The Complex Nature of the Electrode/Electrolyte Interfaces in Li-ion Batteries

Towards Understanding the Role of Electrolytes and Additives Using Photoelectron Spectroscopy

KATARZYNA CIOSEK HÖGSTRÖM
The stability of electrode/electrolyte interfaces in Li-ion batteries is crucial to the performance, lifetime and safety of the entire battery system. In this work, interface processes have been studied in LiFePO$_4$/graphite Li-ion battery cells.

The first part has focused on improving photoelectron spectroscopy (PES) methodology for making post-mortem battery analyses. Exposure of cycled electrodes to air was shown to influence the surface chemistry of the graphite. A combination of synchrotron and in-house PES has facilitated non-destructive interface depth profiling from the outermost surfaces into the electrode bulk. A better understanding of the chemistry taking place at the anode and cathode interfaces has been achieved. The solid electrolyte interphase (SEI) on a graphite anode was found to be thicker and more inhomogeneous than films formed on cathodes. Dynamic changes in the SEI on cycling and accumulation of lithium close to the carbon surface have been observed.

Two electrolyte additives have also been studied: a film-forming additive propargyl methanesulfonate (PMS) and a flame retardant triphenyl phosphate (TPP). A detailed study was made at ambient and elevated temperature (21 and 60 °C) of interface aging for anodes and cathodes cycled with and without the PMS additive. PMS improved cell capacity retention at both temperatures. Higher SEI stability, relatively constant thickness and lower loss of cyclable lithium are suggested as the main reasons for better cell performance. PMS was also shown to influence the chemical composition on the cathode surface.

The TPP flame retardant was shown to be unsuitable for high power applications. Low TPP concentrations had only a minor impact on electrolyte flammability, while larger amounts led to a significant increase in cell polarization. TPP was also shown to influence the interface chemistry at both electrodes.

Although the additives studied here may not be the final solution for improved lifetime and safety of commercial batteries, increased understanding has been achieved of the degradation mechanisms in Li-ion cells. A better understanding of interface processes is of vital importance for the future development of safer and more reliable Li-ion batteries.

**Keywords:** Li-ion battery, LiFePO$_4$/graphite cell, interface, electrolyte additives, solid electrolyte interphase (SEI), photoelectron spectroscopy (PES), synchrotron

**Katarzyna Ciosek Högström, Department of Chemistry - Ångström, Structural Chemistry, Box 538, Uppsala University, SE-751 21 Uppsala, Sweden.**

© Katarzyna Ciosek Högström 2014

ISSN 1651-6214
ISBN 978-91-554-8890-1
urn:nbn:se:uu:diva-219336 (http://urn.kb.se/resolve?urn=urn:nbn:se:uu:diva-219336)
List of Papers

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

I  S. Malmgren, K. Ciosek, R. Lindblad, S. Plogmaker, J. Kühn, H. Rensmo, K. Edström, M. Hahlin
Consequences of air exposure on the lithiated graphite SEI.

II  K. Ciosek Högström, S. Malmgren, M. Hahlin, M. Gorgoi, L. Nyholm, H. Rensmo, K. Edström
The buried carbon/solid electrolyte interphase in Li-ion batteries studied by hard X-ray photoelectron spectroscopy.
*Submitted.*

III  S. Malmgren, K. Ciosek, M. Hahlin, T. Gustafsson, M. Gorgoi, H. Rensmo, K. Edström
Comparing anode and cathode electrode/electrolyte interface composition and morphology using soft and hard X-ray photoelectron spectroscopy.

The influence of PMS-additive on the electrode/electrolyte interfaces in LiFePO₄/graphite Li-ion batteries.

V  K. Ciosek Högström, M. Hahlin, S. Malmgren, H. Rensmo, K. Edström
Aging of electrode/electrolyte interfaces in LiFePO₄/graphite cells cycled with and without PMS additive.
*Submitted.*

Impact of the flame retardant additive triphenyl phosphate (TPP) on the performance of graphite/LiFePO₄ cells in high power applications.


Reprints were made with permission from the respective publishers. Paper I, III and VI were reproduced with permission from Elsevier while Paper VI with permission from American Chemical Society.

The following is a list of publications to which the author has contributed but which are not included in this thesis.

K. Ciosek, S. Killiches, T. Zavalis, M. Behm, P. Johansson, K. Edström, P. Jacobsson, G. Lindbergh

Energy storage activities in the Swedish Hybrid Vehicle Centre.


M. H. Kjell, S. Malmgren, K. Ciosek, M. Behm, K. Edström, G. Lindbergh

Comparing aging of MCMB graphite/LiFePO₄ cells at 22 °C and 55 °C. Electrochemical and photoelectron spectroscopy studies.


Non-uniform aging of cycled commercial LiFePO₄/graphite cylindrical cells revealed by post-mortem analysis.

*Journal of Power Sources* 257 (2014) 126-137.
Comments on my contributions to the papers:

I  I participated in planning, synchrotron PES measurements, analysis and writing.

II I participated in planning, all the experiments, analysis and writing. Responsible for finalizing the manuscript.

III I participated in planning, all the experiments, analysis and writing.

IV I planned and performed all the experiments and analysis. I wrote and finalized the manuscript.

V  I planned and performed all the experiments and analysis. I wrote and finalized the manuscript.

VI I participated in planning, performed and analyzed SEM, full-cell tests and interface characterization, wrote a major part of the paper. Responsible for finalizing the manuscript.
Contents

1. Introduction ........................................................................................................ 9

2. Li-ion batteries .................................................................................................. 10
   2.1 Principle and materials ............................................................................. 10
   2.2 Electrode/electrolyte interface ................................................................. 15
   2.4 Scope of the thesis ..................................................................................... 16

3. Experimental ..................................................................................................... 18
   3.1 Battery preparation .................................................................................... 18
   3.2 Electrochemical characterization ................................................................. 20
   3.3 Photoelectron spectroscopy (PES) .............................................................. 21
   3.4 Near edge X-ray absorption fine structure (NEXAFS) ................................ 24

4. Method development for electrode/electrolyte interface studies .................. 26
   4.1 Non-destructive depth profiling ................................................................. 26
   4.2 Quantitative information and SEI thickness estimation ............................. 28
   4.2 Experimental issues ................................................................................... 30
   4.3 Effect of air exposure on cycled Li-ion electrodes ...................................... 32
   4.4 Binding energy shifts as a function of cycling ........................................... 34

5. Comparing cathode and anode electrode/electrolyte interfaces ................. 36

6. Comparing electrode/electrolyte interfaces formed in standard electrolyte and with the PMS film-forming additive ......................................... 42
   6.1 Electrochemical studies ............................................................................. 42
   6.2 PES depth profile after three cycles ........................................................... 43
   6.3 LiFePO_4 interface - aging study at 21 and 60° C .................................... 46
   6.4 Graphite interface - aging study at 21 and 60 °C ..................................... 48

7. TPP flame retardant additive in the context of high power applications ....... 55

8. Conclusions ..................................................................................................... 59

9. Populärvetenskaplig sammanfattning ............................................................ 61

10. Acknowledgements ......................................................................................... 65

References .......................................................................................................... 68
### Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>ARXPS</td>
<td>Angle-resolved X-ray photoelectron spectroscopy</td>
</tr>
<tr>
<td>EC</td>
<td>Ethylene carbonate</td>
</tr>
<tr>
<td>DEC</td>
<td>Diethyl carbonate</td>
</tr>
<tr>
<td>DMC</td>
<td>Dimethyl carbonate</td>
</tr>
<tr>
<td>IMFP</td>
<td>Inelastic mean free path</td>
</tr>
<tr>
<td>HAXPES</td>
<td>Hard X-ray photoelectron spectroscopy</td>
</tr>
<tr>
<td>NEXAFS</td>
<td>Near edge X-Ray absorption fine structure</td>
</tr>
<tr>
<td>PES</td>
<td>Photoelectron spectroscopy</td>
</tr>
<tr>
<td>PMS</td>
<td>Propargyl methanesulfonate</td>
</tr>
<tr>
<td>SEI</td>
<td>Solid electrolyte interphase</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscope</td>
</tr>
<tr>
<td>TPP</td>
<td>Triphenyl phosphate</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
</tr>
</tbody>
</table>
1. Introduction

Population growth and vast technological development result in huge energy consumption. Over the last twenty years the global energy consumption increased by 52% and it is expected to increase further by 1.5 % per year until 2040 [1,2]. Fossil fuels, such as oil, coal and natural gas, account for 88% of the total worldwide energy consumption [1]. Those energy sources are not renewable; it takes millions of years for nature to produce them and reserves are being depleted at a much faster rate than new ones are being formed. Moreover, the production and combustion of fossil fuels raise environmental concerns; it leads to emission of carbon dioxide, nitrogen oxides, sulfur dioxide, volatile organic compounds and heavy metals. The increased greenhouse effect, acid rain and smog are some of the results.

All these concerns have led to an increased interest in more efficient use of energy and different measures to increase the share of renewable energy production, especially the share of electricity production. These issues have to be supported by technologies that can enable energy conversion and storage, e.g., batteries. Many renewable energy sources (e.g., solar, wind) produce intermittent power, which requires efficient electric energy storage in order to provide a reliable and stable energy supply. Within the transport sector, more efficient vehicles are needed to reduce the emissions of carbon dioxide. This is achieved by the development of hybrid vehicles, which give higher energy conversion efficiencies compared to internal combustion engine vehicles as well as less pollution in cities. Plug-in hybrids and pure electric vehicles could further decrease the dominating position of oil in the transportation sector. However, in order to successfully implement batteries in new applications, further technology development is necessary to ensure low cost, long life and safe systems.
2. Li-ion batteries

2.1 Principle and materials

There are many different energy storage technologies, and they can be classified into four main categories: electrical, mechanical, thermal and chemical [3]. In batteries, chemical energy is converted to electricity through redox reactions. Batteries are quiet, give no pollution during operation, are easily transported, can be recycled and usually have high energy efficiencies [3]. Secondary batteries also have the advantage of repeated use. Discharging and charging the battery is possible when the electrochemical reactions in the cell are reversible.

Lithium-based rechargeable batteries were first demonstrated in the 1970's [4,5]. In the following years, research was focused on developing various lithium insertion materials [6–10], but commercialization was delayed mainly due to difficulties related to metallic lithium negative electrodes that led to non-uniform lithium plating (dendrite formation) and therefore short circuiting and safety issues. In 1991, Sony Corporation commercialized the first Li-ion battery with LiCoO$_2$ as the positive electrode and soft carbon as the negative electrode [11]. Li-ion batteries revolutionized the consumer electronic products; they were originally used in mobile phones, but quickly spread to laptops, cameras and digital media players. They have many advantageous properties, better energy efficiency and higher energy and power densities than other existing rechargeable batteries, such as lead-acid, nickel-cadmium and nickel-metal hydride.

Li-ion batteries typically consist of two lithium insertion compounds as electrodes and an ionically conductive electrolyte. They are called rocking-chair batteries since Li$^+$ ions move, “rock”, between the electrodes. Figure 1 shows a schematic illustration of the processes taking place in a Li-ion battery when it provides electricity i.e., during discharge. Li$^+$ ions are released from the negative electrode (anode, oxidation reaction), pass across the electrolyte and intercalate into the positive electrode (cathode, reduction reaction) while electrons flow from the negative to the positive electrode through the external circuit. During charge the opposite processes take place. In electrochemistry an anode is an electrode at which oxidation takes place (negative electrode during discharge, positive electrode during charge), however
In the battery community, it usually refers to the negative electrode (discharge is the defining process).

\[
\begin{align*}
\text{Negative electrode:} & \quad Li_xC \leftrightarrow C + xLi^+ + xe^- \\
\text{Positive electrode:} & \quad Li_{1-x}FePO_4 + xLi^+ + xe^- \leftrightarrow LiFePO_4 \\
\text{Overall cell reaction:} & \quad Li_{1-x}FePO_4 + Li_xC \leftrightarrow LiFePO_4 + C
\end{align*}
\]

Figure 1. A schematic illustration of a Li-ion battery during discharge and cell reactions for graphite negative and LiFePO\textsubscript{4} positive electrodes.

There are many positive and negative electrode materials which can be used as lithium insertion compounds. Because of that, there are many different Li-ion chemistries, each with its specific power and energy characteristics. In the following part, various Li-ion battery materials will be briefly discussed.

LiCoO\textsubscript{2} was the first commercial cathode material and now, after over two decades, it is still the most often used cathode in Li-ion cells [8,12]. It is a layered cathode material with two-dimensional Li\textsuperscript{+} diffusion in the structure. It has a high potential ~3.9 V vs. Li\textsuperscript{+}/Li, however only ~0.5 Li\textsuperscript{+} per formula unit can be extracted which limits its practical capacity to about 140 mAh/g [13,14]. LiCoO\textsubscript{2} is expensive, contains toxic cobalt, and has safety problems due to its sensitivity to oxygen evolution [15]. Other commercial cathode materials include LiMn\textsubscript{2}O\textsubscript{4} (LMO) [9,10,16], LiNi\textsubscript{0.8}Co\textsubscript{0.15}Al\textsubscript{0.05}O\textsubscript{2} (NCA) [17,18], LiNi\textsubscript{1/3}Mn\textsubscript{1/3}Co\textsubscript{1/3}O\textsubscript{2} (NMC) [19] and LiFePO\textsubscript{4} (LFP) [20]. Their characteristics are presented in Table 1. The research on positive electrodes continues and mainly focuses on developing materials with higher potentials (e.g., LiNi\textsubscript{0.5}Mn\textsubscript{1.5}O\textsubscript{4} with 4.7 V vs. Li\textsuperscript{+}/Li [14,21]) and higher capacities (e.g., lithium-rich layered oxides [22,23] or compounds storing more than one Li\textsuperscript{+} per formula unit as in Li\textsubscript{2}FeSiO\textsubscript{4} [24,25] or Li\textsubscript{2}MnSiO\textsubscript{4} [25]).
The first commercial Li-ion cells utilized petroleum coke as the anode material. Several years later the most commonly used negative electrode was graphite and this has not changed until now [11,28]. Graphite is an intercalation material that is cheap, has a practical capacity of 350 mAh/g (theoretical: 372 mAh/g), low potential (0.1 V vs. Li+/Li), high electronic conductivity and the volume change is less than 10% during cycling. Li$_4$Ti$_5$O$_12$ is an alternative to graphite [29]. It is also an intercalation material, it is cheap, has great cycle life, good rate capability and thermal stability. However, Li$_4$Ti$_5$O$_12$ has a lower capacity (150-160 mAh/g) and high potential (1.55 V vs. Li+/Li) for lithium intercalation which leads to a lower cell voltage and thus the energy of the battery is lower. Materials that can alloy with lithium, e.g., Al, Sn, Sb, and Si, are also studied as anode materials [30]. Recently the main focus has been on Si since it has almost 10 times higher theoretical capacity than graphite. It suffers, however, from a large volume expansion effect and poor life-time when cycled in a battery [30,31]. In 2005 Sony introduced cells with nanostructured Sn-Co-C alloys. In order to buffer the volume expansion of Sn, nanosized intermetallic Co-Sn grains were dispersed in a carbon matrix [32]. Another group of materials investigated as negative electrodes are conversion materials [33,34]. Among the most studied compounds are CoO and Co$_3$O$_4$, which have been shown to reversibly form metallic Co and Li$_2$O on cycling [33–35].

Two main types of electrolytes are used in commercial Li-ion cells: gel and liquid electrolytes. Liquid electrolytes consist of a mixture of a lithium salt in organic solvents whereas gel electrolytes consist of a liquid electrolyte incorporated into a polymer matrix, e.g., poly(vinylidene fluoride-co-hexafluoropropene) (PVDF-HFP) [32]. Batteries with gel electrolytes are usually referred to as gel-polymer or polymer cells. Nowadays, liquid electrolytes are the most commonly used electrolytes in commercial Li-ion batteries. The most widely employed salt is LiPF$_6$. It has good conductivity and gives higher stability of the aluminum current collector used at the positive
It generates, however, hydrofluoric acid (HF) when exposed to a trace amount of moisture. Commercial electrolytes usually consist of at least three to five organic solvents in order to provide the best properties: high conductivity, broad temperature range and good cell performance. The main solvents used in Li-ion cells are organic carbonates, e.g., ethylene carbonate (EC), diethyl carbonate (DEC), dimethyl carbonate (DMC) and ethyl methyl carbonate (EMC). They give the best properties, however they are also volatile and highly flammable which leads to safety issues. The commonly used electrolytes are not thermodynamically stable at the operation voltages of a Li-ion battery. They get reduced and form a passivation film on the negative electrode, termed the solid electrolyte interphase (SEI). SEI formation and processes taking place at the electrode/electrolyte interface will be further discussed in the following chapters.

Small amounts of chemicals, called additives or functional electrolytes are added to the electrolyte to add extra functionality and improve the properties of a Li-ion battery. Depending on their different functions additives can be divided into the following categories:

- Anode passivation film-forming agents – decompose on the anode surface forming an insoluble product and therefore facilitate the formation of the SEI. They usually have higher reduction potentials vs. Li+/Li than electrolyte solvents.
- Flame retardants – used in order to decrease the flammability of an electrolyte.
- Anion receptors – prevent unwanted side reactions by the formation of complexes with the anions, thereby inhibiting their reaction during cycling.
- Redox shuttles – provide an intrinsic overcharge protection by carrying the current in the cell. They are reversibly oxidized/reduced slightly above the normal cell operation voltage and below the electrolyte decomposition voltage.
- Shutdown additives – provide an intrinsic overcharge protection. There are two different types: the first one releases gas which activates a current interrupter device, the second one undergoes polymerization, thereby blocking the ion transport in the electrolyte. Both processes are irreversible and terminate the life of a battery.
- Cathode protection additives – are capable of scavenging water and/or acids in order to decrease the dissolution of the active cathode material.
- Others, e.g., wetting agents, aluminum corrosion inhibitors, ionic solvation enhancers etc.

In this work the focus is on studying how the common electrode materials graphite and LiFePO₄ are influenced by using film-forming additives and flame retardants. The latter are used to improve the long-term stability of the
SEI and therefore Li-ion battery lifetime. Already in the 90’s gaseous products, such as CO$_2$ [44–46], N$_2$O [44] and SO$_2$ [47,48] were shown to form inorganic SEI layers and improve the electrochemical performance of the battery. Later, a lot of interest was concentrated on studying monomers with one or more carbon-carbon double bond which polymerize on the anode surface, e.g., vinylene carbonate (VC) [49–52], vinyl ethylene carbonate [53,54] and vinyl acetate [55,56]. Currently, VC is the most popular anode passivation agent and it is the most used additive in commercial cells. Recently, a new promising additive, propargyl methanesulfonate (PMS) (Figure 2a), has been introduced [57,58]. It improves the cyclability of a LiCoO$_2$/graphite cell and prevents graphite exfoliation in propylene carbonate (PC) based electrolytes [57]. The performance of this additive will be further discussed in Chapter 6.

Flame retardant additives are used to improve the safety of Li-ion cells by decreasing the electrolyte flammability. One of the first investigated flame retardants was trimethyl phosphate [59,60]. It suppresses the flammability of the electrolyte, however it is not stable during cycling and decomposes on the anode surface leading to capacity fading [59–61]. Phosphates with longer or partially fluorinated alkyl groups, as well as phosphates with aryl groups were shown to be more effective flame retardants with better electrochemical stability at low potentials [62–65]. An example of an alkyl phosphate in which the alkyl groups have been replaced with phenyl substituents is triphenyl phosphate (TPP) (Figure 2b) [64]. It was shown to be a promising flame retardant, which lowers the flammability without significantly affecting cell performance for TPP concentrations up to 10-20 wt% [64,66–69]. The performance of this additive will be further discussed in Chapter 7.

![Figure 2. The chemical structures of the PMS film-forming additive (a) and the TPP flame retardant (b).](image)

In commercial cells a combination of many additives is used. Synergy effects between additives have been studied [58,70]; however because of direct commercial interests most of the research on functional electrolytes has never been published. It is well known that the usage of many additives leads to a trade-off between the effectiveness of an additive and cell performance and in commercial cells only small amounts of additives are used (usually up to 5 wt%) [71].
2.2 Electrode/electrolyte interface

A Li-ion battery operates at voltages that are outside the electrochemical stability window of the electrolyte components. During the first charge electrolyte is reduced. It usually decomposes below 0.8 V vs. Li+/Li. Electrolyte reduction products deposit at the negative electrode/electrolyte interface and form a layer called SEI [40,72]. The electrolyte reduction leads to irreversible consumption of Li\(^+\) ions which leads to an irreversible capacity loss for the whole battery. Ideally, the SEI is an electronic insulator, preventing further electrolyte reduction but at the same time it is an ionic conductor, which enables Li\(^+\) to pass through during cycling. The SEI should also protect the electrode from solvent intercalation which for some solvents (e.g., propylene carbonate) causes exfoliation of graphite [73].

The SEI has been extensively studied for more than 30 years; however the processes taking place at the electrode/electrolyte interface are still not fully understood. This is mainly due to the complexity of the system (thin multi-component layer), limited amount of analysis techniques that can be used to detect the chemical components of the layer, and the sensitive nature of the SEI [74]. Solvent and salt reaction schemes leading to SEI formation will be discussed in detail in Chapter 5, whereas several models which have been proposed to explain the complex nature of the SEI will be described below.

Besenhard et al. suggested that electrolyte decomposition products penetrate into the bulk electrode material and remain between the graphite sheets [73], Zaban et al. proposed a multilayer structure of SEI with an inner, compact part composed of several layers and outer, porous part [75]. Peled et al. described a mosaic-type SEI with inorganic microphases in the inner SEI and organic phases in the outer part [76] and Ein-Eli suggested that passive films mimic a double-layer capacitor as the electropositive sites of the electrolyte decomposition products are aligned to the negatively charged graphite anode [77]. Recent models suggest that the SEI consists of an inorganic matrix in the inner part and a porous organic layer in the outer part [74,78]. LiF crystals were also found in the SEI [74,78]. In the earlier studies the thickness of the SEI was suggested to be in the order of few nm [40,79], but more recent publications indicate the formation of a thicker SEI, in the order of a few tens of nm [80,81].

The complex nature of the SEI is further complicated by the fact that it undergoes conversion, stabilization, dissolution/cracking and growth during the entire battery life [82]. It has been shown that different interface processes take place at different electrode potentials [83,84] and that the SEI becomes thicker upon cycling [85]. Furthermore, the SEI is not stable at elevated temperatures [78,86,87] and at low temperatures metallic lithium plating
might take place on the graphite [88,89]. The above issues clearly show that besides being partly responsible for the irreversible loss of capacity, the SEI has a huge impact on the cyclability, rate capability and thermal stability of the whole Li-ion battery [72,90,91]. Moreover, processes taking place at the negative electrode/electrolyte interface are considered as one of the major sources of Li-ion battery aging [82].

The issues described above concern mainly the negative electrode/electrolyte interface. On the positive electrode other processes take place due to the different cathode potentials and different electrode materials. An interface layer will always form on all cathodes cycled in liquid electrolytes; however the main processes are often different for different materials [92]. The most commonly discussed mechanism for positive electrode film formation is electrolyte oxidation. It was shown that the onset potential for oxidation of commonly used electrolytes on various metal electrodes is below 4 V vs. Li+/Li [93,94]. It is important to mention that higher surface catalytic activity could decrease the oxidation potential; other sources claim, however, that the reactions might be inhibited by composite cathodes [95,96]. Acid–base interactions between the cathode material and trace impurities have been shown to cause transition metal dissolution from the active material (e.g., Fe and Mn), other interface processes could involve, e.g., nucleophilic attack of the electrophilic solvent on the transition metal oxide or electrolyte polymerization [92,96].

2.4 Scope of the thesis

This work is focused on how the interface processes involving the electrodes and the electrolyte in LiFePO4/graphite full cells develop during Li-ion battery cycling under different conditions. The electrode materials were selected as baseline chemistry within the Swedish Hybrid Vehicle Centre. The important motivation for the chosen electrode materials is that they are non-toxic, have good safety characteristics and are composed of abundant/inexpensive elements, making them a good choice for automotive applications.

The aim of the research has been two-fold: fundamental research in order to understand, develop and improve a technology for more detailed and consistent studies of the processes taking place at interfaces and applied research where potentially useful materials were studied in Li-ion batteries with this improved technology.

The detailed aim of my study was therefore to combine synchrotron and in-house photoelectron spectroscopy and to perform a unique non-destructive
depth profiling through the electrode/electrolyte interfaces into the bulk materials as a means to better understand the cell system. A more extended goal of this work was to study the influence of electrolyte additives and to improve the understanding of aging processes at interfaces in Li-ion batteries as a function of cycling.
3. Experimental

3.1 Battery preparation

In the present work LiFePO₄/graphite full cells have been studied. In Papers I-V, the LiFePO₄ cathode consisted of 75 wt% hydrothermally synthesized carbon-coated LiFePO₄, 10 wt% conductive carbon black (Super P, Erachem Comilog N. V.) and 15 wt% Kynar binder (vinylidene fluoride trifluoroethylene co-polymer, Arkema). The graphite anode consisted of 85 wt% potato-shaped graphite (Toyo Tanso), 3 wt% KS6 graphite (Timcal), 2 wt% conductive carbon black (Super P, Erachem Comilog N. V.) and 10 wt% Kynar binder. Electrode components were mixed in N-methyl-2pyrrolidone (NMP) solvent, ball-milled and casted on aluminum (cathode) or copper (anode) foils using a Hosen pilot-line, which allowed for good control of the coating thickness. In Paper VI LiFePO₄ and graphite electrode materials were supplied by Quallion LLC.

A high resolution scanning electron microscope (SEM, Zeiss LEO 1550) was used to characterize the structure of all studied electrode materials (Figure 3). Both LiFePO₄ electrodes have a relatively uniform distribution of particles, with particle sizes around 200 nm. Both graphite electrodes have bigger dispersion of particle size, which ranges from few hundred nm to few-tens of μm.

The standard electrolyte used in Papers I-V was 1M LiPF₆ (Ferro) in EC:DEC (Novolyte technologies) in a 2:1 volume ratio. In Papers IV and V an electrolyte, hereafter called PMS, was prepared by adding 1 wt% of the film-forming additive PMS to the standard electrolyte. In Paper VI 1 M LiPF₆ in EC:DEC in a 1:1 weight ratio (LP40, BASF, battery grade) was used. To the electrolyte different amounts of TPP (≥99%, Sigma-Aldrich) flame-retardant additive were added. In total six electrolytes with 0-15 wt% TPP were studied.

Circular electrodes were cut out, moved to an argon-filled glove-box (≤1 ppm H₂O, ≤1 ppm O), and dried for at least five hours in a vacuum oven. Graphite/LiFePO₄ pouch cells (vacuum sealed polymer-coated aluminum bags, Figure 4) were assembled in the glove-box. The electrodes were assembled with 16–20 % overcapacity for the graphite electrode.
Figure 3. SEM images of LiFePO$_4$ cathodes (left) and graphite anodes (right) prepared by me (top) and supplied by Quallion LLC (bottom).

Figure 4. Graphite/LiFePO$_4$ pouch cell.
3.2 Electrochemical characterization

The standard electrochemical test used in Papers I-VI was galvanostatic cycling, also called chronopotentiometry [97]. A constant current is applied between the electrodes and the potential is measured as a function of time (Figure 5a). When the cut-off potential is reached, the current is reversed. The discharge/charge current is expressed as a C-rate, in order to normalize with respect to the battery capacity. A 1C rate means that the discharge current will discharge the battery in 1 hour. A C/10 rate corresponds to full discharge in 10 hours and 5C in 12 minutes. Galvanostatic cycling was generally performed at a C/10 rate. The capacity retention ($C_{-ret}$) in Paper V was calculated from:

$$C_{ret} = \frac{C_{dis}}{C_{1dis}} \cdot 100\% \quad (3.1)$$

where $C_{dis}$ corresponds to the discharge capacity and $C_{1dis}$ to the discharge capacity in the first cycle.

![Figure 5. Schematic summary of electrochemical tests used in this work a) galvanostatic cycling and b) EUCAR test.](image)

In Paper VI a EUCAR Hybrid Pulse Power Characterization (HPPC) test cycle was used [98]. It is a 120 s cycle with +/- 5% difference in state-of-charge and a maximum C-rate 10C (Figure 5b). The EUCAR cycle was used to get insight into the high power performance of the cells. In Papers V and VI the differential capacity during the first charge was calculated in order to track the reduction potentials during the SEI formation. Electrochemical characterization was performed using Digatron BTS-600 galvanostat, Arbin BT2043 and VMP2 potentiostats/galvanostats. The cell voltage discussed in this work refers to that for a LiFePO$_4$/graphite cell.
3.3 Photoelectron spectroscopy (PES)

Photoelectron spectroscopy (PES), also called X-ray photoelectron spectroscopy (XPS) or electron spectroscopy for chemical analysis (ESCA), is one of the most widely used surface characterization techniques [99–101]. PES is based on the photoelectric effect [102]: a sample is irradiated with X-ray photons with well-defined energy ($h\nu$), the material absorbs the photon and emits a photoelectron (Figure 6a). The kinetic energy of the emitted photoelectrons (KE) is measured by an analyzer and the binding energy of the electrons (BE) vs. the Fermi level is calculated from:

$$BE = h\nu - KE - \phi$$

(3.2)

where $\phi$ is a spectrometer work function.

![Figure 6. A schematic representation of the PES process: (a) the material absorbs the photon and emits a photoelectron, (b) the relation between the analysis depth $z$ and photoelectron travel distance in the material $z\sin\theta$.](image)

The general core level electronic structure is unique for the different elements and PES can provide identification of all elements. The binding energies are characteristic for specific electron orbitals in specific atoms and PES spectra (Figure 7) are named using the atomic shell from which the electrons are ejected (e.g., C1s, P2p, O1s). Variations in the binding energy of a specific core level are often referred to as chemical shifts. The chemical shift provides information about the chemical state of the material; it is therefore an important tool for identifying compounds with different chemical environments. The binding energy of an emitted photoelectron is the energy difference between final and initial state of the system. The chemical shift can thus be expressed as the difference between the initial and the final state for one system relative to another. The initial state effect include changes in binding energy due to differences in the system prior to the photoemission process, e.g., due to the formation of chemical bonds. In a simplified model the more electronegative neighbor atoms draw electrons away, which give a more positively charged atom and therefore an increase in the binding ener-
The final state effects include changes in binding energy that arise from processes in the systems taking place after photoemission, e.g., electron relaxation. After the photoemission, the excited system relaxes by e.g., emission of Auger electron or X-ray fluorescence. Auger electrons may be observed in photoelectron spectra (Figure 7). For some materials, interaction between the photoelectron and other electrons leads to energy losses in the photoemission process and formation of plasmons or shake-ups that can be observed in the spectrum. Spin-orbit splitting is also observed in the spectra and it may be considered as a final state effect, which appears for all core levels besides s-subshells. It arises from a magnetic interaction between spin of the electron (up or down) and its orbital angular momentum.

A typical XPS spectrum (Figure 7) is plotted as the number of elastically emitted electrons that reach the detector as a function of binding energy. For flat, homogenous samples the number of detected electrons ($A_j$) is proportional to the concentration of the emitting atom in the sample ($C_j$), the probability of emission from a specific core level, i.e., cross section ($\sigma_j$) and the spectrometer transmission ($T_j$). Another important factor is signal attenuation. The probing depth of the measurement is limited by the distance that emitted electrons can travel in a material without being inelastically scattered, i.e., losing energy. The above factors give the following relationship for the total intensity:

$$A_j \propto C_j \sigma_j T_j \int_0^\infty e^{-z/\left(\lambda sin\theta\right)} \, dz$$  

(3.3)

where $\theta$ is the take-off angle, $z$ is the probing depth (Figure 6b) and $\lambda$ is the inelastic mean free path (IMFP), an average travel distance in a material of...
an elastically emitted photoelectron. The IMFP depends on the material and on the kinetic energy of the photoelectron. Figure 8 shows a graph of the probability that a photoelectron is emitted to vacuum without being inelastically scattered as a function of depth. For $\theta=90^\circ$ $1\lambda$ corresponds to 63% of elastically emitted electrons, $2\lambda$ to 86% and $3\lambda$ to 95% [101,103]. The probing depth is often defined as $3\lambda$. For the in-house XPS instrument, $\lambda$ corresponds to a few nm. In this work polyethylene IMFP values were used [104].

![Figure 8](image)

**Figure 8.** Schematic picture of the probability that a photoelectron is emitted to vacuum without being inelastically scattered as a function of photoelectron travel distance in material.

PES depth profiling is a well-known technique for studying multilayered, heterogeneous surface layers. In order to obtain a depth profile, several measurements with information about different sample depths have to be performed. It can be achieved by three different approaches. In the first method, a depth profile from the surface deep into the material can be obtained by ion etching. Ions (usually noble gases, e.g., argon) bombard the surface, knock off the surface atoms and etch the top layer. Due to different sputtering rates for different compounds it can be difficult to interpret these depth profiles. Moreover, sputtering is a destructive method and leads to damaging of the surface layer and decomposition of interface compounds [101]. A second depth profiling method is angle-resolved X-ray photoelectron spectroscopy (ARXPS). By changing the angle between the surface plane and analyzer ($\theta$ in Figure 6b) the distance that the electron will have to travel in a material ($z/\sin\theta$) varies, resulting in a different analyzing depth ($z$). This method is non-destructive, however it requires a flat surface. The third depth profiling method is based on changing the excitation energy. By increasing the excitation energy the kinetic energy of emitted photoelectrons
and their IMFP increase. This increases the probing depth and a larger yield of emitted photoelectrons comes from the deeper part of the sample. This is a non-destructive method; however it has to be performed at a synchrotron, as the classical in-house XPS instruments usually has one monochromatic X-ray source (Al or Mg anode). At synchrotron facilities the radiation can range from the far infrared to the hard X-ray region, which gives the freedom to choose different excitation energies and therefore change the analyzing depth of PES measurement. The synchrotron-based depth profiling method will be presented in Chapter 4.

PES is the main characterization technique used in this study; it was used in all the papers in order to study changes in the LiFePO₄ and graphite interfaces. PES spectra were fitted using Shirley background and a 70% Gaussian and 30% Lorentzian mix for the Voigt peak shapes. The carbon active material C1s peak, referred to as LiₓC, was an exception; in that case an asymmetric peak shape was used [105]. More details about experimental settings and development of the methodology for studying Li-ion battery electrode/electrolyte interfaces are presented in Chapter 4.

3.4 Near edge X-ray absorption fine structure (NEXAFS)

At synchrotron facilities the possibility of varying the photon energy opens up for the use of other spectroscopic techniques, e.g., NEXAFS. In NEXAFS, the photon energy is scanned and when it matches the energy difference between the ground state and the state where a core level electron is excited to an unoccupied state, the absorption can occur (Figure 9). The absorption process creates a core hole. The core hole is filled by an electron from a higher energy level and the excess energy can be released in two different processes [106]:
- radiatively, by emission of fluorescence. This process may be referred to as bulk sensitive, as it originates from several tens of μm from the surface.
- non-radiatively, by emission of Auger electrons. This process is more surface sensitive and originates from processes within about 10 nm from the surface.

The yield of both processes is directly proportional to the absorption probability, therefore NEXAFS spectra can be obtained by measuring either fluorescence or Auger electrons as a function of photon energy. NEXAFS provides information about the electronic structure; it is element specific and sensitive to the bonding environment of the absorbing atom. For flat samples it can also provide information about orientation of molecules. The method can be used as a fingerprint method for a chemical compound by comparing
the spectrum of the sample of interest to that of reference molecules or materials. Detailed NEXAFS information about the electronic structure of the absorbing atom and geometrical arrangement of its neighbors require complex theoretical calculations. NEXAFS can be used as a complimentary tool to the PES technique, its advantage being the higher sensitivity towards changes in chemical environment of an atom [106].

Figure 9. Schematic picture of the processes taking place during NEXAFS.
4. Method development for electrode/electrolyte interface studies

PES is a powerful technique for studying surface layers, however the electrode/electrolyte interface formed in Li-ion batteries is very complex and special experimental considerations are hence required. A number of issues have to be taken into consideration when performing PES analysis of Li-ion batteries, some of them include: decision on washing or not washing off the residual electrolyte from the sample, radiation damage effects, safe opening and transfer of samples to avoid exposure to air, appropriate choice of excitation energy in order to avoid overlaps with other spectral features, etc. Moreover, the binding energy calibration of photoemission spectra is more complex for Li-ion battery electrodes than for many other samples and some of the binding energy shifts in spectra of cycled electrodes are not completely understood. Below a new approach for non-destructive depth profiling of Li-ion interfaces is briefly introduced and a new method for estimating the SEI thickness on graphite electrodes is presented. Papers I-III describe these issues in more detail.

4.1 Non-destructive depth profiling

Depth profiling of Li-ion battery interfaces has so far mainly been obtained by argon etching. Previous studies and our recent measurements indicate that sputtering is a too destructive method for studying electrode/electrolyte interfaces in Li-ion batteries, as it leads to decomposition of surface species [107]. Neither ARXPS can be used for depth profiling, as the electrode and its interface is not flat enough, and such measurements will therefore not provide satisfactory information. Part of this work was focused on development of non-destructive PES depth profiling using different excitation energies by combining synchrotron and in-house XPS measurements. Figure 10 shows the schematic picture of PES measurements performed in this work. By increasing the excitation energy, the kinetic energy of photoelectron and therefore the IMFP will increase. The following measurements were performed in this study:
• Soft X-ray PES. The most surface sensitive measurements were performed at the I411 beamline at MAX IV Laboratory (Lund, Sweden) [108]. A special focus was on performing measurements with very similar probing depths; the kinetic energy of emitted electrons was therefore kept constant. (~145/590 eV). The resulting excitation energies were: 430/880 eV for C1s, 280/730 eV for P2p, 680/1130 eV for O1s, 835/1280 eV for F1s and 325/770 eV for S2p.

• In-house XPS. More bulk sensitive measurements were performed on a PHI 5500 system with monochromatized 1486.6 eV Al Kα radiation.

• Hard X-ray PES (HAXPES). The most bulk sensitive measurements were performed at the HIKE system (Figure 11), KMC-1 beamline at the BESSY II synchrotron (HZB, Berlin, Germany) [109]. Two excitation energies were chosen: 2300 eV - first order radiation monochromatized by Si (111) and 6900 eV first order radiation monochromatized by Si (422).

---

Figure 10. Schematic representation of PES measurements performed in this study.

Figure 11. The HIKE experimental end-station at the KMC1 beamline in BESSY II synchrotron showing the sample transfer system (a), the analysis chamber (b) and the beamline with incident radiation (c).
Figure 12 shows an example of a C1s depth profile for graphite. Excitation energies in a range from 280 eV to 6900 eV were used, and the probing depth was thus varied in the 2 to 47 nm range. The C1s spectra show only SEI surface compounds for low probing depths and by increasing the probing depth a larger contribution of the carbon active material, Li\textsubscript{x}C, is detected. However, due to signal attenuation, the signal decreases exponentially with depth (Equation 3.3, Figure 8), and therefore the thin surface layer dominates the spectra, even for the measurement with the highest probing depth.

![Figure 12. Schematic representation of a non-destructive depth profile for a lithiated graphite anode. Reprinted with permission from [Paper IV]. Copyright 2013 American Chemical Society.](image)

4.2 Quantitative information and SEI thickness estimation

PES can also be used to obtain quantitative information about all elements except H and He. The relative intensities/amounts of elements (I) can be determined from the photoelectron peak areas (A) corrected by cross section (σ) which describes probability of emission from a specific core level:

\[
I_j(\%) = \frac{A_j/\sigma_j}{\sum_i A_i/\sigma_i} \cdot 100\% \quad (4.1)
\]

In the present work Scofield theoretical photoionization cross section values were used [110]. For the LiFePO\textsubscript{4} cathode, the relative intensity was calculated excluding iron and lithium contributions due to peak overlaps: Fe3p with Li1s and Fe2p with a fluorine plasmon. The PES spectra in this work
are presented with normalized intensity or relative intensity on the y-axis and binding energy on the x-axis. In the former case the spectra are normalized by the area of the respective core level signal, in the latter using the obtained relative intensity \( I_j \) of that element in the sample.

To study the changes at the negative electrode/electrolyte interface a new model was implemented to estimate the SEI thickness. The model is based on the approximation that below the depth \( d \), which corresponds to SEI thickness, the anode consists of carbon active material \((\text{Li}_x\text{C})\) only (Figure 13). By combining Equations 3.3 and 4.1 and taking into account that the concentration \((C)\) varies with probing depth, the SEI thickness was estimated from:

\[
I_{\text{Li}_x\text{C}}(\%) = \frac{I_{\text{Li}_x\text{C}}}{I_{\text{Li}_x\text{C}} + I_{\text{SEI}}} = \frac{\int_{d}^{\infty} C_{\text{Li}_x\text{C}} e^{-\frac{z}{\lambda \sin \theta}} dz}{\int_{d}^{\infty} C_{\text{Li}_x\text{C}} e^{-\frac{z}{\lambda \sin \theta}} dz + \sum_{i} \int_{0}^{d} C_{i} e^{-\frac{z}{\lambda \sin \theta}} dz} = e^{-\frac{d}{\lambda \sin \theta}}
\]

\[
d = -\lambda \sin \theta \ln[I_{\text{Li}_x\text{C}}(\%)]
\]

\[\text{(4.2)}\]

\[\text{(4.3)}\]

Figure 13. Schematic picture of a model used to estimate SEI thickness.

The thickness calculations were based on the relative intensity of the carbon active material peak in the C1s 2300 eV spectrum. This energy was chosen as the graphite signal is clearly detectable and all core levels were measured, which enabled quantitative calculations. The thickness calculations were used to give approximate values in order to compare the relative thicknesses in the different cases.
4.2 Experimental issues

Most of the electrode/electrolyte interface studies were performed on electrodes washed with a solvent, usually DMC, to remove electrolyte residues from the electrode surface. Previous studies suggested that some SEI components are being dissolved when the electrode is washed with DMC and that different SEI components have different solubilities in DMC [111,112]. Despite this, the solubility issue is seldom taken into consideration during post-mortem interface studies. In this work the main focus was on unwashed samples. The pressure in the spectrometer (<10^{-7} mbar) is at least five orders of magnitude larger than the vapor pressure of solvents, EC and DEC [113,114], therefore a majority of these compounds should be removed prior to PES measurement. In a few of the presented studies (Papers I, IV, VI) both washed and unwashed samples were studied in order to get a broader and more detailed picture of interface processes. This was done in order to keep the advantages of both treatments: unwashed samples guarantee that no SEI components are washed off, while washed samples give a useful comparison and guarantee that not only the electrolyte components are being analyzed.

Another experimental aspect concerns the sensitivity of Li-ion batteries to moisture. For example, the LiPF₆ salt forms toxic, highly reactive HF gas upon reaction with water [38,39]. HF could further react with SEI components [115]. Lithium alkyl carbonates are some of the reduction products found in the interface which also decompose in the presence of moisture [95]. The effect of air exposure on cycled graphite electrodes will be further discussed in the next section. In order to avoid electrode contact with air, all the cells were opened in an argon-filled glove-box (≤1 ppm H₂O, ≤1 ppm O) and a special transfer system was built (Paper I) to assure safe transfer of samples from the glove box to the PES instruments. The transfer system is a portable unit (see Figure 14c-g), which easily can be attached to different spectrometers or to a glove-box using a special adapter (Figure 14 a). In order to make the system more versatile, different sample magazines (Figure 14 c and d) can be mounted on a magnetic rod.

Detailed interface studies on cycled electrodes showed that samples are sensitive to radiation during PES measurement. Figure 15 shows that a significant increase of LiF is detected on samples exposed to radiation for longer time. The X-ray induced variations limit the measurement time. Therefore a lot of care was taken to avoid radiation damage by following the development of the spectra with time. Other measures were also taken in order to avoid irradiation related changes: the counts optimization was not performed on the sample, the intensity of radiation was reduced and the spectrometer resolution was adjusted to be only slightly lower than that of the natural peak.
width. Moreover, during soft X-ray PES measurements the slit through which the X-rays were passing was reduced to less than 1 μm and during HAXPES measurements a 25 μm Be filter was used in order to reduce irradiation related damage.

Figure 14. Portable transfer system used in this study. The adapter (a) can be plugged into the glove-box and sealed by a flange (b) or attached to the portable unit (c-g). Reprinted from [Paper I], with permission from Elsevier.

Figure 15. Effect of radiation damage on the graphite F1s spectra. Fresh sample (top), sample after 5 (middle) and 25 (bottom) minutes of exposure to radiation.
With the intention of minimizing the external effects on the samples, the measurements were started very quickly, just after opening the cells and transporting them to the spectrometer. Moreover, the electrodes were transferred to the spectrometer individually. In order to get reproducible data electrodes were measured in a standardized way.

4.3 Effect of air exposure on cycled Li-ion electrodes

Even though it is commonly known that Li-ion batteries are sensitive to moisture, many published post-mortem studies have been performed after exposure of electrodes to air. In Paper I the focus was on understanding the effects of air exposure of cycled graphite anodes. All the spectra supporting the mechanisms described in this section are depicted in Paper I. Four different sample pre-treatments were selected for this study. These are schematically shown in Figure 16. The sample names represent the subsequent steps of treatment prior to the PES measurement: u—unwashed, w—washed, A—exposed to air, V—exposed to vacuum. One electrode was cut into four pieces. Performing different pre-treatments on one electrode guaranteed the same starting material. Two pieces were washed with DMC in order to remove electrolyte residues and two pieces remained unwashed. One washed and one unwashed sample was transferred to a spectrometer (which requires insertion into vacuum), the reference samples uREF (unwashed reference) and wREF (washed reference) were measured. The procedure was followed by a four-minute air exposure, insertion into UHV analysis chamber and PES measurement (uVAV, wVAV). The remaining two samples (one washed, one unwashed) were directly exposed to air for the same time (the exposure took place before insertion into vacuum), and subsequently inserted into the UHV analysis chamber and measured with PES (samples uAV, wAV).

All samples exposed to air displayed lower amounts of carbon active material, which indicate that a thicker surface layer was formed upon air exposure. The relative amount of oxygen also increased for all the air exposed samples. In order to understand these changes two different mechanisms were suggested. For an unwashed sample exposed to air prior to vacuum treatment (uAV), the solvent has not evaporated. It could react upon exposure and form less volatile carbonates and ether-containing compounds. For the rest of the samples (uVAV, wAV, wVAV) volatile solvents were removed during vacuum treatment, therefore a different mechanism was suggested in this case. On all the latter samples a new compound, lithium hydroxide (LiOH), has been observed in the deeper parts of the SEI. It could be formed by delithiation of the lithiated carbon active material upon reaction with water. The results also suggest that decomposition of LiPF₆ salt or its products could
Figure 16. Schematic representation of the air exposure study. The sample names represent the subsequent steps of treatment prior to the PES measurement: u—unwashed, w—washed, A—exposed to air, V—exposed to vacuum. Reprinted from [Paper I], with permission from Elsevier.
take place, however this is not a dominating effect of the air exposure. This study shows how important it is to maintain a proper handling of electrodes for post-mortem analysis and that even a short exposure to air could have a detrimental effects on the studied cells and lead to misinterpretations of the surface composition.

4.4 Binding energy shifts as a function of cycling

Proper binding energy calibration is crucial in order to correctly interpret PES spectra. For poor electrical conductors, a positive charge may build up on the sample because the emission of photoelectrons is not fully compensated. This process can result in shifts of the binding energy and/or asymmetric peak shapes. This could partially be compensated by a low energy electron flood gun; however this does not completely solve the problem for the binding energy calibration and it could also be destructive for sensitive surface compounds. Even for samples that are not charged, the energy alignment of the non-conductive materials will have important consequences for the energy calibration. For cycled graphite electrodes, the conductive carbon active material can align with the Fermi level, while the SEI may align with the vacuum level. Therefore, an internal reference was used in this work; the hydrocarbon feature was set to 284.4 eV and all core levels were shifted accordingly. Paper II further describes the importance of energy calibration and binding energy shifts in the carbon active material as a function of cycling.

Figure 17 shows C1s spectra for a graphite electrode cycled in a standard electrolyte and stopped at different potentials during the first and the third cycle. Interestingly, the binding energy of the carbon active material, Li,C, shifts upon cycling. This binding energy shift can be attributed to two different processes: a chemical shift due to charge transfer in carbon during lithium intercalation and changes in the work function. The latter could be attributed to a potential drop across the carbon active material/SEI dipole layer. The following shifts are observed in the first cycle: at 3.0 V, prior to the first lithium inserted in the carbon active material, the Li,C feature is located at 283.2 eV and it shifts to 282.1 eV at 3.3 V, after the first graphite lithiation plateau. It shows that lithium insertion between 3.0 and 3.3 V leads to a significant binding energy shift (-1.1 eV) of the carbon active material feature relative to the SEI peaks. Previous studies have shown that due to the filling of the π-bands in the graphite upon lithiation, a binding energy shift (0.8 eV) towards higher values relative to the Fermi level takes place [116,117]. At the same time a decrease of the work function occurs (-1.6 eV), which results in a decrease of the binding energy (-0.8 eV) vs. the vacuum level. The internal reference calibration used in our study can to a first
approximation be considered as a vacuum level calibration, therefore the binding energy shift observed here is in agreement with previous studies [117]. The magnitude of the shift observed in our samples is slightly larger, which could indicate a combination of chemical shift and Fermi level changes. The carbon active material, Li$_x$C, shifts further by 0.1 eV to 282.0 eV for fully lithiated samples stopped at 4.2 V and to ~282.3 eV for delithiated samples stopped at 2.7 V.

The higher binding energy for delithiated samples is probably due to emptying of the π-band: it is, however, worth to mention that this value is significantly lower than the binding energy of a delithiated sample stopped at 3.0 V prior to the first lithiation. It indicates that the first lithiation contributes to non-reversible changes adjusting both the work function and the Fermi level. The non-reversible changes could be explained by the fact that the carbon active material is not fully delithiated at 2.7 V and that the Fermi level is set by a low amount of electrons remaining in π-band.

Figure 17. C1s spectra of graphite electrodes stopped at different voltages (a) and the corresponding LiFePO$_4$/graphite cell galvanostatic cycling (b). The probing depth in (a) was 18 nm ($h_0=2300$ eV). The red dots in (b) denote the voltages at which the cells were collected for interface analysis. Graphite electrodes are lithiated in cells charged to 4.2 V, and delithiated in cells discharged to 2.7 V.
This chapter deals with a comparison of the electrode/electrolyte interfaces formed on a LiFePO$_4$ cathode and a graphite anode after three cycles in the full cell configuration. The details of this study can be found in Paper III.

Figure 18. PES spectra of uncycled and cycled LiFePO$_4$ cathodes and graphite anodes. The probing depth was 18 nm ($h\nu=2300$ eV).

Figure 18 shows the PES spectra for uncycled and cycled electrodes, where the intensity is normalized to reflect the relative concentration of the element. The results show that more electrolyte products were present after cycling, both on the anode and the cathode. For both electrodes, higher amounts of ethers and P-F compounds were detected at the interface. The
intensity of the phosphate bulk material (PO$_4$ in Figure 18) did not change significantly after cycling, which indicates that the cathode interface layer was very thin. It confirms previous studies on this material [118,119]. In contrary, at the graphite electrode surface the feature assigned to the carbon active material (LiC in Figure 18) decreased significantly after cycling, as the signal was attenuated by the thick SEI layer. Besides previously mentioned ethers and P-F compounds, the interface on the cycled anode exhibits higher amounts of carbonates. Alkoxides (ROLi), lithium oxide (Li$_2$O), lithium fluoride (LiF) and P-O/P=O compounds are also detected on cycled anodes. To obtain better insight into the processes taking place at both interfaces non-destructive PES depth profiling was performed.

Figure 19 depicts the PES depth characterization for the LiFePO$_4$ cathode. Going from top to bottom in the Figure 19, the measurements were performed with probing depths 2, 7, 18 and 47 nm, respectively. As expected, the contribution from the bulk component, phosphate, increased with increasing probing depth. The bulk phosphate feature on the positive electrode in Figure 19 was detected already in the most surface sensitive P2p spectrum, where the probing depth was 2 nm. The thickness of the interface was therefore estimated to be in the order of a few nm. The intensity of the C-H/C-C feature increased with the probing depth, which indicates that on the cathode this feature mainly originated from the carbon coating and carbon additives in the electrode and not from electrolyte decomposition products.
The intensity of all the cathode interface components: ethers, P-F compounds and LiF, decreased with increasing probing depth, which indicates that a thin homogenous layer was formed on the cathode.

The corresponding PES depth characterization of the graphite anode is shown in Figure 20. The two most surface sensitive measurements show only SEI compounds and the bulk carbon active material, Li$_x$C, was only detected for the two most bulk sensitive measurements. A thickness of the SEI corresponding to 17 nm was estimated using Equation 4.3. The interface formed on graphite is thus much thicker than on LiFePO$_4$.

The feature attributed to the trifluoromethyl group in the binder (~293 eV in C1s spectra) is clearly separated from those of the electrolyte products and can hence be used as a signature to detect the binder contribution. This tiny feature was detected for all the studied probing depths, which indicates that SEI species were deposited in the porous binder matrix.

For the solvents EC and DEC, the most commonly suggested reduction products are lithium alkyl carbonates (ROCO$_2$Li), lithium alkoxides (ROLi) and lithium carbonate (Li$_2$CO$_3$) [120–122]:

$$2(CH_2O)_2CO + 2e^- + 2Li^+ \rightarrow (LiOOCOCH_2)_2 + C_2H_4$$  \hspace{1cm} (5.1)
(CH₂O)₂CO + 2e⁻ + 2Li⁺ → Li₂CO₃ + C₂H₄  \hspace{1cm} (5.2)
CH₃CH₂OCO₂CH₂CH₃+ 2e⁻ + 2Li⁺ → CH₃CH₂OCO₂Li+CH₃CH₂· \hspace{1cm} (5.3)
CH₃CH₂OCO₂CH₂CH₃+ e⁻ + Li⁺ → CH₃CH₂COLi+CH₃CH₂CO₂· \hspace{1cm} (5.4)

Lithium carbonate could further decompose to lithium oxide [123]:

\[ \text{Li}_2\text{CO}_3 + 2 \text{e}^- + 2 \text{Li}^+ \rightarrow 2 \text{Li}_2\text{O} + \text{CO} \] \hspace{1cm} (5.5)

The O1s depth profile shows that ethers are formed in the top parts of the SEI (higher amounts detected for low probing depths), significant amounts of carbonates are present throughout the SEI, whereas lithium alkoxide and lithium oxide are formed in the bottom parts of the SEI (detected only with high probing depth). It suggests the formation of electron-rich compounds in the deeper parts of the SEI, close to the highly reductive graphite.

Significant amounts of P-F and P-O/P=O compounds are detected in the P2p spectra. LiF was also found in the graphite interface layer and F1s depth profile indicates that more LiF was formed in the bottom parts of the SEI. These compounds correspond mainly to salt decomposition products. LiPF₆ is in equilibrium with PF₅ gas and LiF [95,124]:

\[ \text{LiPF}_6 \leftrightarrow \text{PF}_5 + \text{LiF} \] \hspace{1cm} (5.6)

Which could further reduce and/or react with other SEI components [91,118,125–127]:

\[ \text{LiPF}_6 + x\text{e}^- + x\text{Li}^+ \rightarrow x\text{LiF} + \text{LiPF}_{6-x} \] \hspace{1cm} (5.7)
\[ \text{LiPF}_6 + \text{Li}_2\text{CO}_3 \rightarrow 3\text{LiF} + \text{POF}_3 + \text{CO}_2 \] \hspace{1cm} (5.8)
\[ \text{PF}_5 + \text{Li}_2\text{CO}_3 \rightarrow 2\text{LiF} + \text{POF}_3 + \text{CO}_2 \] \hspace{1cm} (5.9)
\[ \text{PF}_5 + \text{ROLi} \rightarrow \text{POF}_3 + \text{RF} + \text{LiF} \] \hspace{1cm} (5.10)
\[ \text{POF}_3 + 2x\text{Li}^+ + 2x\text{e}^- \rightarrow x\text{LiF} + \text{Li}_x\text{POF}_{3-x} \] \hspace{1cm} (5.11)
\[ \text{POF}_3 + x\text{ROLi} \rightarrow x\text{LiF} + \text{P(OR)}_x\text{F}_{3-x} \] \hspace{1cm} (5.12)

Figure 21 shows schematic depth profiles of the cathode and anode interfaces after three cycles. The thickness of the SEI on the anode is in the order of twenty nanometers, whereas on the cathode it corresponds to just a few nanometers. The SEI layer is inhomogeneous; in the vicinity of the highly reductive graphite material Li₂O, LiOR and LiF were found, whereas in the outer layer of the SEI higher amounts of ethers and P-F compounds were detected. The cathode interface was, on the other hand, homogenous and contained mainly compounds found in the outermost part of the SEI on graphite (ethers and P-F compounds). This could indicate partial dissolution of SEI components and interaction with the positive electrode interface.
The processes taking place at the electrode/electrolyte interface were further studied in Paper II using batteries stopped at different potentials during the first four cycles. The LiFePO₄ electrodes showed very little potential-dependent changes in the interface and thus for this set of batteries focus was placed on the graphite anode. Figure 22 shows the HAXPES spectra of lithiated/delithiated graphite electrodes stopped during the first four cycles. The changes that can be observed in binding energy of the carbon active material, LiₓC, upon cycling were discussed previously in Section 4.4. The C1s spectra show a higher relative LiₓC intensity for delithiated samples (cell discharged to 2.7 V) than for lithiated samples (cell charged to 4.2 V). The SEI thickness was calculated from Equation 4.3 and corresponds to 18 and 15 nm for the lithiated and delithiated electrodes, respectively. In addition, a lower LiF intensity and a higher Li₂O intensity were observed for all lithiated anodes compared to for the delithiated samples. These results are a sign of dynamic/reversible changes in the SEI on cycling.

The increased depth sensitivity of HAXPES was used to study the variations in the carbon active material, LiₓC intensity, as a function of the cycling. The LiₓC feature was present in both the C1s and Li1s spectra (Figure 22). The sum of both features was constant for all the samples, even though the intensity of each feature varied substantially between the lithiated and delithiated samples. The maximum amount of lithium that can intercalate graphite, LiₓC, is x=1/6 (one lithium per 6 carbons) [79,128]. Therefore, the C1s LiₓC feature should be at least six times bigger than the Li1s LiₓC intensity. The results showed, however, that the C : Li ratio for LiₓC was close to unity, which implies a local excess of lithium. This is illustrated in Figure 23; an excess of lithium is shown in the vicinity of graphite, which cannot be explained by intercalation of lithium into carbon with the LiC₆ structure or by
SEI formation at the surface. We suggested that the excess of lithium could have been due to deposition of metallic lithium or formation of a distorted lithium-enriched carbon outer layer, which surrounded the LiC₆ bulk structure, similar to previously reported for TiO₂ electrodes [129].

**Figure 22.** HAXPES spectra of graphite electrodes stopped in either lithiated (cell charged to 4.2 V) or delithiated (cell discharged to 2.7 V) state during the first four cycles. The probing depth was 18 nm (hv=2300 eV).

**Figure 23.** Li1s and C1s HAXPES spectra of a graphite electrode cycled for 3.5 cycles and a schematic picture showing excess of lithium at the buried carbon/SEI interface. The relative intensity of the Li,C feature in the C1s and Li1s spectra indicate a C : Li ratio close to unity.
6. Comparing electrode/electrolyte interfaces formed in standard electrolyte and with the PMS film-forming additive

This chapter focuses on comparing the LiFePO₄/graphite cells cycled in a standard electrolyte (the same as in the previous chapter) and in a standard electrolyte with the addition of the PMS film-forming additive (hereafter called PMS electrolyte). The electrochemical performance of the cells together with a detailed interface depth profiling analysis and the evolution of aging at the electrode/electrolyte interfaces will be presented. The details of this study can be found in Papers IV and V.

6.1 Electrochemical studies

Electrochemical tests of LiFePO₄/graphite cells cycled in the standard and PMS electrolytes are shown in Figure 24. The tests were performed at 21 and 60 °C. The differential capacity during the first charge (Figure 24 a) shows that the standard electrolyte at 21 °C reduces at 2.7 V (0.8 V vs. Li⁺/Li). The broad peak at ~2.1 V (1.4 V vs. Li⁺/Li) corresponds to decomposition of PMS. Due to increase in reaction kinetics at 60 °C, both these peaks are shifted to lower cell potentials (i.e. higher reduction potentials vs. Li⁺/Li). This shift is more pronounced for the standard electrolyte cell. Moreover, all cells cycled at 60 °C have larger electrolyte reduction peaks in the differential capacity plot than cells cycled at 21 °C, which indicates that a thicker SEI is formed at the elevated temperature.

The capacity retention for the same set of cells is shown in Figure 24b. In this study, galvanostatic cycling with a wide voltage window (charge and discharge in the 0-100 % state-of-charge range) was used. It leads to faster capacity fade, i.e., accelerates aging. At 21 °C, the capacity retention for the standard electrolyte cell was better at the beginning of the cycling. However, the capacity retention of the PMS electrolyte cell did not decay as rapidly and after approximately the 50th cycle it was better than for the cell cycled without the additive. At 60 °C, both cells had much worse capacity retention; however PMS performed better than the standard electrolyte. The results
clearly show that the PMS additive improves the capacity retention both at ambient and elevated temperatures. To study how the PMS additive influences the electrode/electrolyte interfaces and how the evolution of aging proceeds at the interfaces, a detailed PES study will be presented in the next paragraphs.

Figure 24. LiFePO$_4$/graphite cells cycled with standard and PMS electrolytes at 21 and 60 °C. Differential capacity during first charge (a) and capacity retention (b).

6.2 PES depth profile after three cycles

In this section, the PES depth profiles of LiFePO$_4$ cathodes and graphite anodes cycled with two different electrolytes will be compared. The measurements are performed on cells after three galvanostatic cycles.

Figure 25 shows the PES depth characterization of the LiFePO$_4$ cathode cycled with standard and PMS electrolytes. When comparing the spectra for the anodes cycled with different electrolytes it is clear that all the PMS samples have less intense bulk features: phosphate and C-H/C-C peaks. It indicates that a thicker interface is formed on samples cycled with the additive. Also, higher amounts of ethers and P-F features are found on the samples cycled with PMS. The sulfur spectra were used as a probe for additive decomposition on the cathode; however no direct signs of PMS decomposition products were detected.

The PES depth characterization of graphite electrodes is shown in Figure 26. The LiixC feature of the carbon active material is more pronounced for the standard electrolyte samples, which indicates a thinner SEI than for the PMS electrodes. The SEI thickness was estimated to be 19 and 25 nm for the standard and PMS electrolyte samples, respectively. The compounds formed
in the bottom parts of the SEI, close to the carbon active material, are more attenuated for the PMS electrolyte samples due to thicker SEI. It could be the reason for the lower intensity of alkoxides and Li₂O in the O1s spectra. The samples cycled with the film-forming additive have more constant carbonate to ether ratios at all measured probing depths and much higher intensity for hydrocarbons. The sulfur depth profile for the PMS electrolyte anode is shown in Figure 27. The peak at higher binding energy may correspond to a product with a similar sulfur environment as in the PMS molecule, e.g., sulfonate with a different functional group. The peak at lower binding energy indicate the presence of a compound with less positively charged sulfur,
Figure 26. PES depth profile of the graphite anode cycled with standard and PMS electrolytes. The probing depths correspond to 2, 11 and 18 nm, respectively. Reprinted with permission from [Paper IV]. Copyright 2013 American Chemical Society.

e.g., with an oxidation state of +2. The depth profile shows that this compound is formed in the inner part of the SEI, close to the bulk material. A suggested PMS reduction scheme is shown in Figure 28. During the reaction, the C-O bond is broken and a methanesulfonate anion and a C-C triple-
bonded radical are formed. Both compounds could further react with solvent components.

**Figure 27.** Sulfur depth profile of the graphite anode cycled in the PMS electrolyte. The probing depths correspond to 2, 18 and 47 nm, respectively. Reprinted with permission from [Paper IV]. Copyright 2013 American Chemical Society.

**Figure 28.** Suggested reaction scheme for SEI formation with PMS additive. Reprinted with permission from [Paper IV]. Copyright 2013 American Chemical Society.

### 6.3 LiFePO₄ interface - aging study at 21 and 60° C

In order to study how the evolution of aging proceeds at the interfaces, LiFePO₄ samples were collected after the 3rd, 50th and 200th galvanostatic cycles for HAXPES analysis. Synchrotron-based HAXPES measurements were performed using excitation energy of 2300 eV, corresponding to a probing depth of 18 nm, which enables deeper measurements than with a traditional in-house XPS instrument. For the long-term cycled electrodes this is essential for comparing the changes in thickness of the interface layer, as the signal from the bulk material was fully attenuated when using lower photon energies.
HAXPES P2p spectra for delithiated LiFePO₄ electrodes cycled with standard and PMS electrolytes are shown in Figure 29. The bulk phosphate feature is slightly decreasing with the number of cycles, which shows that an interface layer is continuously growing on LiFePO₄ electrodes upon cycling. A larger decrease of the phosphate bulk signal is observed at 60 °C, which shows that the buildup of an interface layer on the cathode is much more pronounced at the elevated temperature. At 21 °C, a thicker electrode/electrolyte interface is found for the PMS electrolyte cells, whereas at 60 °C, it is the standard electrolyte cell that leads to a thicker interface layer. Moreover, the intensity of a P-F feature increases and a new feature assigned to fluorophosphates, POₓFᵧ, appears and grows during aging. The amount of fluorophosphates on samples that were washed with DMC in order to remove electrolyte residues (not shown here) was much smaller, which could indicate that they are an electrolyte residue. It can be speculated that fluorophosphates might primarily have been formed on the anode; they could have dissolved, changed the composition of the bulk electrolyte and therefore affected the cathode interface.

![Figure 29. P2p core level spectra for delithiated LiFePO₄ electrodes cycled with the standard (top) and PMS (bottom) electrolytes at 21 and at 60 °C. The probing depth was 18 nm (hv=2300 eV).](image)

The relative intensities of detected components for the LiFePO₄ cathode are shown in Figure 30. An increase of C-O containing compounds during aging is observed for both electrolytes cycled at 21 °C. The main difference between the cathodes cycled in different electrolytes is the feature assigned to C-C/C-H bonds. This feature decreased during cycling for the standard electrolyte and increased for the PMS electrolyte samples. For the standard electrolyte, the C-C/C-H feature corresponds mainly to carbon coating and the carbon additive in the bulk electrode and therefore it decreases on cycling while the interface gets thicker. The increasing contribution of the C-C/C-H
feature for the cathode cycled with PMS electrolyte indicates that hydrocarbon intensity increase upon cycling. At 60 °C, very similar aging trends are observed as at 21 °C. The main difference is that the cycling trends are more pronounced due to faster aging at the elevated temperature.

Spectroscopic measurements gave no clear evidence for PMS decomposition on the positive electrode (Paper V). The differences between the spectra for LiFePO₄ cycled in different electrolytes suggest that PMS has a significant impact on the positive electrode interface. However, it was not possible to give a clear answer whether it was due to PMS decomposition on the positive electrode or processes that take place on the anode and influence the whole cell.

Figure 30. Relative intensities of detected features for LiFePO₄ positive electrodes cycled with standard (top) and PMS (bottom) electrolytes at 21 °C and at 60 °C.

6.4 Graphite interface - aging study at 21 and 60 °C

Graphite electrodes were also analyzed with HAXPES in order to understand the changes in the negative electrode/electrolyte interface during aging. Figure 31 schematically shows a summary of the changes in the SEI during
aging for standard and PMS electrolytes at 21 and 60 °C. The yellow area represents SEI and arrows on the sides show changes in the relative intensity of a feature during aging. Each picture shows how the SEI thickness changes with the number of cycles. The schematic picture is based on the Figures 32-34.

**Figure 31.** Schematic picture of the changes in the SEI during cycling with standard (top) and PMS (bottom) electrolytes, at 21 °C (left) and at 60 °C (right). The dashed line in the SEI represents the probing depth when using the 2300 eV excitation energy (95% of total signal). Arrows show changes in the relative intensity of a feature on aging, ↑: small increase, ↑↑: large increase, ↓: small decrease, ↓↓: large decrease.
Figure 32. C1s core level spectra for lithiated graphite cycled with standard (top) and PMS (bottom) electrolytes at 21 and 60 °C. The probing depth was 18 nm ($h\nu=2300$ eV) and 47 nm ($h\nu=6900$ eV). The calculated SEI thicknesses ($d$) are noted in the spectra.

Figure 33. F1s and P2p core level spectra for lithiated graphite cycled with standard and PMS electrolytes at 21 and 60 °C. The probing depth was 18 nm ($h\nu=2300$ eV).
The relative intensity of the carbon active material, Li$_x$C, feature decreased upon cycling as a thicker SEI was formed (Figure 32). As the schematic picture shows, after three cycles at 21 °C, the SEI formed in the standard electrolyte cell was thinner than the SEI formed in the PMS electrolyte; however the difference in thickness became smaller upon cycling and after 200 cycles the SEI formed in a standard electrolyte was thicker. When comparing the SEI thickness after three cycles at 21 °C and at 60 °C, it is clear that a much thicker SEI was formed at the elevated temperature: it was 84 and 17% thicker for the standard electrolyte and PMS electrolyte, respectively. At 60 °C the anodes cycled with PMS had thinner SEI layers than the ones cycled with the standard electrolyte. This was observed both at the beginning of cycling as well as after aging (after 3 and 50 cycles). The above results show that after aging at 21 and at 60 °C, the SEI on graphite electrodes cycled with PMS remains thinner than the SEI formed in standard electrolyte cells. This can be interpreted as a more stable interface formed with the PMS additive.

![Figure 34. Relative intensities of detected features for graphite negative electrodes cycled with standard (top) and PMS (bottom) electrolytes at 21 and 60 °C.](image)

Besides SEI growth upon aging there are additional changes in the interface composition. Features of LiF and P-O/P=O increased on cycling with the standard electrolyte at 21°C (showed in Figure 33 and 34 and as double ar-
rows in Figure 31). It indicates an increase of salt decomposition products upon cycling. For the electrodes cycled with PMS the increase of salt decomposition products was less distinct (shown as a single arrow in Figure 31). For both electrolytes the higher intensity of the P-O/P=O feature during aging was accompanied by a 0.6 eV increase in binding energy (Figure 33). This binding energy shift implies that the P-O/P=O feature was built up by a mixture of slightly different compounds that overlap in the P2p spectra due to small differences in electron density on the phosphorous atom. The shift to the higher binding energy may represent a more dominant character of a compound in which phosphorous is more positively charged, e.g., fluorophosphates containing more fluorine functional groups as in OPF$_2$OR.

Besides many similarities there are also distinct differences in the SEI aging trends at 21 °C for the anodes cycled with standard and PMS electrolytes. The C-H feature decreased upon cycling for the standard electrolyte, which is attributed to thicker interface and attenuation of the hydrocarbon signal. In contrary, the hydrocarbon feature increased upon cycling for the PMS cell. In Section 6.2 it was shown that PMS forms an SEI rich in hydrocarbons. The higher intensity of hydrocarbon upon cycling is therefore interpreted as a continued decomposition of PMS during aging. Figure 35 shows relative intensities of the Li1s core level for lithiated and delithiated graphite electrodes cycled with the standard and PMS electrolytes. The change in the relative amounts of lithium between lithiated and delithiated states was large for the standard electrolyte and a significant increase in the amount of lithium in the SEI was observed during cycling. This indicates bigger loss of cyclable lithium for the standard electrolyte cell. A lower loss of cyclable lithium and a thinner SEI formed during long-term cycling suggest that the PMS electrolyte contributes to the formation of a more stable SEI and therefore the cell cycled with the additive has better long-term capacity retention.

![Figure 35](image_url)

*Figure 35. Relative intensities of the Li1s core level for graphite cells cycled with the standard and PMS electrolytes at 21 °C.*

52
Clear differences in the negative electrode/electrolyte interface composition were observed for the different cycling temperatures. Besides thicker interface layer formed after three cycles at 60 °C, higher relative amounts of carbonates and P-O/P=O features were detected for cell cycled with both electrolytes. This clearly shows that solvent and salt decomposition takes place to a higher extent at the elevated temperature. This could be connected to the reaction equilibrium of LiPF$_6$ with PF$_5$ gas and LiF (Reaction 5.6) [124,128]. PF$_5$ is a strong Lewis acid [129], which immediately reacts with solvent components and the equilibrium moves towards products. This takes place to a higher extent at elevated temperature [124,128] and leads to increased decomposition of salt and solvent components. Interestingly, for all cells cycled at 60 °C the inside of the pouch cell material was covered with a brownish substance. Similar brown colored precipitate was previously reported for cells stored at 85 °C for two days. It has been identified as a mixed carbonate ester formed in an EC ring-opening reaction [128].

Similar interface aging trends were observed for cells cycled at elevated temperatures with the standard and PMS electrolytes. The most significant interface changes upon cycling are: increased amounts of C-H and P-O/P=O features as well as decreased amounts of lithium. Moreover, less significant changes, such as increased amount of the P-F feature and decreased amounts of carbonates and LiF, have been observed during aging at 60 °C. However, the interface aging processes differ significantly for the two studied temperatures: 21 and 60 °C, which imply that aging at elevated temperature differs from aging at ambient temperature. This is also supported by previous work [130]. The interface aging processes at 60 °C were very similar for both studied electrolytes, however thinner SEI with lower amounts of lithium for the PMS electrolyte was probably the reason for the better capacity retention.

NEXAFS measurements were performed to obtain complimentary information about any PMS decomposition products, and the spectra are displayed in Figure 36. The reference NEXAFS spectrum of uncyced graphite soaked in the PMS electrolyte shows a main peak located at 2475.8 eV (Figure 36a). This spectrum resembles a previously measured spectrum for a compound with a similar sulfur environment, i.e. the methanesulfonate anion, CH$_3$SO$_3^-$ [131]. All cycled samples displayed a main peak at approximately the same position as in the reference sample and a small peak at around 2.9 eV lower energy. For cycled samples the main peak could correspond to either a decomposition product with similar environment around sulfur as in the PMS molecule or to the PMS molecule itself, i.e. a compound with an oxidation state of +4. The small peak, which appears at 2.9 eV lower energy could correspond to a compound with a lower oxidation state of sulfur, e.g., +2 [132,133]. This interpretation is supported by PES
sulfur depth profiles after 3 and 200 cycles (Figures 27 and 36c, respectively), where two different sulfur compounds were detected. Moreover, both depth profiles show that the compound that could correspond to sulfur with oxidation state +2 was detected in the bottom parts of the SEI, close to the bulk material. The comparison of different NEXAFS detection modes confirms these findings (Figure 36b). The surface sensitive measurement show lower intensity of the feature attributed to sulfur +2 than bulk sensitive measurement. These results indicate that during PMS decomposition at least two new sulfur compounds are formed. One, with similar structure as PMS, which could resemble a product presented in the reaction scheme depicted in Figure 28, and another one, probably with oxidation state +2, formed in the bottom parts of the SEI. The latter could be formed by further reduction of the products suggested in Figure 28 or it could correspond to a product from a different PMS decomposition reaction (e.g., with broken S-O bond during PMS reduction).

Figure 36. a) S K-edge NEXAFS spectra of graphite electrodes cycled with PMS electrolyte, from the top: unycled reference electrode (soaked in PMS electrolyte), electrodes cycled at 21 °C for 3, 50 and 200 cycles and electrodes cycled at 60 °C for 3 and 50 cycles. b) S K-edge NEXAFS spectra of graphite electrode after 200 cycles at 21 °C. Fluorescence yield mode (bulk sensitive, black line) and total electron yield mode (surface sensitive, grey dots). c) Sulfur depth profile of graphite anode cycled with the PMS additive for 200 cycles at 21 °C. The probing depth was 2, 18 and 47 nm, respectively.
7. TPP flame retardant additive in the context of high power applications

This chapter describes the extensive characterization of a standard electrolyte containing different concentrations of the TPP flame retardant. The aim was to determine whether or not TPP is a suitable flame retardant for Li-ion batteries intended for high power demanding applications, such as hybrid electric vehicles. The study is divided into three parts: electrolyte characterization, LiFePO₄/graphite full cell tests and interface characterization. Full cell tests and interface studies will be discussed in more detail. This chapter summarizes the results presented in Paper VI.

TPP is a flame retardant that is added to the electrolyte in order to decrease flammability and therefore increase the safety of the battery. However, flammability tests showed only a minor decrease in the electrolyte flammability for low TPP concentrations. Even an addition of 15 wt% TPP was not effective enough to create a non-flammable electrolyte (defined as self-extinguishing time below 6 s/g [61]). Electrolyte characterization showed that the addition of TPP to the electrolyte leads to increased viscosity and decreased conductivity. Moreover, solvation of Li⁺ is affected by TPP. Li⁺ seems to coordinate to TPP more preferentially than to EC and DEC, which decreases the mass transport rate in the electrolyte.

LiFePO₄/graphite full cell tests were focused on understanding the impact of TPP on high power performance. Figure 37 shows a EUCAR test for cells cycled with 0-15 wt% TPP. The results clearly show that the addition of TPP leads to increased polarization, which causes lower energy efficiency. The energy efficiency decreased by 8% when 15 wt% TPP was added to the electrolyte. The polarization during the pulse can roughly be divided into two parts [130,134]:

- instantaneous polarization, caused by contact resistance between different materials, activation of the electrochemical reactions, and ohmic potential drop
- time-dependent polarization is the diffusion polarization due to the diffusion resistivity in the electrolyte and in the solid phase.
Table 2. Different polarization contributions for the 10C discharge pulse. Reprinted from [Paper VI], with permission from Elsevier.

<table>
<thead>
<tr>
<th>Electrolyte composition / wt% TPP</th>
<th>Instantaneous polarization /V</th>
<th>Time-dependent polarization /V</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>-0.096</td>
<td>-0.286</td>
</tr>
<tr>
<td>1</td>
<td>-0.082</td>
<td>-0.255</td>
</tr>
<tr>
<td>3</td>
<td>-0.106</td>
<td>-0.259</td>
</tr>
<tr>
<td>5</td>
<td>-0.111</td>
<td>-0.390</td>
</tr>
<tr>
<td>10</td>
<td>-0.138</td>
<td>-0.308</td>
</tr>
<tr>
<td>15</td>
<td>-0.139</td>
<td>-0.481</td>
</tr>
</tbody>
</table>

Table 2 shows the instantaneous and time-dependent contributions for the 10 C discharge pulse while Figure 37b depicts the corresponding cell voltages. The results show that both instantaneous and time-dependent polarization increase with increasing concentration of TPP in the electrolyte. Cells with 0–3 wt% TPP showed similar performance, while cells with 5 and 10 wt% TPP displayed decreased performance, with significant increase in time-dependent polarization. The cell with 15 wt% TPP showed poor performance with high increases in instantaneous and time-dependent polarization, 46 and 68 %, respectively.

XPS measurements were performed in order to understand the influence of the TPP additive on the electrode/electrolyte interfaces. Prior to interface characterization, accelerated cycling of the cells was executed. Figure 38 shows C1s and P2p spectra of LiFePO₄ electrodes cycled with different concentrations of TPP. The electrode cycled without the additive has a very thin interface, as large amounts of phosphate bulk material were detected for both washed and unwashed samples. For unwashed samples, the addition of TPP...
to the electrolyte results in an increase of the hydrocarbon feature and the formation of a broad peak at ~290.5 eV. It is a shake-up, formed by aromatic \( \pi - \pi^* \) transitions in the phenyl groups present in TPP. In the P2p spectra a new feature, TPP*, was formed when TPP was added to the electrolyte. This feature could be attributed to TPP itself or a compound with very similar environment around phosphorous. The spectra show that washed electrodes have thinner interface layers and smaller amounts of TPP* and P-F features in the surface, as electrolyte residues are washed off. Despite that, TPP addition to the electrolyte shows the same trends for washed and unwashed samples.

Figure 38. C1s and P2p spectra of unwashed (UW) and washed (W) LiFePO\(_4\) electrodes. The probing depth was 11 nm \((h\nu=1487\) eV). Reprinted from [Paper VI], with permission from Elsevier.

Figure 39 shows C1s and P2p spectra of graphite electrodes cycled with different concentrations of TPP. For unwashed samples, similar trends during TPP addition were observed as for the LiFePO\(_4\) electrodes: increased amounts of hydrocarbons and the formation of a shake-up. Interestingly, C1s spectra of washed samples differ significantly. Most of the TPP contribution was washed off and a more standard SEI with respect to carbonaceous compounds, such as ethers and carbonates, appeared. The P2p spectra show that addition of TPP lead to the formation of TPP*. After washing, the feature
attributed to P-F decreased, however TPP* was still present in the interface. It suggest that TPP* is an SEI component and not just an electrolyte residue. Even though full cell tests showed no signs of TPP reduction on the negative electrode, TPP could participate in SEI formation by chemical reactions with, e.g., radicals formed during solvent decomposition.

The presented results show that TPP addition to the electrolyte significantly influences the interface chemistry on both the LiFePO$_4$ positive electrode and the graphite negative electrode. The interface films probably contribute to higher polarization of cells cycled with TPP. Big increase in polarization for higher TPP concentrations and low impact on flammability for lower concentrations show that TPP is not a suitable additive for high power applications.

![Figure 39. C1s and P2p spectra of unwashed (UW) and washed (W) graphite electrodes. The probing depth was 11 nm ($hν=1487$ eV). Reprinted from [Paper VI], with permission from Elsevier.](image)
8. Conclusions

This work was focused on studying Li-ion battery interfaces in LiFePO₄/graphite cells. Those electrode chemistries were selected as a baseline within the Swedish Hybrid Vehicle Centre for understanding parameters affecting the lifetime of batteries to be used in hybrid electric vehicles.

The first part of this thesis was dedicated to the development and improvement of a photoelectron spectroscopy methodology for studying electrode/electrolyte interfaces. Since these are very sensitive chemical systems, extra attention was given towards understanding the parameters influencing post-mortem analysis of Li-ion battery interfaces and improving the measurement procedure. Binding energy shifts of photoemission spectra as a function of cycling and the effect of air exposure on cycled Li-ion electrodes were discussed.

A powerful technique for non-destructive depth profiling was used in order to study electrode/electrolyte interfaces in LiFePO₄/graphite full cells. A combination of synchrotron and in-house photoelectron spectroscopy has enabled depth profiling from the outermost surfaces into the electrode bulk and gave an improved understanding of the surface chemistry. For example, a comparison of cathode and anode interfaces after three cycles in a standard electrolyte showed that the thickness of the SEI is in the order of twenty nanometers, whereas on the cathode interface it corresponds to just a few nanometers. Moreover, the cathode interface is rather homogenous, whereas the anode SEI is inhomogeneous. Li₂O, LiOR and LiF were found in the vicinity of the highly reductive graphite surface, whereas in the outer layer of the SEI higher amounts of ethers and P-F compounds were detected. Moreover, the SEI species deposit in the porous binder structure, which acts as a matrix for the SEI. The LiFePO₄ electrodes showed very little potential dependent changes in the interface, while dynamic changes in the SEI on cycling and accumulation of lithium close to the carbon surface in the negative electrode have been observed.

In the next part of this work the propargyl methanesulfonate (PMS) film-forming additive was studied. It was shown to improve capacity retention at ambient and elevated temperature (21 and 60 °C). The additive influences the interface on both positive and negative electrodes with thicker interface
layers formed after three cycles at 21 °C. A thorough study on the development of the interface aging on anodes and cathodes cycled with and without the PMS film-forming additive, at ambient and elevated temperature was presented. The aging trends and specifically the influence of PMS on the surface reactions were discussed. Higher stability of the SEI formed with PMS leading to lower loss of cyclable lithium in the interface is probably a main reason for the better capacity retention of the battery.

Finally, the flame retardant triphenyl phosphate (TPP) was studied in the context of high power demanding applications, such as hybrid electric vehicles. The study showed that TPP is not a suitable additive for such applications. Flammability tests showed only a minor decrease in the electrolyte flammability for low TPP concentrations; even with an addition of 15 wt% TPP did not create a non-flammable electrolyte. The energy efficiency of the cells decreased with addition of TPP; diffusion resistivity was the main source of losses. Moreover, addition of flame-retardant leads to a thicker interface layer on the cathode. Although TPP did not reduce on the graphite surface, it affected the interface chemistry on the anode.

This thesis shows that reliable photoelectron spectroscopy results on such sensitive systems as the electrode/electrolyte interfaces formed in Li-ion batteries can be obtained as long as care is taken to maintain careful sample handling and measurements. Although the additives studied may not be the final solution to improved lifetime and safety of commercial batteries, an increased understanding of the mechanisms that degrade the SEI has been achieved. Better understanding of these mechanisms is of great importance to the future development of improved additives to stabilize the SEI, and it is the hope of the author that this thesis will bring us one step closer to safer and more reliable Li-ion batteries in the future.
Världens växande befolkning och den snabba tekniska utvecklingen har lett till ett enormt och fortfarande ökande energibehov. De fossila bränslen som tillhandahåller en stor del av denna energi kommer inte att räcka i framtiden, och dessutom medför såväl deras produktion som förbränning belastningar på miljön. Ökad växthuseffekt, surt regn och smog är bara några exempel på negativa miljöeffekter, och senare års kraftigt stigande oljepriser kan ses som en indikator på att världen redan nu börjar få svårt att tillgodose sitt energibehov.

De negativa miljöeffekterna såväl som risken för kraftiga prisuppgångar på energi i takt med att vi får allt svårare att möta vårt energibehov med minskande tillgångar av fossila bränslen har lett till ett ökat intresse för energieffektiviseringar och förnybar energiproduktion. Speciellt risken för klimatförändringar till följd av en ökad växthuseffekt har varit en viktig faktor i debatten på senare tid.


Av de laddningsbara batterierna har liitiumjonbatterier den högsta energitättheten, och är därmed den batterityp som ger den bästa räckvidden. Dessutom klarar de kraftigare effektuttag än andra batterier för en given fysisk storlek. Att de även har högre verkningsgrad gör att värmeöverföringen minimeras med liitiumjonbatterier. Detta gör dem till en huvudkandidat även för ett annat område, nämligen som buffer till intermittenta förnybara energikällor, såsom sol- och vindkraft.

Litiumjonbatterier är redan idag helt dominerande i telefoner och annan bärbar elektronik. Om de ska kunna slå på bred front även för större applikat-

---

9. Populärvetenskaplig sammanfattning

Världens växande befolkning och den snabba tekniska utvecklingen har lett till ett enormt och fortfarande ökande energibehov. De fossila bränslen som tillhandahåller en stor del av denna energi kommer inte att räcka i framtiden, och dessutom medför såväl deras produktion som förbränning belastningar på miljön. Ökad växthuseffekt, surt regn och smog är bara några exempel på negativa miljöeffekter, och senare års kraftigt stigande oljepriser kan ses som en indikator på att världen redan nu börjar få svårt att tillgodose sitt energibehov.

De negativa miljöeffekterna såväl som risken för kraftiga prisuppgångar på energi i takt med att vi får allt svårare att möta vårt energibehov med minskande tillgångar av fossila bränslen har lett till ett ökat intresse för energieffektiviseringar och förnybar energiproduktion. Speciellt risken för klimatförändringar till följd av en ökad växthuseffekt har varit en viktig faktor i debatten på senare tid.


Av de laddningsbara batterierna har liitiumjonbatterier den högsta energitättheten, och är därmed den batterityp som ger den bästa räckvidden. Dessutom klarar de kraftigare effektuttag än andra batterier för en given fysisk storlek. Att de även har högre verkningsgrad gör att värmeöverföringen minimeras med liitiumjonbatterier. Detta gör dem till en huvudkandidat även för ett annat område, nämligen som buffer till intermittenta förnybara energikällor, såsom sol- och vindkraft.

Litiumjonbatterier är redan idag helt dominerande i telefoner och annan bärbar elektronik. Om de ska kunna slå på bred front även för större applikat-
ioner, såsom elbilar och buffertar till kraftverk, måste de dock förbättras ytterligare. Kostnaden måste minska och livslängden öka. Dessutom måste även säkerheten förbättras, då dessa batterier blir mycket större än de som är vanliga idag.

En viktig faktor för batteriets funktionalitet är den tunna film som bildas i gränsytan mellan elektrod och elektrolyt. Denna tunna film förhindrar att elektrolyten bryts ner i kontakt med elektroden. Den film som bildas på anoden (minuspolen) kallas vanligen för solid electrolyte interphase (SEI). SEI har en helt avgörande betydelse för batteriets prestanda, livslängd och säkerhet.

Den här avhandlingen handlar om dessa filmer och fokuserar på två områden: dels utvecklades metoder för att använda fotoelektronspektroskopii (PES) för att studera SEI och katodfilmen, dels användes de förbättrade metoderna för att undersöka vilka effekter några additiv som tillsätts i elektrolyten gav på filmerna. PES är en analytiskt dit där fotoner, röntgenstrålning, används för att emittera elektroner, som sedan kan detekteras och ge information om materialet de kom ifrån.

Som modellsystem valdes ett batteri med anod av grafit och katod av litium-järnfosfat. Dessa elektroder används som grundsystem i Svenskt hybridfordonscentrum (SHC). De är ogiftiga, förhållandevis säkra och tillverkas av lättillgängliga och billiga råmaterial, vilket gör dem till bra kandidater för fordonsbatterier.

Synkrotroner kan generera röntgenstrålning av varierande energi och därmed PES-detectionsdjup. Genom att använda synkrotroner vid PES-mätningarna på SEI och katodfilmen var det möjligt att skapa en bild av hur filmerna såg ut på olika djup utan att filmerna förstördes (Figur 1). Detta ledde till en ökad förståelse av de kemiska processer som äger rum i gränsytorna mellan elektroderna och elektrolyten. SEI visade sig vara inhomogen och betydligt tjockare än katodfilmen. Dynamiska förändringar av SEI när batteriet laddades och laddades ur (cyklades) och litium anrikades nära grafitanodens yta diskuteras.

Små mängder av olika additiv tillsätts ofta till ett batteris elektrolyt för att lägga till eller förbättra någon funktion. I den här avhandlingen studerades propargylmetansulfonat (PMS, Figur 2a), som bidrar till att bilda de tunna filmerna på elektroderna, och trifenylofosfat (TPP, Figur 2b), som är ett flamskyddsmedel.
**Figur 1.** Schematisk skiss över framtagandet av en icke-förstörande djupprofil på en grafitanod. Reprinted with permission from [Paper IV]. Copyright 2013 American Chemical Society.

**Figur 2.** De kemiska strukturerna för filmbildaren PMS (a) och flamskyddsmedlet TPP (b).

PMS minskade batteriets degradering, både vid 21 och 60 °C. Additivet påverkade gränssytona på båda elektroderna. I en utökad studie undersöcktes åldringseffekterna för båda elektroderna och vid båda temperaturerna. Med PMS höll sig tjockleken av gränssytan på anoden mer konstant när batteriet åldrades. PMS hade en gynnsam effekt genom att stabilisera SEI, vilket ledde till ett hållbarare batteri.


Även om de studerade additiven inte visade sig vara den slutgiltiga lösningen för att förbättra livslängden och säkerheten för kommersiella batterier, så har studierna lett till en ökad förståelse för de processer som bidrar till nedbrytningen av litiumjonbatterier. En bättre förståelse för dessa gränssyterepro-
cesser har stor betydelse för den kommande utvecklingen av säkrare och pålitligare litiumjonbatterier.
10. Acknowledgements

First of all, I would like to thank my supervisor Kristina Edström for giving me the opportunity to work with this project and for her guidance, encouragement and enthusiasm during these years. Håkan Rensmo, my co-supervisor, thank you for your support and for sharing your spectroscopy knowledge. Leif Nyholm, my co-supervisor, thank you for the interesting discussions and for proof-reading my thesis. Maria Hahlin, we should have worked more often while having fika in city center! Thank you for your contribution to this work and for being a ‘super-hero’ and saving a few ‘super important’ samples :) Finally, Sara Malmgren, we have gone together through a very bumpy road. Many hard times, but even more laughs. I will always remember the bed from styrofoam that you made for me. Thank you for sharing this journey!

Torbjörn Gustafsson, thank you for all-the-different-kinds of discussions. It is great to have a person who knows everything about batteries and all the practical details in the same corridor. Josh Thomas, thank you for a warm welcome to the battery group and for still being there for us, whenever needed :) Daniel Brandell and Fredrik Björefors, thank you for taking care of the practical issues within the battery group and for creating a great working environment.

Mihaela Gorgoi, thank you for your support in Bessy and for reading our articles in the ‘last minute’ :) Frédéric Thébault and Patrik Johansson are acknowledged for the PMS additive. Patrik, thank you for your engagement in the TPP project and for providing very detailed comments. Henrik Lundgren, Susanne Wilken and Tommy Zavalis, thank you for collaboration and all the interesting discussions and phone meetings. I would also like to thank the rest of co-authors I have been working with during the last years: Mårten Behm, Per Jacobsson, Göran Lindbergh, Rickard Eriksson, Maria Hellqvist Kjell, Matilda Klett, Jens Groot, Pontus Svens, Rakel Wreland Lindström, Helena Berg, Rebecka Lindblad, Stefan Plogmaker and Julius Kühn.

I would also like to acknowledge Robert Kostecki for giving me the opportunity of performing the experiments in his group in Lawrence Berkeley
National Laboratory. Nick Norberg, Ivan Lucas, Jarosław Syzdek, thank you for your support in the laboratory and for the nice company.

Henrik Eriksson, thank you for taking care of our battery lab. Kristina Israelsson and Eva Larsson, thank you for support with all the administrative procedures and Peter Lundström for IT support. Anders Lund is acknowledged for support with our in-house XPS and Pertti Knuuttila for making teaching labs much easier.

I would like to acknowledge the Swedish Hybrid Vehicle Center (SHC) for financing this work and for giving me a great opportunity to join the network. BESSY II and MAX IV Laboratory are acknowledged for allocation of synchrotron radiation beamtimes for enabling the measurements. ÅForsk, Liljewalchs, Wallenberg Foundation and Graduate School in Advanced Materials are acknowledged for the travel grants.

Gabi, thank you for being a great friend who is always ready to help. Anti, I think you introduced me to all the ‘sauna-having-fun’ activities. We should repeat it soon! Bertrand, it was fun to work with you in the synchrotrons. Thank you for discovering jelly sweets and for help with the uncountable amount of transfers that we did together. Maybe some chair race in 3303? ;) Reza and Chao are also acknowledged for help in the synchrotron. Stéven, thank you for support with organic chemistry and David for your SEM time. Mario, Solveig, Sara Mu. and Matt, thank you for great parties! Adam, you are the next, it is my time for teasing! ;) Also to the rest of battery group: Alina, Rickard, Fredrik L., Cesar, Julia, Mohammed, Jeff, Andreas, Fabian, Tim, Viktor, Bing, Habtom, Taha, Jia, Wei, Jonas M., Girma, thanks for a great atmosphere and all the fun we had together, all the laughs and after-works. All the previous group members, especially Wendy, Sigita and Kenza are also acknowledged. I want to thank everyone in the inorganic chemistry group for fikas, chats, trips and friendly environment in the whole department!

I would like to thank my friends who prevented my social life from disappearing completely during the last, though year. Justyna and Daniel, Kasia Z-N. and Grzegorz, Kasia P-B. and Petter, Marta K. and Björn, Beata and Łukasz, thank you for all the fikas/games/dinners. Of course, the rest of the mafia girls also have to be acknowledged! Agata N., Agata Z., Kasia K., Marta B., Kasia Ro., Gabrysia, Ewa, Ania L, Ola, Alicja, Kasia Ra., Ania M., Krysia… (wow, I hope I remembered all of you! ;)… thank you for all the laughs, girly chats, dinners, parties and complaints on ‘life in science‘ ;) The X-section gang of friends, thank you for the nice times we have together!
I would also like to thank to all my friends who stayed in Warsaw (and the ones that are spread in the world), it is great that we still keep in touch! Ania and Dieter, Mirja and Jussi, even though the distance is a bit bigger now, I hope to see you soon again!

Most of all, I want to thank my family.

Mamo, dziękuję, że zawsze, wszędzie, niezależnie od wszystkiego wspierasz mnie i jesteś tak blisko jak tylko można być będąc oddzielonym przez morze i tysiące kilometrów. Patrycja, dzięki za to, że zawsze mogę na Ciebie liczyć i że dajesz mi do zrozumienia, że problemy naukowe to nie koniec świata. Dziękuję też Babci, Darkowi, Antosiowi i całej reszcie rodziny za wsparcie i uśmiech na każdym kroku.

Min svenska familj: Britt-Marie, Peter, Gunnar, Jennifer, Magnus, Britta, Sigvard och Kerstin, tack för att Ni finns och att Ni gjorde att det var så lätt att kalla Sverige mitt hem.

And finally, Jonas, for being a great supporting husband. For reminding me that science is not everything and helping in the most difficult times. I love you. Buzi.

Kasia

Katarzyna Ciosek Högström
References


A doctoral dissertation from the Faculty of Science and Technology, Uppsala University, is usually a summary of a number of papers. A few copies of the complete dissertation are kept at major Swedish research libraries, while the summary alone is distributed internationally through the series Digital Comprehensive Summaries of Uppsala Dissertations from the Faculty of Science and Technology.