For the cathode side of the Li-ion battery, LiFePO4 [28] has taken a leading role among olivine structured materials, mainly due to its low material cost and excellent chemical stability. The only obvious drawback for LiFePO4 is the poor rate capability. The rate capability of LiFePO4 is restricted by the following: (i) LiFePO4 and FePO4 are two separate phases and the phase boundary might impede Li-ion diffusion, and (ii) LiFePO4 has rather poor electrical conductivity.

There are, however, ongoing efforts to improve the olivine type of cathode materials. Not only by reducing the size of and carbon coat the LiFePO4 particles, but also through the introduction of other cations than Fe in the olivine structure. One of the most promising candidates so far is LiMnPO4, which has an electrochemical activity of Mn3+/Mn2+ at 4.1 V vs. Li/Li+, while the Fe3+/Fe2+ redox couple shows 3.4 V vs. Li/Li+. However, because the electrical conductivity of the LiMnPO4 is less than 0.1% that of LiFePO4, it cannot be easily used for high-output devices. It has, however, proved to be difficult to overcome these shortcomings for LiMnPO4 cathodes, mainly due to unclear effects of particle sizes, carbon additives, geometries of the battery cells, and other extrinsic properties. Fig. 4.7 shows a model of the LiMnPO4 structure.

4.2 Copper corrosion and nuclear waste storage

Cu corrosion by groundwater is of current interest due to plans of storing spent fuel from nuclear power plants in canisters with an outer liner of Cu in an underground repository at 500 m depth [35]. In Fig. 4.8 a drawing of the storage is shown.
Figure 4.6: (a) The structure of LiCoO$_2$. The Co atoms are inside the octahedra and the O atoms are colored red. The Li atoms, which are able to move into and out of the material end up in-between the layers, and are colored violet. (b) The structure of Li$_x$MnPO$_4$. P atoms are inside the yellow, Ti inside the dark blue, and Ni inside the green volumes. The O atoms are colored red and Li atoms light blue.

Figure 4.7: The structure of the LiMnPO$_4$ material.
Although oxygen free, groundwater contains sulfides in solution that may attack the Cu surface and break it down during the planned duration of 100,000 years until activity has declined to biologically negligible levels. The canisters will consist of a cast iron insert, which enables the canister to withstand great mechanical loads, as well as a 5 cm thick Cu liner. Cu is very corrosion-resistant in atmospheric environments but it is less clear how well Cu withstands the aqueous environment and the redox conditions of the repository [36] when considering that the containers must be able to withstand its corroding surroundings for a long period of time.

There will initially be some oxygen in the storage from the time of construction and filling of the repository. Once oxygen is depleted within a repository, the presence of sulphide species, produced from nearby Fe$_2$S and remotely from SO$_4^{2-}$ via sulphate reducing bacteria may present an ongoing corrosion issue, as Cu sulphide formation may be coupled with water reduction [37]. It has been shown that electrochemically prepared Cu$_2$O/CuOH surfaces are slowly converted to Cu$_2$S in aqueous sulphide solutions over a number of hours [38]. This result suggests that the oxide/hydroxide layer may be partially passivating the surface upon exposure to sulphides; unfortunately, this is poorly quantified at this point. Cu speciation among oxides/hydroxides and sulphides/bisulphides has not been performed, nor have mixed CuO/Cu$_2$O starting materials been used for these reactions. These are all motivating elements to our work, as we are attempting to accurately characterize various oxidized Cu surface species and their behavior when exposed to sulphides exposure to sulphides.

During the time of writing of this thesis there is an intense media debate on the Cu canisters’ corrosion resistance. Swedish Nuclear Fuel and Waste Management Company (SKB) submitted applications for the repository pro-
gram to the Swedish Radiation Safety Authority (SSM) in March 2011, and the commotion grew larger the closer to the submission date we came.

We have done experiments aiming at building knowledge about how Cu and its surface oxide react with aqueous sulfide solutions. We used a combination of XAS and RIXS spectroscopy to study polycrystalline Cu that had been ex-situ oxidized both by thermal treatment and by electrochemical treatment. The oxidation state of Cu was controlled by the duration and temperature of the heat treatment. The method to produce the Cu(I) oxide- and Cu(II) oxide-containing surfaces was by placing the polycrystalline Cu foil (0.05 mm thick, 99.9+% pure, from Goodfellow Cambridge Limited) onto a heating plate in air at ambient pressure. For some of the samples we applied a moderate flow of oxygen over the samples during the heat treatment. The heating plate was held at a temperature of 230°C, resulting in a temperature for the samples of 190°C, while exposed to a flow of O₂. This was done briefly (about 2 min.) until a visible layer of oxide formed. Several samples with different thicknesses (different interference colors) were prepared and checked by O K- and Cu L_{III,II}-XAS. All of them showed identical spectral features. Another set of Cu foil samples was heated to the same temperature for a prolonged time (about 20 min.) until a thick black layer of CuO had formed visibly. This produced a sufficiently pure and thick Cu(II) oxide film as the comparison with the O K- and Cu L_{III,II}-XAS of a CuO reference sample showed.

For the electrochemical experiment we used different potentials and durations to build up different oxidation states. We also tried to strip off the oxides by applying reducing potentials for different durations. The electrochemical setup consisted of a polycrystalline Cu metal foil (0.05 mm, purity 99.9 %) as working electrode, a platinum foil as counter electrode, and an Ag/AgCl electrode as reference, all in a single compartment cell as shown in Fig. 4.9. All potentials are quoted against the standard hydrogen electrode (SHE) [Ag/AgCl potential is -0.197 V vs SHE]. Potentials were controlled using a Gamry Reference 600 potentiostat. All solutions were prepared using deionized Millipore water (18.1 MΩ·cm). Prior to further treatment, nitrogen was bubbled through the solutions for one hour. This was done in order to minimize the amount of dissolved O₂ that could participate in the corrosion process, mimicking the eventual oxygen-free groundwater conditions. We prepared a 0.1 mM NaOH solution for creating oxidized Cu surfaces on Cu foil. Oxidized samples (e.g. from each potential) were then directly exposed to solution containing 1 mmol L⁻¹ Na₂S and 0.1 mol L⁻¹ NaCl for 8 h and analyzed using XAS.

Another try with in situ measurements was performed, using a similar liquid cell as discussed in chapter 4.1. Cu was evaporated in vacuum onto a Si₃N₄ window, as a counter electrode a Pt metal foil was used, and a silver wire was inserted into the side of the cell and used as a reference electrode. This design was only partly successful, due to the Cu films tendency to peel off at potentials close to the Cu(II) formation threshold. This did not occur gradually.
as a stripping process, but rather as a peeling of the whole Cu layer in one
rapid process. The thickness of the Cu film on the Si$_3$N$_4$ window varied from
50-100 nm between different samples. We also tried to evaporate a thin (20
nm) Al film as an intermediate layer to see if Cu had better adhesion to Al at
elevated potentials but the peel-off problem remained.

4.3 Hydrolysis using a Co catalyst

Photosynthesis is a process that converts carbon dioxide into organic com-
pounds, using the energy from sunlight. This is done by rearranging the bonds
of water:

$$6\text{CO}_2 + 6\text{H}_2\text{O} \stackrel{\text{light}}{\longrightarrow} \text{C}_6\text{H}_{12}\text{O}_6 + 6\text{O}_2 \quad (4.3)$$

This process, i.e. rearranging the bonds of water, is also a process of im-
portance to artificial systems that perform “water splitting”. Such systems are
interesting due to their ability to produce O and H gas, which could be an im-
portant characteristic in potential future hydrogen economy. The splitting of
the water molecule into O and H gas by letting an electric current pass through
the water is called electrolysis.

If the rate of a reaction is increased by the presence of a substance, this
substance is called a catalyst. This also implies that the catalyst itself is not
consumed during the reaction. A recently proposed method \[39\] to increase
the rate for H gas production during electrolysis of water involves an \textit{in situ}
formation of a catalyst containing phosphate and Co$^{2+}$-ions. If the kinetics of
the electron transfer at the electrodes in the electrochemical setup are rapid,
they can be assumed to be at equilibrium with the electrode potential and
hence governed by the Nernst equation for the half-cell reaction:

$$\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightleftharpoons 2\text{H}_2\text{O}$$

$$4\text{H}^+ + 4\text{e}^- \rightleftharpoons 2\text{H}_2$$

$$2\text{H}_2\text{O} \rightarrow 2\text{H}_2 + \text{O}_2 \quad (4.4)$$

The electrodeposited catalyst material I have studied is intended to be used
in solar-to-fuel conversion and is an interesting candidate for an efficient
water-splitting catalyst. The electrochemistry in this method must operate
close to the Nernstian potentials (E) for the H$_2$O/O$_2$ and H$_2$O/H$_2$ half-cell
reaction:

$$E = E^0 + \frac{RT}{nF} \cdot \ln \frac{C_O(x = 0)}{C_R(x = 0)} \quad (4.5)$$
where \( O \) is the species to be reduced, as in \( O + ne^- \rightarrow R \). \( C \) in Eq. 4.5 is concentration, and \( x \) is the distance from the electrode surface.

The electrochemical setup I used was very straightforward. However, even for simple setups there are numerous factors that influence the reactions during an experiment. In Fig. 4.9 the variables that may affect the electrochemistry are shown. The electrodes in the electrochemical setup are Indium-Tin-Oxide coated glass slides (ITO) as working electrode and a Pt foil as auxiliary electrode, both in KPi electrolyte containing phosphate and Co\(^{2+}\). Electrolysis was carried out at 1.29 V (NHE) and a reference electrode was placed close to the working electrode. During this experiment a Co-containing dark coating forms on the ITO electrode and this is the catalyst material I have studied with both XAS and RIXS measurements.

![Figure 4.9](image)

**Figure 4.9:** The electrochemical setup used for preparing Cu oxides as well as electrolysis experiments. The figure also shows the important variables affecting electrochemical reactions.

The basic electrochemical recipe is identical to what is described in reference [39]. We have, though, altered the recipe slightly for some of the samples in an attempt to shed some light on which criteria govern the formation of the catalyst. In table 4.1 it is shown what potentials has been used to drive the formation of the catalyst material, and also what pH the solution had. Potentials were measured against a Ag/AgCl reference and converted to NHE potentials by using \( E(\text{NHE}) = E(\text{Ag/AgCl}) + 0.197 \text{ V} \). In reference [39] the potential was 1.29 V (versus NHE), and a 30 wt% KOH solution was used to buffer the electrolyte to pH 7.0. In other words, sample \( b \) is as good a copy of the samples in reference [39] as we could achieve, and samples \( a, c, \) and \( d \) have one or more variables altered.
Table 4.1: This table shows from left to right the different potentials (versus NHE) under which the samples \((a – d)\) are produced, the pH of the buffer solution, and lastly the wt% of KOH in the buffer solution.

<table>
<thead>
<tr>
<th>sample</th>
<th>potential [V]</th>
<th>pH</th>
<th>buffer [wt%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>1.387</td>
<td>7.0</td>
<td>5</td>
</tr>
<tr>
<td>b</td>
<td>1.287</td>
<td>7.0</td>
<td>30</td>
</tr>
<tr>
<td>c</td>
<td>1.287</td>
<td>4.45</td>
<td>5</td>
</tr>
<tr>
<td>d</td>
<td>1.387</td>
<td>7.0</td>
<td>30</td>
</tr>
</tbody>
</table>
5. Results

In order to present the most important results from the articles in this thesis I will in this chapter shortly summarize the results my from studies on battery electrodes, Cu corrosion, and catalysis materials. A word should maybe be said about beam damage while measuring with soft X-rays. I have made tests, by performing repeated scans at the same spot and searching for any differences between the scans. For experiments on ex situ battery electrodes I have not been able to see any beam damage effects on the samples. For Cu corrosion experiments I have seen beam damage effects. This makes sense, since the species that was susceptible to beam damage was most likely Cu(OH)\(_2\) which has, compared to other possible compounds in this example, much weaker bond and is converted to the more stable compound Cu\(_2\)O. As discussed earlier, during in situ experiments, both on battery materials and Cu corrosion, beam damage is an issue.

5.1 Battery materials

For all three battery material experiments presented below, the aim has been to shed light on the charge uptake process during intercalation of the materials. The electrochemical data from cycling of the batteries tells you at what potentials and for how long different chemical reactions occur inside the battery, but you need to make a qualified guess to say anything about which atom is active in the charge uptake during any given period of the intercalation, and that is where XAS and RIXS come into play.

Paper I

The most important result for this electrode material is that Co indeed plays an electrochemically active role and Ni is much less active in the charge uptake than reported from TM-K edge measurements [40, 41]. Furthermore, we find that both the unoccupied as well as the occupied O 2\(p\)-states are heavily influenced by the charge compensation process.

For the delithiation process between \(x=1.0\) and \(x=0.2\), we tentatively find that the transition metals undergo the following transitions: (i) Ni\(^{2.2+}\) to Ni\(^{2.5+}\), (ii) Co\(^{3+}\) to somewhere between Co\(^{3+}\) and Co\(^{4+}\), (iii) whereas Mn remains fairly unchanged at Mn\(^{4+}\). This means that, depending on the
delithiation state of Li$_{x}$Ni$_{0.65}$Co$_{0.25}$Mn$_{0.1}$O$_2$, the effective charge transfer to the O-ion sites corresponds to about 1.6-1.8 electrons, in the case where Co changes from Co$^{3+}$ to Co$^{4+}$, and to 1.5-1.8 electrons if Co does not change its oxidation state at all. The actual value for the change in valence number is likely somewhere in the middle of this interval, resulting in a change in effective charge on the O of about 0.24 charge units.

Co L$_{III}$-RIXS is also sensitive to the delithiation process with a substantial energy shift of the main peak 5.1. The main peak shifts down in the valence band as more charge becomes available, which is ascribed to a corresponding upward shift of the Fermi level.

![Energy spectrum of RIXS CoL-edge](image)

*Figure 5.1: RIXS on Li$_{x}$Ni$_{0.65}$Co$_{0.25}$Mn$_{0.1}$O$_2$ at different degrees of lithiation.*

**Paper II**

For the electrode material Li$_{x}$Ni$_{0.25}$TiOPO$_4$ we have studied the first lithiation and delithiation of the material. We know that this material has a first lithiation curve (see Fig. 4.4) which is very different compared to subsequent ones. It has three plateaus while all subsequent curves show a single larger plateau, more like the delithiation curve in Fig. 4.4. Our experimental data shows that one cannot easily assign any of the two first plateaus to a single species changing its valence. An initial assumption was otherwise that Ni should be associated with the first plateau and Ti with the second. The third plateau is situated at such low potential that it is likely that SEI formation and other reactions involving the electrolyte takes place.

For the lithiation process between $x=0.5$ and $x=2.5$, we find that Ni changes its oxidation state from Ni$^{2+}$ ($x=0.5$) to Ni$^{1+}$ ($x=2.0$) and finally to metallic Ni ($x=2.5$). Delithiation of the material only incompletely reverses the changes from the lithiation process at Ni. Even for the maximally delithiated sample Ni
has only changed its valence number back to Ni$^{1+}$. We find moderate intensity variations in the first two Ti $L$-XAS peaks during the first lithiation/delithiation cycle.

Ti-ions show an incomplete reversal of the lithiation process. The Ti $L$-RIXS spectra clearly show how the Ti $d$-band receives and loses charge in the lithiation/delithiation process. It is, however, not a monotonic function of the degree of lithiation as can be seen in Fig. 5.2.

![Figure 5.2: RIXS on Li$_x$Ni$_{0.25}$TiOPO$_4$ at different degrees of lithiation.](image)

Also the O-ions participate in the uptake of charge, but, in contrast to both Ni and Ti, this happens at a later stage in the lithiation (at $x \geq 1.5$).

Our results show that there exists considerable “crosstalk” between different atomic species, i.e. Ni, Ti, and O, regarding the response of the electronic structure to the lithiation/delithiation process. For this material, we must abandon the expected picture of a linear and sequential process in which a
rigid band is filled up and emptied as a simple function of $x$. We conclude that Ni and Ti respond not sequentially, but simultaneously, to the lithiation/delithiation process. The irreversible changes that we found for the first cycle at the Ni-ion sites have, most likely, an inhibiting effect on subsequent battery cycles, especially suggesting a reduced activity of the Ni sites. Finally, we point out that our systematic investigation shows that the combination of XAS and RIXS is a powerful approach for extracting details of the lithiation process in complex transition metal-oxide Li-ion battery materials such as Li$_x$MnPO$_4$.

As a consequence of the spectroscopic results from these first lithiation batteries, it would be very interesting to do a similar experiment, but with batteries at different stages in the second lithiation.

**Paper III**

From our experiments presented in this paper, we found that Mn $L$-edge XAS, in both Li$_x$MnPO$_4$ and Li$_x$Mn$_0.9$Fe$_{0.1}$PO$_4$, shows Mn$^{2+}$ character independent of the degree of lithiation. Initially we anticipated finding evidence for much larger changes at the Mn $L$-edge XAS, so these results were unexpected. In Fig. 5.3 we can see XAS spectra from the Li$_x$MnPO$_4$ electrode at three different degrees of lithiation, and also three reference spectra showing Mn compounds with different oxidation states.

**Figure 5.3:** Top traces show XAS at the Mn $L$-edge on Li$_x$MnPO$_4$ for $x=1.0$, 0.6, and 0.2. Bottom traces show XAS at the Mn $L$-edge for references MnO and LiMnO$_2$ (adapted from [42]) and MnO$_2$ (adapted from [43]).
There are small changes observed in O K-XAS of Li$_x$MnPO$_4$ but these cannot account for the entire charge compensation process. Mn L- and O K-RIXS spectra corroborate this picture even if there are indeed some smaller changes in the local electronic structure that evades detection using XAS. In paper I and II we have showed that a significant amount of charge compensation in the lithiation process may take place on O sites. However, compared to these similar studies the spectral shape changes are still relatively minute, considering that one must account for a transfer of 0.8 electrons per Mn$_0$Fe$_{0.1}$PO$_4$-unit in the complete lithiation process. This suggests that the other atomic species in the material (P and Li) may play a more active role than commonly assumed.

Replacement of 10% of Mn by Fe in Li$_x$MnPO$_4$ affects the discharge curve by a small voltage offset at the beginning and by the occurrence of an additional voltage plateau between $x = 0.75$ and $x = 1$. This was attributed to a Fe$^{3+}$/Fe$^{2+}$ redox process. However, our Fe L-XAS and -RIXS results showed that Fe is involved in charge compensation already from the start of the lithiation process and, in contrast, to pure FePO$_4$ [44], Fe is not completely reduced from Fe$^{2+}$ (Li$_{0.2}$Mn$_{0.9}$Fe$_{0.1}$PO$_4$) to Fe$^{3+}$ (LiMn$_{0.9}$Fe$_{0.1}$PO$_4$).

Fe L-RIXS (and, by virtue of hybridization, also Mn L-RIXS) showed that states in the electronic gap of Li$_x$MnPO$_4$ lying close to the Fermi level (within 0.5 eV) are created, which is expected from previous calculations [45]. This may partly explain the improved conductivity of the iron-substituted species. However, the maximum filling of these states seems to occur well before the lithiation process is complete and, thus, increased Fe-substitution may not improve electronic conductivity. Instead, other dopants such as Mg or Zn [46] could be useful to this end.

In conclusion, our comparative study of Li$_x$MnPO$_4$ and the iron-substituted Li$_x$Mn$_{0.9}$Fe$_{0.1}$PO$_4$ revealed that the redox reactions during lithiation/delithiation of these materials are complex and involve repopulation of charges for all constituent elements and consequently also involve Li- and P-sites in the charge compensation.

5.2 Copper corrosion

Paper IV

Our main conclusion is that sodium sulfide effectively reduces Cu(II) oxide to Cu(I) compounds after several hours of exposure. The XAS and RIXS spectra of the exposed surfaces closely resemble those of the Cu$_2$O reference sample with the notable exception of their Cu L$_{III,II}$-RIXS spectra. Therefore, Cu evidently forms a Cu(I) compound with O but with a Cu 3d-band of much reduced width, pointing to the possibility of a more complex compound containing sulfur. Fig. 5.4 (5.5) shows XAS (RIXS) spectra from thermally prepared Cu(I) and Cu(II) surfaces before and after exposure to Na$_2$S solution.
Figure 5.4: XAS at the Cu L_{III,II}-edge in TFY mode on thermally prepared Cu(I) and Cu(II) surfaces before and after exposure to Na$_2$S solution.

Figure 5.5: RIXS on thermally prepared Cu(I) and Cu(II) surfaces before and after exposure to Na$_2$S solution.

Our study suggests that further examination of the sulfide exposed Cu oxides is warranted in order to assess the consequences for long term underground storage of Cu canisters. Especially, the question of mass loss of such surfaces during the reduction process could be addressed, for instance, by combining X-ray spectroscopy studies with \textit{in situ} quartz crystal microbalance metrology [47].
Preoxidation of Cu electrodes in 0.1 M NaOH has been applied earlier [38] to yield oxidized Cu surfaces with known composition and characteristics. A voltammetric scan for Cu is shown in Fig. 5.6. At the first oxidation peak during the scan (U₁), a base layer of Cu₂O is formed, whereas at the second peak nucleation and growth of Cu(OH)₂ takes place and beyond the second peak (U₂) a partially passivating mixture of CuO/Cu(OH)₂ is expected.

Prior studies have applied Raman spectroscopy for spectral analysis, whereas our study uses XAS, which offers the advantage of being elementally and chemically specific. As shown in paper IV, that thermal treatment of Cu surfaces in air or pure oxygen also leads to distinct oxide layers, depending on the length of heating time. However, in contrast to the thermally treated Cu(II) sample IV, the electrochemically oxidized sample Cu@U₂ does not form a surface of pure Cu(II) oxide. The thermally oxidized sample exhibits a thick layer of single phase CuO, whereas the Cu²⁺-signature of the Cu@U₂ is weaker than the Cu¹⁺-signature. It is also, from studying the voltammetric scan (Fig. 5.6), reasonable to say that the Cu(OH)₂ layer that initially forms in the U₂ region is not to any substantial degree converted to CuO. This could mean that in our electrochemical experiment the reaction,

\[
\text{Cu} + 2\text{OH}^- \rightarrow \text{Cu(OH)₂} + 2e^- \quad (5.1)
\]

is favored to the alternative reaction,

\[
\text{Cu} + 2\text{OH}^- \rightarrow \text{CuO} + \text{H}_2 + 2e^- . \quad (5.2)
\]
In other words, the outermost layer of our samples consists mostly of Cu(OH)$_2$.

Moreover, the Cu(II) oxide phase is converted by X-ray irradiation and may be completely reduced electrochemically within four hours, possibly due to the weaker bonding of a hydroxide phase Cu(OH)$_2$. These results are compatible with the conclusions by [38] that a porous trilayer of a base layer of Cu$_2$O, a thin intermediate layer of CuO, and an outer deposit of Cu(OH)$_2$. However, any CuO is virtually undetectable in our experiment.

Both Cu@U$_1$ and Cu@U$_2$ surfaces are chemically converted into surfaces mainly containing Cu$_2$S by exposure to a Na$_2$S solution. This corroborates the conclusions of reference [38] for the conversion of preoxidized Cu to CuS. Additionally, we observe small amounts of remnant Cu$_2$O, where the Cu@U$_2$ surface contains the lesser amount than the Cu@U$_1$ surface.

5.3 Hydrolysis using a Co catalyst

While performing the bulk electrolysis, effervescence from the coating on the electrode occurred for all samples. By simple visual examination of the samples, only sample $b$ stands out by having less material deposited onto the ITO covered glass substrate and a more shiny metallic color. The other samples are of a lusterless black or dark gray color. It is noteworthy that sample $b$ did not turn out as good as expected. Most probably this had to do with less favorable geometry in our setup, compared to the setup used in reference [39], and therefore a slightly higher driving potential was needed to drive the bulk electrolysis. From the above mentioned we conclude that sample $d$ has the best chances of performing well as a catalyst.

SEM images of all samples is shown in Fig. 5.7. It is, from the SEM images, clear that sample $d$ has a rather different morphology than the other samples. The black coating, built up during the electrolysis, consists in this case of approximately 10 $\mu$m long and 1 $\mu$m thick rods.

XAS results show very small difference between the four samples. RIXS spectra, recorded at two different excitation energies, which show much greater variations in the spectra at the Co $L$-edge, are shown in Fig. 5.8. The three upper traces in the figure are emission spectra with an incidence energy of 775.67 eV, which is the energy that corresponds to a shoulder on the right hand side of the absorption peak in Co $L$-edge XAS. The three lower traces are emission spectra with an incidence energy of 774.88 eV, which corresponds to the top of the absorption peak.

From both the SEM images and the XAS and RIXS measurements it is clear that the potential, pH, and buffer concentration is of great importance for what compound we will grow on the electrode during electrolysis. The work on this catalyst material is in its infancy and more experiments are needed in order
Figure 5.7: SEM images of samples a – d.

Figure 5.8: X-ray emission spectra (Co L-edge) of the Co catalyst.
to achieve better understanding of the self-evolving process and the catalyst process under varied electrolysis conditions.
6. Conclusion and Outlook

In my research soft X-ray spectroscopy techniques (XAS and RIXS) have proven to be valuable and powerful tools for studying the processes of charge compensations in battery electrodes and Cu corrosion mechanisms. The bothersome complication that the experiments have to be performed in vacuum is well compensated by the, otherwise unaccessible, data obtained from this technique. This thesis aims at shedding new light on redox reactions in Li-ion batteries, Cu corrosion, and a novel Co catalyst. Some of the less expected results are summarized below.

Generally, oxygen plays a more important role in the charge uptake than commonly assumed, but also the transition metals and other species depart from expected behavior. The main result from the Li-ion battery material studies is the justification to abandon the view of valences as integers. This is true for all battery electrodes examined in this thesis. For the battery electrode material \( \text{LiNi}_{0.65}\text{Co}_{0.25}\text{Mn}_{0.1}\text{O}_2 \) we find that Ni changes its valence number, but considerably less than commonly assumed. Co, on the other hand, is changing its valence number during the delithiation process more than commonly assumed. Mn remains fairly unchanged which is in line with expectations. This implies that the resulting change in effective charge on O is about 0.24 charge units during lithiation/delithiation of the cathode material \( \text{LiNi}_{0.65}\text{Co}_{0.25}\text{Mn}_{0.1}\text{O}_2 \).

The anode material \( \text{Li}_{0.5}\text{Ni}_{0.25}\text{TiOPO}_4 \) exhibits, during the first lithiation of the material, two distinct plateaus initially believed to stem from separate oxidation processes of Ni and Ti. Our results show that the situation is more complicated and that there exists considerable “crosstalk” between different atomic species, i.e. Ni, Ti, and O, regarding the response of the electronic structure to the lithiation/delithiation process. For this material, we must give up the expected picture of a linear and sequential process in which a rigid band is filled up and emptied during lithiation/delithiation. We conclude that Ni and Ti respond not sequentially, but simultaneously, to the lithiation/delithiation process, even for the first cycle.

For both cathode materials \( \text{Li}_x\text{MnPO}_4 \) and \( \text{Li}_x\text{Mn}_{0.9}\text{Fe}_{0.1}\text{PO}_4 \), Mn \( L \)-edge XAS reveals \( \text{Mn}^{2+} \) character independent of the degree of lithiation. Initially we anticipated finding evidence for much larger changes in the Mn \( L \)-edge XAS, so these results were unexpected. As a consequence of this and analysis of the changes occurring at O, we find it justified to say that the lithia-
tion/delithiation involve repopulation of charges for all constituent elements and consequently also involve Li- and P-sites in the charge compensation.

One *ex situ* battery experiment that could increase our understanding of the complex processes in for instance $\text{Li}_x\text{Ni}_{0.25}\text{TiOPO}_4$ would be to repeat the experiments for this material, but for the second cycle instead of the first. The second cycle has only one voltage plateau during lithiation and is similar to the delithiation curve for the first cycle. This is to compare to the lithiation curve for the first cycle, which has two, or even three, plateaus (see Fig. 4.4).

An interesting idea that has been discussed is to do soft X-ray spectroscopy on model systems containing Li in an attempt to get better understanding of how the Li-ion is behaving in different environments and also to possibly retrieve a data base of spectroscopic “fingerprints” for Li in various environments. An attractive model system would be an ionic crystal incorporating Li, from which Li is extracted in a similar fashion as during lithiation of the electrode materials discussed in this thesis. This is however very difficult since crystals have a tendency to break during the extraction.

Another important task is of course to continue the development of the *in situ* technique for measurements on batteries during cycling. As discussed in this thesis, this is a time-consuming and difficult project, but one that would further expand our understanding of the redox reactions during cycling.

The conclusion from the Cu corrosion experiments is that sulfide effectively reduces Cu(II) oxide to Cu(I) compounds and possibly forms a compound containing both oxygen and sulfur. Also, the thickness and inhomogeneity of the copper oxide surface layers are of great importance for the corrosion mechanisms, including passivation.

The results from electrochemical oxidation of Cu are compatible with the theory that at strongly oxidizing potentials, a porous trilayer consisting of a base layer of Cu$_2$O, a thin intermediate layer of CuO, and an outer deposit of Cu(OH)$_2$ is formed. However, at both stronger and weaker potentials, the resulting surfaces consisted largely of Cu$_2$O. At the more strongly oxidizing potential, an admixture of Cu$^{2+}$-containing phases – mostly Cu(OH)$_2$ – was detected. Sulfide exposure of both surfaces was found to completely reduce the surface from Cu$^{2+}$ to Cu$^{1+}$ and resulted in the formation of Cu$_2$S with an admixture of Cu$_2$O.

To be able to perform *in situ* measurements with the liquid cell for Cu corrosion studies would be valuable, but similar to the battery experiments, there are a few obstacles that must be overcome in order to attain good data from *in situ* measurements. The biggest issue, in my opinion, is the insufficient adhesion of the Cu film onto the Si$_3$N$_4$ window. In addition, the difficulties regarding measuring and controlling small currents and potentials at a synchrotron facility, with its excess of interfering electric fields, must be resolved.
7. Acknowledgments

I would like to acknowledge a few people in a vaguely time-resolved fashion. Consequently, I’ll begin by thanking Joseph Nordgren for letting me become a Ph.D. student in your group. You proved to be quite the philanthropist that helped me out when I needed it.

Next, a huge THANKS to the most important person during my Ph.D. studies, who not only showed me how to do soft X-ray spectroscopy but also put up with my quirks: Laurent Duda. Thank you for calming me with your resonant voice when we, after 14 hours straight at the beamline, feared that we were illuminating two gratings and – it finally happened – we’d gone slightly mad... 😵

I would not have been working with such interesting samples if it wasn’t for Kristina Edström and Torbjörn Gustafsson and your extended network of chemists worldwide. Thanks for letting me pick your brain when it comes to structural chemistry and batteries. Also, thanks for putting up with my unconventional ideas on valence numbers.

My incredible liquid cell would not have been born without you, Calle Englund, although I still have not quite accepted your love of United States customary units.

During my time in the Soft X-ray group I’ve spent time at beamlines with several persons: Laurent, Johan F., Johan V., Paw, and Pete. Thank you for making these sojourns memorable. In hindsight you can’t even remember how tired you were at the time. Instead you tend to remember how incredibly huge the Eisbein, Schweinshaxe, and Sauerkraut servings are at this one restaurant in Berlin. Or how weird it is that you need to tell the cashier the number of your shopping cart every time at Kaufland.

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With people from the Soft X-ray group and, nowadays, from the new division Molecular and Condensed Matter Physics I’ve discussed physics, watched sports, shared rooms, been to lunch, had coffee and beer, rolled in
the snow after a sauna session, and been to small jazz clubs. Thank you everyone!

Lastly, in a greater context than physics and thesis writing, I would like to thank Malin for her patience and support during my synchrotron tours and thesis writing, and to Freya for accepting a lot of “not right now sweetie, I have to finish this book...”. I love you both.
8. Summary in Swedish

Redox reaktioner vid cykling av Li-jon batterier och i Cu korrosion studerat med mjukröntgenspektroskopi

Om man vill studera den materia vi har runt omkring oss, eller för den delen den materia vi själva är uppbygda av, så är spektroskopi en kraftfull metod. Spektroskopi är ett mycket vitt begrepp, men ofta när man säger spektroskopi menar man experimentella metoder där man uppdelar elektromagnetisk strålning (fotoner) i olika våglängder (energi) för att studera materia. Elektromagnetisk strålning inom energiområdet 50-1500 eV brukar man kalla för mjukröntgen. Denna strålning ligger i ett energiområde under hårdröntgenstrålning, vilket är den röntgen som t.ex. tandläkare använder sig av. Mjukröntgen däremot, kan inte färdas rakt genom tänderna utan absorberas lätt t.o.m. i luft. Detta medför att alla mjukröntgenexperiment måste utföras i vakuum. Efter energiuppdelningen har jag sorterat mina fotoner med hjälp av en spektrometer. Med denna kan man titta på hur energin fördelar sig hos de fotoner som kommer ut från det studerade materialet efter att man bestrålat det med röntgen. Man kan dessutom studera hur många av de inkommande fotonerna som absorberas i ett material vid olika inkommande fotonenenergi. Utifrån dessa experiment kan man dra intressanta slutsatser om elektronstrukturen hos undersökta material. Röntgenstrålning penetrerar långt in i atomerna och interagerar med ”core” elektronerna, d.v.s. de elektroner som finns i de innersta orbitalerna runt atomkärnorna. De elektroner som växelverkar med inkommande fotoner kommer att få extra energi som gör att de hoppar till en ledig orbital med högre energi. De innersta elektronbanorna är hårt bundna till atomkärnan och information som kommer från växelverkan med dessa kommer att vara unik för just det specifika atomslaget, eller riktiggare, för alla atomer av den sorten som befinner sig i en likvärdig omgivning. Detta är en av de avgörande fördelarna med just spektroskopi med röntgenstrålning: att man kan urskilja kemiska skift för ett specifikt atomslag. I min grupp vid Ångströmlaboratoriet utförs forskning och utveckling kring mjukröntgenspektrometrar och spektroskopiska metoder. Denna forskning är i sig fängslande, men blir än mer intressant om man får möjlighet till att undersöka något nytt material. Turligt nog är det aldrig svårt att hitta spännande projekt i Ångströmslaboratoriets tvärvetenskapliga miljö. Dessa projekt har i mitt fall oftast varit tillsammans med andra forskargrupper med material och frågeställningar väl lämpade för den spektroskopiteknik jag har arbetat
med. Mitt första samarbete var med en grupp experter inom avancerade Li-jon batterier vid Institutionen för Materialkemi. De har frågeställningar där mjukröntgenspektroskopisk information och bidra till ökad förståelse kring de komplicerade processer som sker i ett Li-jon batteri. I dess elektroder ska Li-joner kunna vandra in och ut i elektrodens struktur under batteriets laddning och urladdning. Med varje Li-jon kommer en elektron att rora sig på batteriets utsida om vi har en slutren krets (se figur 4.1). Dessa elektroner driver t.ex. en mobiltelefon eller laptop. När elektronerna kommer till elektroden på andra sidan i battericellen ska det materialet ta hand om de extra laddningarna som nu finns där. Detta påverkar laddningsfördelningen kring de ingående atomerna i elektrodmaterialet och det är denna process jag kan följa i mina experiment. Att förstå vilka atomslag som i vilken period under upp- respektive urladdning är mest aktiva kan hjälpa batteriforskarna att skräddarsy material för batterielektroder på bästa sätt. Mina resultaten har bl.a. visat att i elektrodmaterialet LiNi0₆Co0₂₅Mn0₁O₂ så är Co mer aktivt än man trott och O hjälper genom sin starkt hybridiserade karaktär till väsentligt i elektronupptagningsprocessen. För elektrodmaterialet Li₀₅Ni₀₂₅TiOPO₄ har mina resultaten visat att det inte, under den första urladdningen, är Ni och sen Ti som i tur och ordning ändrar oxidationstal, utan en kontinuerlig dynamisk växelverkan mellan Ni, Ti och O som avgör var elektronupptagenheten sker. De sista två elektrodmaterialer, som är nära besläktade, är LiMnPO₄ och LiMn₀₉Fe₀₁PO₄. Dessa, i vilka Mn torde stå för en ansenlig del av arbetet med att akkommodera laddningarna under litiering, upphittrade resultatet: Mn är i det närmaste inaktivt, vilket innebär att ett större ansvar läggs över på de övriga ingående atomslagen. Slutsatsen efter noggrann analys av all data, är att inte bara O tar över Mn atomens roll utan att även P är aktivt. Dessutom kan man ifrågasätta riktigheten i att anta att Li är envärt joniserat i elektrodmaterialet. Istället bör man överväga möjligheten att Li behåller kontakten med sin yttersta elektron och får ett oxidationstal någonstans mellan 0 och 1. Ett annat projekt initierades tillsammans med Svensk Kärnbränslehantering AB (SKB). SKB har som uppgift att designa ett slutlager för använt kärnbränsle och deras system för slutlager ska prövas enligt både kärntekniklagen och miljöbalken. Den 16 mars ska SKB lämna in ansökningarna till Strålsäkerhetsmyndigheten och Miljödomstolen och ju närmare detta datum har kommit desto omtycktar man debatten i media bli vit. Denna debatt handlar om korrosion av de kopparkapslar som är tänkta att vara barriär runt de använda bränsletavarna. Man kan till en början tro att vi redan vet allt vi behöver om kopparkorrosion. Men premisserna för korrosion av kapslarna är i detta fall speciella. Först och främst är slutlageret tänkt att placeras 500 m ner i det svenska urberget. Där är grundvattnet syrerik, d.v.s. det finns inget löst syre i vattnet, men det finns små mängder sulfid i det. Huruvida sulfid kan korrodera koppar är ganska enkelt att kontrollera: lägg bara ner en bit koppar i grundvatten från urberget och vänta och se. Problemet är bara att slutlageret skall vara säkert i 100 000 år. Så länge har ännu ingen haft tid att vänta för att
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