Si negative electrodes for Li-ion batteries

Aging mechanism studies by electrochemistry and photoelectron spectroscopy

FREDRIK LINDGREN
Abstract

This thesis is focusing on the challenges when using Si as a possible new negative electrode material in Li-ion batteries. The overall aim is to contribute to a general understanding of the processes in the Si electrode, to identify aging mechanisms, and to evaluate how they influence the cycling performance. Another objective is to investigate how photoelectron spectroscopy (PES) can be used to analyze these mechanisms.

LiPF₆ based electrolytes are aggressive towards the oxide layer present at the surface of the Si particles. With the use of fluoroethylene carbonate (FEC) as an electrolyte additive the cycling performance is improved, but the oxide layer is still affected. A recently developed salt, lithium 4,5-dicyano-2-(trifluoromethyl)imidazolide (LiTDI), is shown not to have any detrimental effects on the oxide. The SEI with FEC and vinylene carbonate (VC) as contains a high concentration of LiF and polymeric carbonate species and this composition seems to be beneficial for the cycling performance, but the results indicate that additional aging mechanisms occur. Therefore, electrochemical analysis is performed and confirms a continuous SEI formation. However, it also reveals a self-discharge mechanism and that a considerable amount of Li is remaining in the Si material after standard cycling.

PES is used in this work to analyze the SEI-layers as well as the surface and the bulk of the Si material. With this technique it is hence possible to distinguish changes in the Si material as a function of lithiation. To improve the data interpretation of PES spectra, a range of battery electrode model systems are investigated. These results show shifts of the SEI peaks relative to the electrode specific peaks as a result of the SEI thickness and the presence of a dipole layer. Also other electronically insulating composite electrode components show relative peak shifts as a function of the electrochemical potential.

To summarize, these studies investigate a number of well recognized aging mechanisms in detail and also establish additional processes contributing to aging in Si electrodes. Furthermore, this work highlights phenomena that influence data interpretation of PES measurements from battery materials.

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List of Papers

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


III Lindgren, F., Xu, C., Marcinek, M., Niedzicki, L., Gustafsson, T., Björefors, F., Edström, K., Younesi, R. (2016) SEI Formation and Interfacial Stability of a Si electrode in a LiTDI Based Electrolyte with FEC and VC additives. *Submitted manuscript*

IV Lindgren, F., Rehnlund, D., Younesi, R., Xu, C., Edström, K., Nyholm, L. (2016) Aging mechanisms of composite nano-Si electrodes in a Li-ion battery half-cell. *In manuscript*

V Maibach, J., Lindgren, F., Eriksson, H., Edström, K., Hahlin, M. (2016) The electric potential gradient at the buried interface between lithium-ion battery electrodes and the SEI observed using photoelectron spectroscopy. *Submitted manuscript*


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Contributions to the papers

Paper I  Contributed to the experimental work and took part in all discussions

Paper II  Planned and performed most of the experimental work, took part in all discussions and wrote the manuscript.

Paper III  Planned and performed most of the experimental work, took part in all discussions and wrote the manuscript.

Paper IV  Planned and performed most of the experimental work, took part in all discussions and wrote the manuscript.

Paper V  Contributed to the discussions on PES data interpretation and the manuscript.

Paper VI  Planned and performed the experimental work, took part in all discussions and wrote the manuscript.
Other publications to which the author has contributed that are not included in the present thesis:


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Grundämnet kisel har en möjlighet att ersätta och förbättra dagens negativa elektrodmaterial i litium-jonbatterier. Detta skulle innebära att batteriet kan lagra mer energi per vikt och volym och att batteriernas prestanda ökar. Därför kan lagring av förnybar energi från sol och vindkraft bli mer lönsam samtidigt som fossila bränslen i exempelvis fordon kan ersättas med bättre batterier.

Kisel är ett av de vanligaste grundämnen på jorden och ingår i bland annat sand och många mineral. Tillgången är alltså god och kisel har inga negativa effekter på miljö eller människors hälsa. Tillverkningen av rent kisel sker redan på stor industriell skala inom halvledarinstrustrin där det till exempel används i olika elektronikkomponenter och solceller.


Det finns många sidoreaktioner som bidrar till att ett batteri tappar kapacitet eller ”åldras”. För just Li-jonbatterier är ett vanligt exempel på en sådan sidoreaktion bildandet av ett ytskikt som i batterisammanhang kallas för ”solid electrolyte interphase” eller kort SEI. Detta SEI-skikt bildas på negativa elektrodmaterial på grund av att de lösningsmedel som används i elektrolyten inte är stabila vid de låga spänningar som dessa elektroder arbetar vid. När SEI-skiktet bildas genom nedbrytning av lösningsmedel förbrukas också batteriets laddning och batteriets prestanda försämras. För att inte batteriet ska tappa kapacitet är det viktigt att SEI-bildandet avstannar. SEI-

![Figur 1. Urladdningskapacitet som en funktion av antal laddningscykler för ett batteri där den positiva elektroden består av litiumjärnfosfat och den negativa elektroden är baserad på nanometerstora kiselpartiklar.](image-url)

Också saltet i elektrolyten påverkar kiselpartiklarnas yta och det traditionellt sett mest användna saltet för Li-jonbatterier, LiPF$_6$, kan vara aggressivt mot den naturliga oxiden på partiklarnas yta. I den här avhandlingen har ett nytt salt, LiTDI, prövats tillsammans med kiselelektroder. Ytanalyser har då visat att dessa sidoreaktioner försvinner. Även om detta är en mycket positiv effekt är det svårt att visa hur detta påverkar en kiselelektrod i det långa loppet. Detta beror på att det finns många andra sidoreaktioner som har större inverkan på elektrodens prestanda än bara partiklarna ytstabilitet.

I detta arbete har även en annan process som bidrar till att kapaciteten minskar i kiselelektroden identifierats. Detta sker genom att Li hålls fast i kiselmaterialet och blir svårt att extrahera. Med långa urladdningsperioder går en stor del av detta Li att få tillbaka men det är troligt att en ännu större del ändå finns kvar i kiselpartiklarna.
Många av de reaktioner som pågår i en kiselektrod sker på partiklarnas ytor. Därför är ytanalys av dessa ett av de bästa verktygen för att spåra de reaktioner som skett och följa, bland annat, hur SEI-lagret byggs upp.


Avslutningsvis har detta arbete ha bidragit med att påvisa effekter från traditionella elektrolyter. Dessutom har ett nytt elektrotylalternativ baserat på saltet LiTDI utarbetats och dess egenskaper för kiselbaserade elektroder påvisats. Vidare har många processer och sidoreaktioner i en kiselelektrod identifierats och deras påverkan på elektrodens prestanda har utvärderats. Högenergetisk fotoelektronspektroskopi är en av få metoder som kan användas för att analysera kisel och dess reaktionsprodukter när de används i litiyumjonbatterier. En ökad insikt i hur resultat från sådana mätningar påverkas av olika elektrodmaterial och processer som pågår i batterier kommer också bidra till en förbättrad tolkning av framtida resultat.

Förhoppningen är att denna avhandling leder till vidare undersökningar av de mekanismer som påverkar kiselelektrodens funktion. Högenergetisk fotoelektronspektroskopi är ett verktyg som kan påvisa hur kiselektroden påverkas under upp- och urladdningar och ytterligare mätningar kan bidra till en ökad förståelse för processer som bidrar till försämrad kapacitet. Inte heller arbetet med att kartlägga de mekanismer som påverkar kalibreringen av fotoelektronspektroskopidata slutar här utan är en process som komemr att behöva uppdateras, i synnerhet när nya elektrodmaterial analyseras.
Introduction

Our society relies on a continuous energy supply to function properly. At present, a large fraction of this energy comes from fossil resources and greenhouse gas emissions from these threaten the stability of our climate. To mitigate these effects, more renewable energy need to be implemented in the energy system [1]. Examples of renewable energy sources are: biopower, hydropower, as well as wind and solar power [2]. A challenge for all these systems is the energy storage. Biomass degrades over time and requires well developed infrastructure [3]. Hydropower requires large water reservoirs which affect nature and wildlife [4]. Solar and wind power produce energy only when the sun is shining or when the wind is blowing. If the energy is not used right away, some kind of storage is needed.

A wide variety of energy storage systems are currently in use and these stretch over a broad range of technical solutions. Hydropower and pumped hydro rely on the potential energy of water at elevated altitudes. Electro-mechanical storage utilizes both the potential energy in e.g. compressed air but also the kinetic energy in flywheels etc. Thermal energy storage is used both domestically but also on larger scales. In batteries, electrical energy is transformed to chemical energy by electrochemical reactions [5].

In Figure 2 the worldwide energy storage for cycle durations longer than four hours is considered. The installed capacity from pumped hydro accounts for a quantity on the GWh scale while the capacities of the other techniques are better presented in MWh. However, the expansion of pumped hydro storage technology is limited to a few geographical locations and requires large infrastructure investments. To enable a more delocalized and versatile energy storage from renewable sources, electrochemical storage in batteries is a possible approach which fairly easily could be implemented in the power grid [6]. Batteries can even offer a mobile energy storage system that already today powers e.g. electric vehicles.
Figure 2. Installed energy storage worldwide designed for energy delivery durations longer than 4 h [7].

Although batteries present a promising way of storing energy, it is so far an expensive technology. Also the environmental impact from battery production should be considered for the whole life cycle of the battery [8]. By improving the performance and lowering the cost of Li-ion batteries, more renewable energy can replace fossil fuels and thus decrease the environmental impact from human activities.
Li-ion batteries

A battery is a device that uses chemical reactions to produce electric energy. If it is possible to reverse the chemical reactions by supplying electrical energy, the device can be recharged and is then referred to as a secondary battery. The very first battery was constructed by Volta in 1799 and was built up by zinc and silver discs using cardboard soaked in acid as separator and electrolyte, respectively [9]. Many different battery systems have been constructed since then. Some examples of the more familiar ones in the category of secondary batteries are the so called nickel cadmium batteries, lead acid batteries, nickel metal hydride batteries and the family of Li-ion batteries [10]. Each battery chemistry has different properties, but the Li-ion batteries generally offer higher capacities and longer lifetimes compared to the others and yet the performance of these kinds of batteries is still expected to improve [11]. The benefit of using Li in batteries stems from the high eagerness of Li to share its electron and its low atomic weight and size [12].

Li has been used in battery research since the 1970s [13] and the first commercial Li-ion battery was developed by Sony and released in 1991 [14]. This battery used lithium cobalt oxide as positive electrode and a carbonaceous material on the negative side [15]. More or less the same materials are still in use but nowadays also other alternative materials have reached the commercial stage [12]. Examples of commercialized positive electrode materials are lithium iron phosphate and various types of lithium metal oxides based on nickel, manganese and cobalt. The negative side is still dominated by carbon-based compounds but lithium titanate and also small additions of silicon (3-5%) is being used for commercial cells [16]. The electrolyte is mainly based on organic carbonates and a lithium salt but commercial cells usually have many different additives to achieve certain properties [17].

The Li-ion battery can be produced in various sizes and shapes depending on the application. Some different examples of Li based batteries are presented in Figure 3. The variety of electrode materials and electrolyte compositions also allow for many different possible combinations to make up a complete Li-ion battery. Each different material has its unique properties and by careful choice of materials, certain properties can be enhanced to render a battery suitable for specific conditions.
Figure 3. Different kinds, formats and shapes of Li based batteries. 1 - Lab scale half-cell (Li-metal vs. Si), 2 - Cell phone battery, 3 – Laptop cell (18650-type) 4 – Primary Li-metal button cell, 5 – Laptop cell, 6 – Electric vehicle cell.

For all batteries, cost, safety and environmental impact are crucial parameters. Anyhow, batteries for electric vehicles require high safety even more and also fast charge and discharge possibilities. Batteries for large scale storage, on the other hand, may have other systems to control safety, thus cost and environmental impact are perhaps the most important parameters. Batteries for consumer electronics require high volumetric capacities but are less cost sensitive.

The safety concern is a righteous one due to incidents reported for consumer electronics, electric vehicles as well as aircrafts relying on these batteries [18]. Indeed, a battery as an energy provider is in general a risky device as the two reacting components (negative and positive electrode) are kept at micrometer distances in a container. In this aspect, batteries are very similar to explosives where both fuel and oxidizers are kept together and the energy can be released by relatively low activation energy. When a battery is working according to plan, the separator makes sure that both electrodes are not in contact and the outer circuit restricts the rate of the chemical reactions to avoid excess heat and detrimental side products. In the case of unforeseen actions such as overcharging, overheating or short circuit, the reactions may
proceed spontaneously and the risk of thermal runaway resulting in fire or explosion of the flammable organic solvents is impending. However, a lot of work has been conducted in order to improve Li-ion battery safety and with proper means and precautions the safety seems to be within control [19-20].

If energy storage in Li-ion batteries should become more implemented in the energy system, it must be assured that the production, use and recycling of these actually have a positive impact on the climate. In this sense, life cycle assessment of battery systems should be performed from the harvest of new materials to the recycling process. To reveal the true impact of the use of batteries, any emissions from production and recycling should be divided by the total capacity delivered by the battery over its lifetime. Indeed, Li-ion batteries have a good lifetime relative to other battery technologies and for this reason, they also have a relatively low environmental impact [21]. However, it should be emphasized that nothing is gained, in terms of environmental impact, unless it is renewable energy that is stored in the batteries.

Also, when considering the cost, the most important parameter is the lifetime of the battery. If the initial cost is divided by the amount of energy that the battery can store during its lifetime, the true cost of the battery is revealed. With this in mind, a battery that has an infinite lifetime could be allowed to have a very high initial cost. Unfortunately, the lifetime of Li-ion batteries is not infinite. Perhaps even worse, the lifetime is very complicated to predict. Thus, it is challenging to make environmental and economical predictions. However, it is clear that the performance and the lifetime of Li-ion batteries are parameters that need to be further improved.
Li-ion battery construction and operating principles

The Li-ion battery is comprised of a positive and a negative electrode that both can store Li. It also requires an electrolyte for Li-ion transport between the electrodes and an external circuit for electron conduction. In the charged state Li is stored in the negative electrode. During discharge the external circuit is closed and a Li-ion and an electron will leave the negative electrode and start to move towards the positive electrode material. However, the ions can only be transported through the electrolyte and electrons are only able to flow in the external circuit. When the electrons are moving through the circuit they can be used to power an electrical device. A schematic illustration of this is presented in Figure 4.

In a secondary Li-ion battery, the Li-ion and the electron are possible to force in the reversed direction by applying an external potential and by doing this, the battery is charged. These processes can be repeated over and over again and a Li-ion battery can maintain most of its original capacity for thousands of cycles [22].

In Figure 4, the so called half-cell reaction that takes place at the negative electrode during cycling is

\[
LiC_6 \rightleftharpoons C_6 + Li^+ + e^- \quad (1)
\]

and the half-cell reaction proceeding at the positive electrode is the following

\[
2 Li_{1/2}CoO_2 + Li^+ + e^- \rightleftharpoons 2 LiCoO_2 \quad (2)
\]

Together these two half-cell reactions results in the overall cell reaction

\[
LiC_6 + 2 Li_{1/2}CoO_2 \rightleftharpoons C_6 + 2 LiCoO_2 \quad (3)
\]

When discharging the cell, these reactions proceed from left to right until the graphite material is basically empty or the LiCoO₂ is full. At that point the cell potential decreases abruptly and the discharge operation is terminated. An example of how this appears in a typical cycling curve is presented in Figure 5 for a cell using a LiFePO₄ positive electrode and a Si based negative electrode.

When charging the battery, reaction schemes 1, 2 and 3 proceed from right to left. During the charge, the cell potential increases slowly until the point where the negative electrode material is fully lithiated or when the positive material is completely empty. As this happens, the cell potential will increase rapidly and the charge is stopped at a certain cut off value. Also this is depicted in Figure 5.
The overall cell reaction proceeds at different rates depending on battery specific factors such as electrode material, electrical conductivity and electrolyte properties but also on external factors such as temperature etc. If these reactions can occur at high rates it allows for large charge and discharge currents, which means that the battery can be charged and discharged within short time frames. However, if these reactions proceed at too high rates, excess heat will be produced with the risk of battery degradation and failure. A common metric for batteries is the C-rate describing the current required for a certain charge or discharge duration. The discharge rate C/10 e.g. means that the full capacity of the battery is delivered over 10 hours. At 1C the capacity is extracted in one hour and at 10C the discharge lasts for only one tenth of an hour.

However, even with moderate C-rates, also unwanted reactions occur in the battery that are not completely reversible and over time these may worsen the battery functionality. All these reactions and mechanisms that degrade the battery performance are commonly called aging. To make the Li-ion battery work better, it is important to identify the aging mechanisms and to find materials that can minimize side reactions.

Figure 4. Schematic picture of a Li-ion battery with a LiCoO$_2$ positive electrode and a graphite negative electrode during discharge.
Materials in the Li-ion battery

To achieve a battery with a high energy density, both the cell potential and the electrode capacities should be high. The cell potential ($E_{cell}$) is the difference between the half-cell reaction potentials for the two electrodes and can be expressed as:

$$E_{cell} = E_{\text{positive electrode}} - E_{\text{negative electrode}}$$

(4)

The resulting cell potential for a full cell Li-ion battery can thereby be deduced from Figure 6 for some selected electrode materials. An example of a cell comprised of a LiFePO$_4$ (LFP) positive electrode and a Si negative electrode is presented in Figure 5 where the cell average working potential is about 3 V vs. Li$^+$/Li.

In Figure 6 also the electrode gravimetric capacities are presented. This capacity is determined by the amount of Li that can be cycled reversibly (in theory or in practice) divided by the mass of electrode material. Note that, in Figure 6, the scale of the positive electrode materials is one tenth of that for the negative electrode materials. The gravimetric capacity should normally be considered relative to the weight of the entire battery unit. However, in research on electrode materials, gravimetric capacities are usually given for the electrode materials that are the focus of the research.

![Figure 5. Cycling curve of a lab scale battery comprising a LFP positive electrode vs. a nano-Si negative electrode. The capacity as a function of cycle number for this cell is presented in Figure 1.](image-url)
Positive electrodes

The positive electrode materials are dominated by transition metal oxides and lithium poly-anionic compounds. The very first commercial cathode material used was LiCoO$_2$ and this material is still employed today [12]. Cobalt, however, has some drawbacks in terms of structural stability [23] and mining of cobalt is many times a questionable business [24]. To circumvent these issues other metal oxides such as LiMnO$_2$, LiNiO$_2$ and LiFeO$_2$ have been investigated but they all suffer from poor stability and insufficient cycling performance [25]. By synthesizing oxides with mixed metals, the structural stability can be increased and nowadays there are examples of commercial cathode materials such as LiNi$_{0.8}$Co$_{0.15}$Al$_{0.05}$O$_2$ and LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$. Also other types of oxides have been investigated, and spinel LiMn$_2$O$_4$ (LMO) is one example that has reached the commercial market [16].

Instead of relying on the O$_2^2-$ anion, larger poly-anions such as SiO$_4^{4-}$, PO$_4^{3-}$ and SO$_4^{2-}$ may provide increased structural stability [26]. A well known member of the poly-anionic class of positive electrode materials is the olivine type LiFePO$_4$ (LFP). The successful commercialization of this material, despite its relatively poor electronic and ionic conductivity, is possible due to nano-sized particles and conductive coatings [27]. The achievements regarding LFP have triggered research on similar poly-anionic materials such as Li$_2$FeSiO$_4$ (LFS) [28], LiFeSO$_4$F [29] etc. and it is possible that future positive electrodes will stem from this group of materials.

Figure 6. Potential and gravimetric capacities for different positive and negative electrode materials.
Negative electrodes

The ideal negative electrode for the Li-ion battery would be metallic Li. This would give both high volumetric (2047 mAh cm\(^{-3}\)) and gravimetric capacity (3862 mAh g\(^{-1}\)) [30], a high cell potential and no need of an additional current collector. Unfortunately, the use of metallic Li is a risky choice because during charge, uneven deposition of Li may form so called dendrites which could lead short circuit and thermal runaway [31]. There have been attempts to avoid dendrite formation by employing different additives in the electrolyte and by replacing the liquid electrolyte with a solid electrolyte or a protective membrane [32-34]. A commercial example of the solid polymer electrolyte used with lithium metal electrodes is the batteries provided by Bolloré [35]. Even if this is a step forward for the Li metal negative electrode, the solid polymer electrolytes do not allow for the high charge and discharge rates required in all applications.

To circumvent dendrite problems, various types of carbon materials are used as negative electrodes which can significantly decrease the dendrite formation problem. The first commercial Li-ion battery comprised a petroleum coke amorphous carbon negative electrode [15] although nowadays, natural graphite power the majority of commercial Li-ion batteries. Compared to lithium metal, carbon materials have a slightly higher lithiation voltage and the theoretical capacity for the fully lithiated graphite is 372 mAh g\(^{-1}\). Although this capacity is more than twice as large as those for most cathode materials, it is about ten times lower compared to the value for metallic lithium. In the graphite structure, Li-ions are intercalated in between graphene layers and up to one Li for each six C atoms can be stored, forming the LiC\(_6\) phase [36]. Also synthetic graphite has been investigated and the properties of this material can be tuned to suit certain electrochemical applications, but the production requires high temperatures and it is not a cost competitive alternative. Hard amorphous carbons have higher reversible gravimetric capacities but the volumetric capacities are worse than for graphite [37-38].

Another intercalation material that is successfully commercialized as a negative electrode is Li\(_x\)Ti\(_5\)O\(_{12}\) (LTO) [16]. The electrochemical performance of LTO offers a flat lithiation plateau at 1.55 V vs. Li\(^+/Li\) and a theoretical capacity of 175 mAh g\(^{-1}\) [39]. The relatively high lithiation potential and the low gravimetric capacity result in an electrode with a fairly low energy density compared to graphite. On the other hand, the high potential results in almost no side reactions with the electrolyte [40] and also enables the use of aluminum current collectors. This is both a cheaper and lighter alternative compared to the copper current collectors used for most other negative electrodes [41]. Although LTO is a poor electron conductor and the lithiation kinetics is fairly slow, modifications such as particle size decrease and surface coatings now present LTO as a material with high charge and
discharge rate capabilities [16]. Cycling of LTO negative electrodes has been successful for more than ten thousand cycles [42].

A second class of materials relies on the formation of intermetallic or alloy compounds with lithium. This could potentially increase the performance of the Li-ion battery since the theoretical volumetric and gravimetric capacities are considerably higher than for the intercalation compounds [30]. Materials that are included in this group are i.e. Si, Sn, Sb, Al and Mg and mixtures of them. Among these Si has the highest energy densities and has therefore been the subject for intense research efforts. Common for all these materials is the large volume expansions that make reversible cycling problematic and commercially only small additions of Si in negative electrodes have been reported [43]. Since Si is the main focus in this thesis, more in depth information will be shared in a coming section.

A third class of possible future negative electrode materials also exists and includes so called conversion type materials. A wide variety of compounds such as transition metal oxides, hydrides, fluorides, carbonates and many more have the possibility to take up and release Li-ions reversibly. These materials are generally simple and cheap to produce and offer higher capacities than graphite. On the downside, the voltage hysteresis is relatively large and the charge and discharge processes thus feature a poor energy efficiency [44].

Electrolytes

In commercial batteries the most widely used electrolyte system is based on a Li salt dissolved in an organic carbonate liquid phase. This is a fairly simple electrolyte with excellent Li transport properties. However, the organic carbonates operate outside their stability window on the negative electrode side and are depending on the formation of an efficient solid electrolyte interphase (SEI). Also the flammable nature of these carbonates poses a safety concern [15]. Polymer electrolytes have been used commercially as mentioned earlier and are a safer alternative but require slower charge and discharge rates [45]. A gel polymer electrolyte is a mixture of the solvent based electrolyte and the solid polymer electrolyte and thereby combines the properties of the two [46] and has also been utilized in commercial cells [47].

The development of the existing electrolyte alternatives is an ongoing research field but investigations of new classes of possible future electrolyte systems are also in progress. Among these, ceramic [45] and ionic liquid electrolytes [48] have unique properties that may be suitable for certain battery applications. In this thesis organic carbonate electrolytes are used with both well known and newly introduced salts as well as additives aimed to improve the electrode performance.

Several salts have been investigated for use in Li-ion batteries with varying success. These stretch from purely inorganic salts such as LiAsF₆, LiPF₆ and LiClO₄ etc. to more organic salts like lithium bis(trifluoromethyl)
sulfonimide) (LiTFSI) and lithium 4,5-dicyano-2-(trifluoromethyl) imidazolide (LiTDI). The structural formula of LiPF₆ and LiTDI are presented in Figure 7. A number of the salts are considered toxic or explosive while other yield inefficient SEI layers while some have negative effects on aluminum current collectors [49]. The most widely used salt in commercial Li-ion batteries is undoubtedly LiPF₆ although the chemical and thermal stabilities of this compound are questioned. Also, in case of battery malfunction and accidents the LiPF₆ salt may form toxic substances [50]. It is worth mentioning that different electrode material may have special requirements in terms of salt properties and it is important that possible decomposition products are not harmful to any components in the battery.

Solvents for electrolytes must have a polarity high enough to allow Li salt dissolution and at the same time withstand the potentials present in the Li-ion battery without decomposing. These requirements are not easily fulfilled since a range between 0 and 5 V vs. Li⁺/Li is reality for most Li-ion batteries. In commercial cells mixtures of e.g. ethylene carbonate (EC), diethyl carbonate (DEC), dimethyl carbonate (DMC) etc. are usually used which yield a good solubility of Li salts [51]. The structural formula of DMC and EC is presented in Figure 7.

Electrolyte additives are used to provide different properties related to SEI formation, safety and overcharge protection. SEI forming additives such as FEC and VC (also in Figure 7) can form polymeric species improving the stability and the safety of the negative electrode. Also flame retardant additives as well as overcharging redox shuttles have been investigated in order to enhance safety. Commercial cells may have a complicated electrolyte composition with many additives to ensure specific properties of the battery [17].

![Figure 7. Structural formula for LiPF₆, LiTDI, DMC, EC, VC and FEC.](image-url)
Inactive battery components
The previously mentioned materials are all active in the chemical reactions. To support these materials a number of inactive battery components are required which also are crucial to the battery performance. These are e.g. binders, conductive additives, separators, current collectors and the outer casing.

Modern Li-ion battery electrodes are so called composite electrodes. These usually consist of micro- or nanometer sized particles, a polymeric binder and a conductive additive. The purpose of the binder is to keep the active particles together and attached to the current collector. Binders are traditionally based on polyvinylidene difluoride (PVdF) but the benefits of using water soluble binders are becoming more and more apparent, especially in the research on new negative electrode materials. Replacing solvent based chemistries with water based alternatives is good from both a health and an environmental perspective. To enhance the electrical wiring a so called conductive additive is usually included in the composite. These comprise various types of soft carbons, carbon nanotubes or fibers that are dispersed in the composite coating.

To keep the positive and the negative electrodes apart a so called separator is required. This is usually an electronically insulating and porous sheet that allows for Li-ion diffusion. Many times these comprise a polymeric membrane based on polyethylene or polypropylene. The separator is subject to a considerable amount of research since it is an expensive component. Also, the possibility to stop dendrite formation by the separator is considered a viable way for metallic Li to be used in commercial cells.

Electrode composites are deposited on the current collector (a metallic foil) that governs the electron transport out of the battery. The positive electrode usually uses an aluminum current collector while the negative electrodes are coated on copper. This part of the battery has a major impact on the overall environmental and cost balance since aluminum production is an energy demanding process and copper is expensive due to limited resources.

Finally some kind of packaging is required to protect the components from air and moisture which otherwise would destroy the battery. Materials used for packaging usually include air and moisture tight metallic and plastic containers.
Reactions and aging mechanisms in the Li-ion battery

An example of the full cell reaction in a Li-ion battery is given in Scheme (3). The redox reactions of the active materials are the primary reactions in the battery and ideally these would be the only ones. However, as observed in the example of LiCoO₂, only half of the Li-ions in the material are possible to cycle reversibly. If more than half of the Li-ions are extracted, the atomic structure of the host material may collapse and the battery will lose capacity. The structural instability of the materials is only one of many sources for battery degradation or aging. In Figure 1, a typical plot of the capacity vs. cycle number shows decreasing capacity due to one or several aging mechanisms. Another rather familiar observation of aging is the inflation of Li-ion batteries due to internal gas evolution as a result of overcharging and decomposition of electrolyte solvents [52]. One such example of an inflated Li-ion battery is shown in Figure 8.

![Figure 8. Gas evolution inside a Li-ion battery due to overcharging (left) and an identical cell before overcharging (right)](image)

Aging mechanisms for positive electrode materials are often connected to changes in the crystallographic structure as in the example of the LiCoO₂ above. The intercalation mechanism of these materials also depends on a stable structure to maintain a good Li-ion transportation. Another mechanism that degrades the performance is the cation dissolution into the electro-
lyte. In this process, the redox active metal is lost from the active material and the amount of redox active sites decreases and in turn, the capacity fades [53]. Another problem associated with the cation dissolution is that cations may end up at the negative electrode and cause an acceleration of the SEI growth on the negative electrode, also resulting in a fading capacity [54].

SEI formation is indeed a major source for aging in negative electrodes [55]. It is necessary that the SEI offers good Li-ion conductivity and electrical insulation. The SEI should also be an impermeable layer that prevents solvent diffusion to the electrode. The SEI layer usually consist of compounds such as LiF, Li alkyl carbonates, Li₂O etc. In the formation of these compounds, charge is irreversibly consumed and the battery capacity will decrease. Therefore, the SEI properties are crucial and the SEI formation must be kept at a minimum level to avoid capacity losses in full cell batteries. Also the structural integrity is threatened in, e.g. graphite negative electrodes as not only Li may be intercalated into its structure. An exfoliation of the graphene sheets may occur as result of intercalation of larger molecules such as solvents, also resulting in decreased performance [56].

Even the integrity of the entire composite electrode and inactive components may be subject to aging mechanisms. This could be due to, i.e. mechanical stress as a function of volume changes during cycling [55] or due to binder decomposition resulting in deterioration of the composite structure [57].

All aging mechanisms mentioned herein may affect the electron and Li-ion transport in the electrolyte and in the active materials. If the kinetics of these processes is hindered this would result in an increasing overall cell resistance. In turn the half-cell reaction potential would be shifted and the energy efficiency would decrease. Also any cutoff limits would be reached earlier meaning that the battery effectively will lose capacity.

To summarize, the Li-ion battery may be subject to many different side reactions that may impair its performance and each component of a battery has its individual aging mechanisms. Efforts on many fronts are therefore required to mitigate battery aging and to improve the lifetime. By increasing the lifetimes, the cost and environmental impact of batteries may be decreased.
Si as negative electrode material

Si is one of the most abundant elements on earth, it is non toxic, cheap, and is produced in large quantities for the semiconductor industry. The very first electrochemical lithiation of Si was performed at elevated temperatures in the 1970s and proved that reversible cycling was possible [58]. During lithiation several crystalline phases corresponding to the Li-Si phase diagram have been observed in the galvanostatic cycling curve. The most lithiated phase, Li$_{4.4}$Si, has a theoretical gravimetric capacity of about 4200 mAh g$^{-1}$ which even exceeds that for lithium metal itself [59-60].

At room temperature the lithiation of crystalline Si appears differently and none of the phases observed at elevated temperatures are present. Instead, the lithiation of crystalline Si has a flat plateau around 0.1 V vs. Li$^+/Li$, see Figure 9, indicating that a two phase addition reaction is taking place. It is shown by XRD that during this two-phase reaction, the crystalline Si is transformed into an amorphous Li-Si compound [61]. By the end of the lithiation, when approaching 0 V vs. Li$^+/Li$ the crystalline Li$_{3.75}$Si phase has sometimes been observed [62-64] and sometimes not [65-66]. The formation of Li$_{3.75}$Si proceeds through the following reaction scheme:

$$3.75 \text{Li} + \text{Si} \rightleftharpoons \text{Li}_{3.75}\text{Si} \quad (5)$$

and the resulting theoretical capacity for this phase is 3579 mAh g$^{-1}$. Even though this phase is sometimes detected and sometimes not, its presence is revealed during de-lithiation where the curve experiences an extra plateau around 0.45 V vs. Li$^+/Li$. This short plateau is also observed during the first de-lithiation (Figure 9).

Figure 9. The first lithiation and de-lithiation of a crystalline nano Si electrode. The inset presents the details during the SEI formation at an early stage in the lithiation step.
The presence of this phase seems to depend on the cycling rate as it is formed during lithiation at low C-rates [43]. If this phase is avoided, either by a cutoff value or by the use of high cycling rates, the de-lithiation curve exhibits a more sloping shape with two quasi plateaus [64, 67]. The lower potential quasi plateau has been suggested to stem from de-lithiation of an environment where the majority of the closest neighbors are Li atoms while the higher plateau would stem from de-lithiation of an environment where the Si atoms make up the closest neighbors [68-69]. Likewise, during lithiation the higher quasi plateau would be insertion of Li with mainly Si neighbors and the lower plateau, Li insertion with mainly Li in the closest vicinity. The overall sloping behavior of the cycling curve resembles the lithiation and de-lithiation curves seen for a solid solution [43]. The detailed local order in Li-Si materials formed at room temperature in Si electrodes is complex and numerous investigations have presented a wide variety of local Li-Si arrangements [70-74].

When inserting as much as 3.75 Li for each Si atom, a volume increase in the range of 280% is expected [62]. This is schematically depicted in Figure 10 where a gradual transformation of Si to Li$_{3.75}$Si is presented from left to right. This causes internal stress and may result in fractures of the Si material which in turn may lead to loss of electrical contacts and poor cycling performance [75]. By decreasing the Si particle size to the nanometer scale major improvements have been achieved [76-78]. For Si particles, the upper size limit to avoid fractures has been reported to be in the range of 150 nm [79]. Even with particles of approximately this size reports have indicated formation of smaller particles [80]. A similar example from this work is presented in Figure 11 where SEM micrographs before and after 100 cycles reveal a particle size decrease as a function of cycling.

![Simulation of the lithiation reaction of crystalline Si (left) gradually transformed to Li$_{3.75}$Si (right). Reprinted with permission from [81]. Copyright (2012) American Chemical Society.](image-url)
Rather poor cycling performance of Si based electrodes is achieved when using PVdF based binders [77, 82], which otherwise are the standard binding agents for other electrode materials. By substituting the PVdF binder with water based polymeric binders such as Na-CMC [82-84], poly acrylic acid [85-86] and alginate [87] major improvements have been achieved concerning the cycling performance. One common denominator for these binders is the carboxylate group which has been attributed to have good binding properties towards the active Si material [84, 87], a binding mechanism that can be improved further by the use of a pH 3 buffered solution during the composite preparation step [88-89].

The electrolytes used for the vast majority of research on Si based electrodes are undoubtedly based on the LiPF₆ salt in different carbonate mixtures [90-97]. Only a few studies of alternative electrolyte salts have been reported with some improvements in cycling performance [92, 98-99]. However, the major improvement in the cycling performance of electrolytes for Si-based electrodes came with the introduction of SEI forming additives such as FEC and VC into the electrolyte [100-104].

The SEI formed by LiPF₆ based electrolyte on Si consists of e.g. Li alkyl carbonates, LiF, Li₂CO₃, Li₂O, etc. from the breakdown of the electrolyte [90-97]. In general the products that make up the SEI on Si electrodes are the same as those found in the SEI on graphite and Li-metal negative electrodes [105]. This is perhaps not surprising as the electrolytes investigated so far have similar compositions. However, the volume changes for Si electrodes during cycling are much more significant than for graphitic electrodes. With volume expansion new surfaces may be exposed which require further SEI formation and this may become a continuous process. Another important aspect is that graphite electrodes generally consist of micrometer sized particles while Si electrodes often are comprised of nanometer sized particles. This means that the overall surface area of a Si electrode is many times larger and since SEI formation occurs on surfaces, the amount of SEI formation will increase with smaller particles.

With FEC additions to the electrolyte, the amount of LiF in these SEI layers increases significantly. Also, both FEC and VC have the possibility to form polymeric carbonates [101-104]. These two additives have attracted the largest interest and with the use of these, the cycling performance is enhanced. The benefit of these additives is generally considered to be due to the thinner and more resistant SEI. This suggests that an inorganic and polymeric rich SEI layer is preferred.

Although the above just mentioned concept may be the general consensus regarding the Si SEI, other studies report somewhat different results. Also FEC free electrolytes have shown SEI layers with high LiF contents (from LiPF₆ decomposition), good passivating properties and relatively low levels of other Li carbonate-like species. However, in this study an electrolyte with the FEC additive was suggested to further enhance passivation due to the
polymeric decomposition product rather than LiF [99]. Similar results were reported where the actual benefit of FEC addition were suggested to include the formation of a polymeric layer closest to the particles surface [106]. The SEI thickness has also been investigated using in situ ellipsometry and it was actually reported to be thicker with FEC and VC additives [107]. In addition, in this study the SEI was found to be dynamic in the sense that it was increasing during lithiation and decreasing during de-lithiation. Similar results are obtained by ex situ PES during the first cycle of Si electrodes [90] as well as on graphite electrodes [108]. An explanation for this behavior could be the dissolution of SEI components into the electrolyte [109-110].

It is important to emphasize that almost all investigations on Si electrodes have been performed in half-cells with a Li metal counter electrode, meaning that a large surplus of Li (and charge) is available. Thus, any consumption of Li in SEI formation will not lead to a capacity decrease of the Si material as new Li can be retrieved from the Li metal whenever required. However, if a thicker SEI results in slower Li transport, an increased polarization of the cell would be seen. With increased polarization the cutoff voltage is reached earlier and it will appear as a capacity loss.

Nonetheless, in a full cell the Li resources are limited and the continuous SEI formation is a feature that prevents Si electrodes from being commercialized. However, continuous SEI formation is by far not the only aging mechanism that exists for Si electrodes. As mentioned earlier, HF generated from the LiPF₆ and water is able to decompose and etch the Si oxide surface [91, 97, 111-112]. It seems reasonable that such an effect would be detrimental to the electrode but exactly how the oxide layer and its composition influence the cycling performance of Si based electrodes remains unclear [113-114].

Other mechanisms responsible for fading capacity are often connected to the volume variations during cycling resulting in decreased electrical contacts within the composite matrix or by complete loss of active material [115]. However, careful cycling data analysis has identified incomplete de-lithiation as the largest source for irreversible capacity in Si electrodes [116]. Li remaining within the amorphous Si material after de-lithiation has also been suggested [117] and recently detected with neutron reflectometry [118]. In connection with this, the slow reaction kinetics of Li-Si phases [67] and also the capture of Li by unsaturated Si atoms [119] could be a reasonable explanation. A similar discussion also exists for other intermetallic negative electrode materials [120-122].

Although a tremendous amount of work has been spent on finding the failure mechanisms of Si based electrodes and the SEI formation, a clear picture has not yet been realized. This indicates the importance to continue the research in new ways with different electrolytes and alternative approaches.
Figure 11. SEM micrographs showing the porous structure and the Si nanoparticles of a composite electrode in pristine condition at three different magnifications (a, c and e) and an identical electrode after 100 cycles in LiTDI based electrolyte with FEC and VC additives (b, d and f). From the top and down the magnification increases. From Paper III.
Scope of the thesis

This thesis is focusing on Si and some of its challenges associated with its use as a possible new negative electrode material in Li-ion batteries. The overall aim is to contribute to the general understanding of processes taking place in the Si electrode during lithiation and de-lithiation. One of the main objectives is to identify and pinpoint different aging mechanisms and how they influence the cycling performance. The purpose with this is to map the most important negative effects in order to establish where the effort for further improvements should be concentrated. One specific aging mechanism that should be addressed is the detrimental side effects on the Si material when LiPF$_6$ based electrolytes are used.

This thesis also targets to assess the desired properties of a more efficient SEI layer in order to provide a better insight of the functionality of this layer. A wider understanding of the SEI layer may be useful also for other battery materials.

Another main purpose with this work is to contribute to the knowledge base when using different kinds of PES as tools to investigate Si and its SEI formation. More specific, fundamental insights are required in the energy calibration of PES spectra not only for Si based electrode materials but also for other battery materials in general.
Methods

Half-cell assembly

To be able to evaluate the Si material during cycling, composite electrodes were produced according to the following procedures. The basis for these electrodes was a Si material, a binder and a conductive additive. The binder was a Na-CMC salt dissolved in a water:ethanol mixture or in a pH 3 buffered solution of KOH and citric acid. An amorphous carbon was also used to increase the electronic conductivity of the composite. These components were mixed thoroughly by ball milling to ensure a homogeneous mixing. The resulting paste was bar coated on Cu foil and dried. Also other types of electrodes were produced in this way to obtain electrodes with different active materials. Composite electrodes with positive electrode materials were fabricated in the same way with the same carbon black conductive additive but the binder in these cases was PVdF-HFP dissolved in N-methyl-2-pyrrolidone (NMP). These composite slurries were bar coated on Al foil. The active material made up roughly 80 wt% of the dry components, the binder about 10% and the carbon black (CB) conductive additive also about 10%. With the use of the buffered solution, the Si active material comprised 67% of the dried composite mass. In some experimental setups the working electrode was a pure Au or Cu disc.

All electrodes were dried under vacuum inside an Ar containing glovebox for at least 5 h at 120°C to remove water residues. Half-cells were then assembled where a lithium foil and the electrode were separated by a porous polyethylene sheet. A schematic drawing of this is presented in Figure 12. The two electrodes and the separator were placed in an aluminum reinforced plastic bag with metal tabs connected to the backside of the electrodes. The separator was soaked in electrolyte before sealing the pouch under vacuum.

Since one of the main focuses of this work was the interfacial stability of the active Si-material and the electrolyte, some different electrolytes have been used. LiPF₆ based electrolytes were used for Si electrodes as well as the positive electrode materials and the electrolyte based on LiTDI was investigated for Si-electrodes. Additives and their effect on the electrochemical performance on Si material were investigated for both salts.
Electrochemical characterization

Electrochemical methods are naturally the main analysis techniques for battery materials. By monitoring the potentials during the lithiation and delithiation steps, information regarding the development of the active material can be retrieved. A wide range of electrochemical tools for battery analysis exist and the ones used in this thesis are briefly described below.

Galvanostatic cycling or cyclic chronopotentiometry

In galvanostatic cycling a constant current is applied or extracted from the battery [123] and the cell voltage as a function of time is recorded. This presentation is a so called cycling curve and examples of cycling curves are presented in Figure 5 and Figure 9. The information obtained from cycling curves includes overall reaction potentials, kinetics and also the amount of charge or capacity that can be inserted or extracted during repeated cycling procedures. By comparing the charge obtained during the lithiation and delithiation processes, the amount of irreversible reactions can be monitored. The ratio of charge extracted divided by the charge inserted into the working electrode during a cycle is usually referred to as the cycling efficiency or coulombic efficiency.

In this work, galvanostatic cycling is the major technique used for battery evaluation and sample preparation for PES measurements. Depending on the material and the desired test, different currents, cutoff voltages or limited cycling capacities were used. For Si electrodes, both cutoff voltages as well as charge limited cycling were evaluated. The first cycle of Si based materials was generally performed with a considerably lower current than that used for extended cycling to allow for the initial amorphisation of Si.

Cyclic voltammetry

In cyclic voltammetry (CV) the voltage of the working electrode is increased or decreased at a constant rate between defined voltage values and the cur-
rent response is recorded [123]. The resulting voltammogram reveals the potentials required to achieve oxidation and reduction. CV was used as a complementary technique to form SEI-layers on metallic substrates.

**Chronoamperometry**
Chronoamperometry is a potentiostatic technique where a constant voltage is applied and the current response as a function of time is recorded. In this work, voltage steps were applied to extract residual amount of Li from the Si electrode and also to mimic continuous SEI formation.

**Electrochemical impedance spectroscopy**
This technique records the current response as function of a wide range of sinusoidal alternating voltage frequencies. Results from this technique are generally challenging to interpret but could provide details of the kinetics of processes within the active material and the SEI. However, in this work impedance spectroscopy was merely used to get a general overview of the total impedance of half-cells.

**Scanning electron microscopy**
In the scanning electron microscope (SEM), an electron beam is directed onto the sample and a detector collects the scattered electrons which are converted to a micrograph over the surface. SEM was used to get an overview of the surface morphology as a function of cycling for electrodes. Sample transfer to the SEM analysis chamber could not be made completely inert but the atmospheric exposure was minimized to about 1 minute.

**Photoelectron spectroscopy**
PES utilizes the photoelectric effect where high energy photons radiate a sample which responds by emitting photoelectrons. The energy of the emitted photoelectrons can be detected and yields a spectrum over the photoemissions as a function of binding energy. This process is schematically presented in Figure 13 where different energy levels result in a photoemission of a certain binding energy. The resulting binding energies can be used to identify the elemental composition of the sample and all elements except hydrogen can be subject to PES analysis.
Figure 13. Schematic representation of the photoelectric effect and the resulting PES spectrum of Cu.

Depending on the closest neighbors of a certain atom, the measured binding energy of a specific core level may vary to some extent. This variation is enough to get a hint on the character of the surrounding atoms. Together with core level spectra of other atoms in the sample, a picture of the composition can be obtained. An illustrative example showing the possibilities to distinguish between different chemical surroundings is presented in Figure 14 from the C1s photoemission of ethyl trifluoroacetate. Different neighboring atoms give rise to a peak shift - this is what usually is referred to as the chemical shift. The chemical shift arises due to the variation in core levels that are altered with the number of neighboring atoms and their electronic properties. In ethyl trifluoroacetate in Figure 14, the more electronegative surrounding of the carbon atoms results in a more positive chemical shift. As a result of this, the measured binding energies of these carbons increase with a more electronegative surrounding.
The spectrum is generated by analyzing the kinetic energy of the emitted photoelectrons from the sample. Binding energies are correlated to the kinetic energy by the following equation

$$E_K = h\nu - E_B - \phi_S - q\phi$$  \hspace{1cm} (6)

where $E_K$ is the measured photoelectron kinetic energy, $h\nu$ is the incoming photon energy causing the photoemission (excitation energy), $E_B$ is the binding energy of the emitted photoelectron, $\phi_S$ is the spectrometer workfunction, $q$ is the electron charge and $\phi$ is the surface potential of the studied photoemission. Out of these parameters, the kinetic energy is measured but the excitation energy as well as the spectrometer workfunction are known. For the sake of simplicity, the surface potential is many times set to zero allowing the binding energy to be calculated. For highly conducting samples this is an appropriate simplification but for insulating materials this surface potential should be considered and a further discussion on this topic is presented in a later section. A schematic energy diagram of the relationship between these parameters is presented in Figure 15. In this figure the Fermi level ($E_F$) of the sample and the spectrometer are aligned since they are in electrical contact.
Surface sensitivity

Photoelectrons that travel through a sample are likely to interfere with other atoms and may then lose some of their kinetic energy. These are the so-called elastically scattered photoelectrons which will produce a background in the spectrum. Photoelectrons that manage to reach outside the sample without losing its energy are the inelastically scattered photoelectrons and they give rise to the emission lines or peaks observed in the spectra as in, e.g. Figure 13 and Figure 14. The intensity ($I$) of photoelectrons from the distance ($d$) into the sample can be expressed by the following equation

$$I(d) = I_0 e^{-(d/\lambda \sin \Theta)} \quad (7)$$

where $I_0$ is the intensity due to photoelectrons at the very surface, $\lambda$ is the inelastic mean free path (IMFP) for a photoelectron moving through the sample and $\Theta$ is the angle between the sample surface and the detector. In Figure 16a, the probability of a photoelectron to reach the surface is depicted as a function of distance into the sample expressed in $\lambda$. The major part of the photoelectrons that manage to escape the sample without being elastically scattered thus originate from the atoms close to the surface. According to Equation 7, the probability for inelastically scattered electrons decays exponentially and therefore 95% comes from a distance of $3\lambda$ within the sample.
Figure 16. a) The probability of inelastically scattered photoelectrons as a function of \( d \) expressed as IMFP or \( \lambda \). b) How the IMFP varies as a function of electron kinetic energy for pure elements, inorganic and organic compounds as described by Seah and Dench [126].

The value of the IMFP depends on the kinetic energy of the emitted photoelectron and in Figure 16b, the relationship between IMFP and photoelectron kinetic energy is presented. In PES photoelectrons of kinetic energies from 100 eV up to 10 000 eV are analyzed.

The kinetic energy of the photoelectron can be altered by changing the energy of the incoming photon. With soft x-rays (hundreds of eVs) this implies that \( \lambda \) is less than 1 nm. With Al K\( \alpha \) radiation (1.49 keV) the same number is 1 - 2 nm and with hard x-rays (2 keV to 10 keV) it is possible to obtain \( \lambda \) values in the range of 3 – 10 nm. By varying the incoming excitation energy a depth resolved picture can be obtained. This is schematically depicted in Figure 17 where an idealized layered structure is presented. It should be noted that these interpretations are valid for a specific photoemission, a constant IMFP and where each layer has a unique chemical shift. Nonetheless, this figure illustrates the concept of depth resolved PES analysis using different excitation energies.

If the sample is built up by a random distribution of components with different chemical shift, the appearance of the spectra will be independent of the excitation energy. This is further illustrated in the random structure sample presented in Figure 17 where the different components have different chemical shift and thus appear at different binding energies.
In this work PES is used to analyze mainly composite electrodes with a three dimensional structure of particles in the nano- and micrometer sized regime. Since the size of the analyzed surface is many times larger than that of a single particle, this means that the escape angle of the photoelectron is effectively independent on the sample angle vs. the analyzer. Another effect that should be considered for PES on a nanomaterial is the relative increase in signal from surface layers compared to flat surfaces [127]. This effect as well as the changing surface morphology makes surface layer thickness estimations complex.

PES in this work is used with different excitation energies to achieve a depth profile of the surface layers. The HIKE end station [128] at the KMC-1 beamline at the synchrotron facility BESSY II operated by the Helmholtz-Zentrum Berlin [129], was used for achieving high kinetic energy photoelectrons. Low kinetic energy PES is performed at the MaxIV synchrotron facility in Lund, Sweden, beamline I411 [130]. Also in-house PES (or XPS) was used with a AlKα radiation source of 1486.7 eV.

Figure 17. Schematic representation of a layered and a randomly structured material and the corresponding PES spectra when analyzed with different excitation energies.
Results and discussion

The basis for this thesis is work presented in six articles. A short summary of the basis for this thesis and the general findings follows here.

The etching of the Si surface by the use of LiPF$_6$ based salts is a recognized aging mechanism for Si electrodes. To address this issue, the FEC electrolyte additive and the resulting SEI layer is investigated for Si based electrodes. Although FEC enhances the cycling performance, the surfaces of the particles are still affected by the electrolyte (Paper I). A new electrolyte salt (LiTDI) is therefore investigated and the Si is shown to be stable towards this salt and its decomposition products. However, the cycling performance with this electrolyte is poor (Paper II). By using FEC and VC additives together with the LiTDI salt, a cycling performance comparable to that for LiPF$_6$ based electrolyte with FEC is achieved and the Si surface is not affected by etching (Paper III).

Although the LiTDI based electrolyte with additives presents a more stable alternative, the cycling performance is not significantly increased. Thus, other aging mechanisms must be more important. In order to evaluate other possible aging mechanisms, a thorough electrochemical analysis is performed. This study reveals a self-discharge mechanism during storage in the lithiated state and also that a significant amount of Li is lost in the Si material during standard cycling (Paper IV).

To get further insights into the mechanisms behind aging of the Si material, more analysis tools are required. One such tool that is able to probe both the formation of SEI layers, the surface of the active material and also a part of the bulk material is HAXPES. Although general PES is a well established technique, battery materials are a relatively new class of samples that require further insights to provide accurate interpretations. Therefore, a model to explain the effects observed in PES spectra due to SEI formation is presented (Paper V). To further highlight the effect of SEI formation and other parameters influencing the measured spectra, a series of model systems is investigated (Paper VI) and the results indicates the influence of local potential variations within the electrode.

The following sections will more deeply explain and discuss the results of this work.
The SEI

The SEI formation is investigated with different kinds of PES at synchrotron facilities as well as with in-house PES. With different incoming photon energies a depth profiling of the material is achieved which indicates the buildup of the SEI, similar to what is described in Figure 17. Although these investigations have included different salts, solvents and additives, the formation of the SEI has several features in common.

*Initial SEI formation and continuous formation during cycling*

In the cycling curves, the first SEI formation is indicated already at 1.6 V vs. Li⁺/Li, see e.g. the inset in Figure 9. With the most surface sensitive measurements electrolyte decomposition is observed at 0.9 V (Paper I) but the major SEI formation occurs at potentials around 0.5 V and is clearly observed in cycling curves, as exemplified by Figure 9.

The initial SEI formation is completed when the lithiation plateau of Si is reached at about 0.1 – 0.2 V. At this stage the Si material is starting to increase in volume and if the SEI is not persistent, new surfaces will be exposed to electrolyte and form more SEI. This is what is considered continuous SEI formation due to volume changes. Another kind of continuous SEI formation is suggested to originate from solvent diffusion through the SEI and where it is reduced on the Si surface in a self-discharge mechanism.

The continuous SEI formation is proceeding throughout the first 50 cycles as indicated by the changes in the C1s spectra in Figure 18. Between 50 and 100 cycles the C1s spectra is almost identical and the SEI composition is stable. It is challenging to conclude which of the two continuous SEI formation mechanisms that is dominating and both of them may occur simultaneously. The decrease in particle size and the rearrangement of the composite electrode would suggest that new surfaces are formed while in coming sections both self-discharge and continuous SEI formation is observed.

One effect that is observed with more cycling is that the relative amount of CB signals decreases. This is observed in Figure 18 (black peak) and Figure 20 (yellow peak). This could simply be explained by an increase in the SEI layer thickness. However, another possible explanation is that with cycling, more surfaces are formed that also need to be passivated by SEI formation. Thus, the relative amount of SEI vs. CB increases and thereby the relative CB signal should decrease, although the SEI layer may be of the same thickness. Again, both mechanisms are probable.

When observing the SEM micrographs in Figure 24, significant morphological differences are observed between electrodes cycled with and without the FEC additive. Despite this difference, the corresponding spectra reveal rather similar CB signals (Figure 20, yellow peaks). This suggests that the CB signal is perhaps not the most reliable indication of SEI layer thickness.
The chemical composition of the SEI

Since the SEI is composed of the decomposition products from the electrolyte, it is not surprising that different electrolytes result in different SEI layers. Without the FEC and VC additives, the composition of carbon and oxygen containing compounds is essentially the same both for LiPF$_6$ and for LiTDI-based electrolytes. Mainly Li alkyl carbonates, LiF, and other solvent decomposition products are observed. With these electrolytes the LiF content is approximately 4%. If FEC is added to either of the electrolytes, the LiF content increases significantly to 15-20%.

It is interesting to compare the relative Li and F content. As the major part of F in the SEI is present as LiF, the amount of Li available for other compounds can be roughly estimated. Without additives, about 10% Li is available for other compounds such as Li alkyl carbonates while with additives, about 5% and even less Li is found in something other than LiF. The SEI layers with additives also comprise more of a compound considered to originate from the FEC and VC decomposition into polycarbonate-like species.
This confirms the decomposition mechanisms suggested for these additives [102, 138]. The peak due to these compounds is located at around 291 eV and is present in both Figure 18 (green peak) and Figure 20 (red peak).

The SEI structure

It is interesting to know how the SEI is built up as it reflects the SEI formation process. The depth profiling is achieved using different excitation energies during PES analysis. It is also valuable to analyze samples frequently during the SEI formation to be able to follow the development of new features.

Without the use of additives, the buildup of the SEI is essentially homogeneous. This is observed as different excitation energies result in similar spectra, see Figure 19 and Figure 20. The buildup of an SEI layer can be followed by the spectra in C1s, Figure 18, from the LiTDI based electrolyte with FEC and VC additives. A layered structure is observed already after the first cycle as there is a difference concerning the relative amounts of the polycarbonate (green in Figure 18) and Li alkyl carbonates (yellow) between the two excitation energies. With more cycling, the polycarbonate species are increasing in relative amounts closer to the surface. This can be observed since the green peak is more intense relative to the yellow peak at 2005 eV than it is at 6015 eV. The same observation is made also for LiPF₆ based electrolytes when additives are used, see Figure 20.

With the most surface sensitive measurements in Paper I, the formation of this polycarbonate compound is found to occur at higher potentials, or before, the formation of other carbonate-like species in the first cycle. With this observation in mind, it is interesting that Li alkyl carbonate species at a later stage are formed beneath this layer, or closer to the surface of the Si material. This is interpreted as a result of two different mechanisms. The first is the possibility of dissolution of Li alkyl carbonate species from the outermost SEI layer into the electrolyte, thus enriching the more stable/less soluble polymeric carbonates. In the other mechanism solvent molecules are diffusing through the SEI layer and are reduced on the electrode surface. This continuous SEI formation would then consume charge from the electrode in a self-discharge process.
Stability of the electrolyte salt

Both LiTDI and LiPF$_6$ salt decomposition is observed already after assembling the half-cells and storing them at the open circuit potential. This is revealed by the presence of LiF in the electrodes stored in the pure electrolytes as the only source of F in these cases is the LiTDI or LiPF$_6$ molecule.

Other decomposition products are observed by monitoring the salt specific photoemissions. For LiPF$_6$, P is unique for the salt in these electrolytes and decomposition products such as phosphates are observed. With the use of FEC, an additional peak is observed in the P1s spectra in Figure 20. This indicates that a different decomposition product is present with the use of the FEC additive. The HF formation in this electrolyte is indicated due to the silicon-oxygen/fluoride species observed in the Si spectra in Figure 28. Thus, the FEC does not provide protection of the silicon oxide surface.

Also the LiTDI salt is shown to decompose but little is known about the degradation reactions of this salt. One decomposition product of this salt is LiF as indicated by the F1s spectra with pure LiTDI electrolyte in Figure 19.

Figure 19. Comparison of PES spectra from electrodes cycled 50 times with LiTDI based electrolyte either with FEC and VC additives or without additives (pure LiTDI electrolyte). From Paper III.
Also an additional peak (grey in Figure 19) is indicated in the N1s spectra both with and without the use of additives, revealing that a new N surrounding exists.

To summarize these findings on SEI characterization: the SEI composition, structure and electrode morphology are clearly affected by the choice of electrolyte. With the use of additives a layered SEI structure is observed but the salt decomposition continues. Also the SEI formation is a continuous process that may proceed due to different mechanisms. In the following sections it will be demonstrated that the additives provide an enhanced cycling performance. Therefore it is at hand to suggest that the layered SEI, rich in polycarbonates and LiF is preferable over mainly a homogeneous SEI formed by Li alkyl carbonate-like compounds.

![Figure 20. PES results from SEI formed on Si electrodes by LiPF$_6$ based electrolytes with additives (black spectra) and without additives (blue spectra). From Paper I.](image)

Cycling performance and aging of the Si material

Cycling of the composite Si electrodes in this thesis is performed galvanostatically with either a charge limited lithiation or a lithiation to a fix cutoff voltage. By restricting the lithiation with these limits only a part of the available Li storing capacity is utilized and volume variations are therefore limited. De-lithiation is in all cases performed with a cutoff value of 0.9 or 1.0 V vs. Li$^+/\text{Li}$.

With the use of electrolytes without additives, the capacity losses in each cycle are fairly high. This is especially the case for pure LiTDI electrolyte which has a coulombic efficiency of only 96% and also a poor overall cycling performance. The LiPF$_6$ based electrolyte yields a higher coulombic efficiency but the major improvement is achieved with the use of FEC and VC additives. With these, coulombic efficiencies of about 99% can be achieved and it even increases slightly with cycling. With capacity limited
cycling to 1200 mAh g\(^{-1}\) of Si, it is possible to achieve more than 200 cycles with the LiTDI based electrolyte with additives. It is a considerable improvement compared to electrolytes without additives but still, 99% coulombic efficiency indicates far too much side reactions and lost capacity.

By monitoring the voltage profiles from extended cycling, presented in Figure 21, it is observed that the lithiation plateaus are shifted to lower voltages with more cycles. The voltage profile during de-lithiation is essentially unaffected but the quasi-plateau is extended and the voltage increase towards the end of these curves becomes sharper with more cycles. These observations are in line with the conclusion that Li is remaining in the Si material even after the de-lithiation [116].

![Figure 21. Cycling curves for a composite Si electrode lithiated to 1200 mAh g\(^{-1}\) and de-lithiated to 1.0 V vs. Li\(^+\)/Li. The electrolyte is 0.6 M LiTDI with FEC and VC additives. From Paper IV.](image)

**Incomplete de-lithiation of the Si material**

To investigate the possibility that Li is remaining in the Si material after cycling, a constant voltage step is added to the standard cycling procedure. After every 10\(^{th}\) or 20\(^{th}\) de-lithiation the voltage is maintained at 1.0 V until the current reaches below 1 µA. During such a step, additional time is allowed for slow processes to occur and release Li. The extracted capacity is presented in Figure 22a) as the sum of the standard de-lithiation capacity and the capacity extracted by the voltage step.

It is obvious that a considerable amount of capacity is possible to extract with these voltage steps. With more cycles, the capacity that is possible to extract increases and after 200 cycles an additional 330 mAh g\(^{-1}\) of Si is re-
trieved. Interestingly, the time and the capacity in each voltage step are correlated and increase similarly, see Figure 22b). This suggests that with even longer step durations, more capacity would be possible to extract. Therefore the true amount of “lost” Li could be higher and this experiment merely reveals that a considerable amount of Li remains in the Si after cycling.

In the cycling curves before the voltage step (Figure 22c) it is observed that the major part of the cycling curve is in the first quasi-plateau and that the second quasi-plateau is reached at the end of the cycle. In Figure 22d), the cycling curves after a voltage step is presented. In these cycling curves it is apparent that essentially the first quasi-plateau is extended and the second quasi-plateau is not possible to observe. The capacity lost in the following cycles is also obvious as the de-lithiation plateau is shortened.

Figure 22. Standard cycling with voltage step. In a) the lithiation and de-lithiation capacities as a function of cycle number are presented. Also the additional capacity extracted in the potential step is shown as well as the capacity loss in the cycle following a potential step. In b) the capacity extracted by the potential step and the potential step duration is presented as a function of cycle number. In c) and d) the cycling curves before and after selected potential steps are presented, respectively. From Paper IV.

Self-discharge in the lithiated state

As mentioned earlier, a self-discharge process by a continuous SEI formation is suggested by PES results on the SEI. In order to estimate the magnitude of this process and the amount of capacity it consumes, a self-discharge experiment is evaluated. This is done for the LiTDI electrolyte
with additives used in paper IV. An electrode is paused for a number of hours in the lithiated state during cycling. After the pause, the standard de-lithiation step is performed and the capacity extracted is plotted against the pause time, see Figure 23a). This procedure is repeated but with increasing pause time durations.

A significant capacity loss is observed with longer pauses. However, the rate at which capacity is lost decreases with the pause time according to a non-linear relationship. If the self-discharge is governed by a linear diffusion, the de-lithiation capacity vs. the square root of the pause time should result in a linear relationship. This presentation is given in Figure 23b) and a decent approximation is achieved. If the de-lithiation capacity is instead plotted vs. time$^{0.7}$, an almost perfect linear relationship is observed (see Paper IV). This suggests that the self-discharge process very well may be diffusion controlled, but perhaps not in a strictly linear fashion.

The origin of this self-discharge mechanism is not established but it is possible that continuous SEI formation and other mechanisms are responsible. Nonetheless, the capacity losses due to shorter pauses are significant and if these processes are active also during cycling, this mechanism should be responsible for a major part of the capacity losses in each cycle.

![Figure 23](image)

**Figure 23.** a) De-lithiation capacity as a function of pause time in the lithiated state. b) De-lithiation capacity as a function of the pause time in the lithiated state$^{1/2}$. From Paper IV.

In summary, the cycling performance of the Si electrode is depending on the electrolyte where FEC and VC additives enhance the cycling performance a great deal. Still, with the use of additives and non aggressive salts, a large capacity loss is observed during cycling. The electrochemical methods with potential step de-lithiation and the self-discharge test indicate the presence of effects that can explain large fractions of the capacity losses in each cycle. Thus it is clear that more than the electrolyte needs to be considered to obtain efficient Si electrodes.
Electrode morphology

The pristine composite electrode has a porous structure without cracks and individual particles are easily distinguished. Examples of this are presented in Figure 11a), c) and d) and also in Figure 24a) and b). After cycling the morphology of the electrodes are heavily altered. With LiPF$_6$ based electrolyte without additives, the porous structure is significantly changed (Figure 24d) and cracks are observed with low magnification (Figure 24c) after 85 cycles. When the FEC additive is used, the electrode still has the porous structure after 85 cycles and the particles appear less smooth, presumably due to SEI formation and surface reconstructions. There is no indication of crack formation or loss of active material with the use of the FEC additive.

Similar observations are also made for LiTDI based electrolytes with and without additives. In Figure 11, a larger Si particle size is used and it is observed that the overall particle size is decreasing upon cycling. Similar observations are also reported in the literature [80].

Thus, with the use of additives, the porous structure is effectively maintained and there is no sign of cracks or loss of active material that would explain the capacity losses. The decrease in particle size is easily observed with the larger particles but it is possible that also the smaller nanoparticles may decrease in particle size due to extended cycling, although it is more challenging to observe by SEM.

![Figure 24. SEM micrographs of a pristine electrode (a and b), an electrode cycled in a LiPF$_6$ based electrolyte without FEC additive (c and d) and with FEC additive (e and f) after 85 cycles. From Paper I.](image-url)
The Si material analyzed by PES

The active Si material in this thesis is based on Si particles with a size of either about 50 nm (paper I and II) or 100-200 nm (paper III and IV). The spectra for the Si1s signal of a pristine electrode are presented in Figure 25. With low electron kinetic energy, the SiO₂ signal is strong and also non-stoichiometric oxides (SiOₓ) are observed. With 6015 eV excitation energy the bulk Si peak is now more intense and the SiO₂ peak is only a small fraction of the total signal. This confirms that a thin native oxide layer is covering the Si particles. From this data it is challenging to estimate the oxide thickness [127] but native oxides for Si materials are thin and generally in the range of only a few atoms thick [131].

![Figure 25. The Si1s photoemissions measured at 2005 and 6015 eV of a pristine composite Si electrode. The spectra are uncalibrated. Previously unpublished data.](image)

With thick SEI layers the Si signal is heavily attenuated. However, the high kinetic photoelectron energies obtained in HAXPES makes it possible to probe Si materials covered by relatively thick SEI layers. Although it is possible to measure the photoemission spectra from the Si particles, the interpretation of the spectral changes due to a lithiation reaction is complex. This is due to fundamental aspects of Si being a semiconductor, the nature of Li-Si compounds and the lack of stable energy reference points.

The lithiation mechanism studied by PES

In the first lithiation the particles undergo a transformation from crystalline Si to amorphous LiₓSi: this is evident due to the lithiation plateau in e.g. Figure 9 [62]. In order to investigate how this lithiation mechanism proceeds and what the corresponding spectral response is, several electrodes at different state of lithiation are analyzed. The spectrum from electrochemically lithiated electrodes and reference Si wafers with different treatments are presented in Figure 26.

The reference Si wafer, where the non analyzed side had been allowed to react with Li metal (Figure 26b), revealed a shift to higher binding energies and a similar shift is also observed for the Si electrode after SEI formation (Figure 26e). This could be interpreted as a doping effect where the Fermi
level of the Si is increased. With increasing lithiation of the Si electrode, a new, presumably more lithiated phase emerges, indicated with a yellow to brown peak, denoted Li$_x$Si, in Figure 26f to i. With increasing lithiation, the highly lithiated peak increases in relative intensity. At the same time, both the grey (Li$_x$Si) peak and the more lithiated phase (Li$_z$Si) are shifted similarly to lower binding energies.

Figure 26. Si1s and Cls spectra for a pristine Si wafer a), Li doped Si wafer b), lithiated Si wafer c) and composite electrodes at different degrees of lithiation (d to i). The spectra from wafers are uncalibrated, the pristine electrode d) is calibrated with respect to the SiO$_2$ peak in the pristine wafer a) and the other electrodes (e to i) are calibrated vs. the lithiated oxide signal in the lithiated Si wafer c). The calibration required to place each spectra at the current position is indicated, for d) the calibration shift was -0.5 eV, for e) the shift was -0.3 eV etc. From Paper VI.
The lithiated and de-lithiated states of Si electrodes are also presented in Figure 27 (from paper IV) after the first, 25th and 50th cycle (at 1200 mAh g\(^{-1}\) of Si). It is seen that more and more of the highly lithiated phase is required to achieve the desired lithiation capacity. Also in this case both bulk peaks are shifted to lower binding energies with more cycling, a sign that the overall Li content in the Si increases. This observation is in good agreement with the hypothesis regarding remaining Li within the Si material as discussed in a previous section. However, in the de-lithiated state, practically no similar peak shifts are observed although presumably more and more Li should be present in the electrode with more cycles. This could be explained if the remaining Li is located in the interior of the particles or deeper in the electrode and does not allow for detection. Alternatively, the Li remaining in the structure is evenly distributed so that all bulk Si atoms has identical surroundings and thus only one chemical shift.

![Figure 27](image-url)

*Figure 27. Si electrode in the pristine state as well as lithiated and de-lithiated electrodes after the first, 25th and 50th cycle with capacity limited cycling. The electrolyte is 0.6 M LiTDI with FEC and VC additives. After 50 cycles, in the lithiated state, a new peak is observed attributed to a more lithiated oxide, indicated with a * in the figure. From Paper IV.*
Si surface reactions
The active Si materials have also been analyzed by PES to trace the surface stability and the formation of new phases. It is shown in other studies that the Si surface is affected by the LiPF$_6$ based electrolytes where presumably water residues results in HF formation which then gives rise to etching of the oxide surface and the formation of new species [91, 111-112]. This is also seen in Figure 28 (unpublished data) where oxygen and fluorine containing Si compounds are formed after 70 cycles in a LiPF$_6$ based electrolyte.

With the use of LiTDI based electrolytes there is no sign of the formation of fluorinated Si species or other unwanted reaction products at any stage. Thus, this salt and its decomposition products seem to be harmless towards the Si material.

The relative amount of silicon oxide is increasing with cycling. This can be observed in Figure 27 but also in another study with a different electrolyte [92]. One reason for this increase may be due to the particle size decrease, as revealed by SEM. This would result in relatively more surface area and since PES is surface sensitive technique, the surface signal would increase. A thicker oxide layer could also explain the increase in the oxide signal.

The reversible cycling of different silicon oxides is demonstrated in a number of studies e.g. [132-134]. It is therefore a reasonable assumption that also the thin oxide layer in the nanoparticles electrode may be able to reversibly cycle Li. By comparing the oxide signal for lithiated and de-lithiated electrodes in Figure 27, only a small peak (indicated *) positioned in between surface oxide and bulk peaks is observed after 50 cycles. This peak only tells us that minor or insignificant amount of a more lithiated oxide exists and this phase should give only a minor contribution to the overall cycling capacity. However, also the major oxide peak could potentially store some Li. To be able to differentiate between a lithiated and a de-lithiated oxide, a different spectrum calibration is required.

![Figure 28. Si 1s spectrum measured at 2600 eV excitation energy of a nano-Si electrode after 70 capacity limited cycles. The electrolyte is 1 M LiPF$_6$ with FEC and VC additives. Previously unpublished data.](image-url)
One challenging aspect for the PES analysis of composite Si electrodes is the choice of energy reference point. When the surface hydrocarbon peak is used as the energy reference, the formation of the SEI layer results in relative peak shifts of the underlying material which is why this calibration is unsuitable. The CB peak offers a good option as it should be in good electrical contact with the active material and the relative peak position of CB is also well established. However, the CB material may likewise undergo a lithiation reaction and how this affects the measured binding energy is not fully understood. The native oxide on the Si particle is indeed also in good contact with the bulk Si but the oxide may be subject to a binding energy change due to a reaction with Li. This makes the comparison between spectra in the lithiated and de-lithiated state virtually impossible and calibrations should be specific for the lithiated or the de-lithiated state, respectively. Still, with the oxide as the internal reference, relative binding energy changes are probed and provide valuable information regarding changes in the bulk material with respect to the surface oxide.

HAXPES is a useful tool to probe the changes in a Si material as a function of cycling and both bulk and surface changes can be observed. However, the changes in the Si occurring during lithiation are not fully understood. A more fundamental insight into the lithiation mechanism would provide meaningful details to the aid data interpretation.
Energy calibration in PES

The basis of all data interpretation in PES measurements is the energy calibration of the spectra. These interpretations enable the assignment of peaks to certain compounds. If the energy calibration is not carefully performed, the interpretations may be incorrect. In this section some phenomena occurring in PES analyses of battery electrodes affecting the binding energy and energy calibration are exemplified.

Peak shifts and changes due to the degree of lithiation

When analyzing active materials in the Li-ion battery, a change in chemical shift is expected due to lithiation or de-lithiation. These shifts depend largely on the involved mechanisms. As an example, LMO electrodes follow a fairly well defined redox chemistry with increasing/decreasing peaks as a response to the lithium content (Paper VI). In this sense, lithiation of Si is more complex with both new peaks and shifting peak positions. The difference can be explained by the different lithiation mechanisms involved. LMO is an intercalation material where one Li is inserted for each formula unit while lithiation of Si results in an intermetallic compound where also the semiconducting properties of the material may change when up to 3.75 Li for each Si is inserted.

For the LMO example, only the +IV oxidation state is expected in the de-lithiated state. However also +III and +II oxidation states of Mn exist. With increasing Li content the +III and +II oxidation states increase as expected. A detailed peak de-convolution is necessary to provide a well resolved picture of the changes in the active material. With LMO, the spectral changes are due to the insertion of Li⁺ which increase or decrease the amount of Mn atoms with a certain oxidation state. In these spectra, the peak position from the CB conductive additive is stable and effectively no internal energy referencing is needed for these peaks.

Peak shifts due to SEI formation

It is well known from other areas of PES that insulating layers on conductive substrates are subject to relative peak shifts as a function of layer thicknesses [135-138]. The formation of a SEI layer on a more conducting electrode is a similar situation and peak shifts relative to underlying materials due to SEI formation are seen for Si electrodes in Paper II and for graphite and Ni₀.5TiOPO₄ electrodes in Paper V.

To further establish the relationship between the SEI formation and the peak shifts, the build-up of an SEI layer on a Au electrode is investigated. The uncalibrated spectra from this system are presented in Figure 29a) and c). These investigations allow for a combined measurement of both the bulk Au4d₅/₂ peak and the SEI components in the C1s spectra. The decrease in Au4d₅/₂ peak is proportional to the increase in SEI thickness. Indeed, the
peaks for the SEI components are shifted to higher binding energies for thicker SEI layers. However, the peak shift is most pronounced (1.4 eV) in the first cycle. This is observed by comparing peak positions for the pristine Au-disc sample with those for the “1 cycle” sample in Figure 29c. The Au4d\(_{5/2}\) peak decreases to about one third for these samples. Comparing the Au4d\(_{5/2}\) peak after 1 and 150 cycles, the intensity decreases to less than one tenth and yet the peak shift is “only” 0.5 eV. Thus, the main part of the observed peak shift is due to the formation of a surface dipole layer that is established during the first cycle.

Figure 29. a) and b), combined Au4d\(_{5/2}\) and C1s spectra recorded for SEI deposited on gold for increasing amount of CV cycles. c) and d) show the C1s region for the spectra in a) and b), respectively. Spectra in a) and c) are uncalibrated and b) and d) are calibrated vs. surface hydrocarbons. From Paper VI.
With this dipole layer, the local potential of the SEI layer will be shifted with respect to the spectrometer and therefore shifted in binding energy. In Figure 15 and Equation 6, this surface potential would be represented by $\phi$. A more detailed representation of how the energy levels and the results are affected by such a dipole is presented in Paper V.

In Figure 29b) and d) the spectra are calibrated vs. surface hydrocarbons set to 285 eV. This kind of calibration is meaningful for further analysis of the SEI components where characteristic SEI compounds such as Li alkyl carbonates now align at ~290 eV. With this calibration the Au4d$_{5/2}$ peak is shifted to lower binding energies. This illustrates how inappropriate surface hydrocarbon calibration is for the bulk materials as the shift would suggest that the Au material is subject to e.g. a chemical shift due to a chemical reaction, which is not the case.

The influence of the electrode potential

As discussed earlier, changes in the spectra are expected for the active materials as a function of lithiation. However, also peak positions shifts for electrochemically inactive components are observed between the lithiated and de-lithiated states in e.g. the Ni$_{0.5}$TiPO$_4$ electrodes in Paper V. This effect is perhaps even more pronounced when the material has a large potential difference between lithiated and de-lithiated states. To further investigate this effect, a composite electrode with four different materials was assembled. This allows the electrode to be stopped during cycling at four well-defined potentials at which the electrode is analyzed with PES.

The results, presented in Figure 30, reveal that inactive components such as the PVdF binder (green peaks in Figure 30a) and b) are shifted as a function of electrode potential. However, a similar shift is also observed for the LTO active material (Figure 30c) while peak positions from the CB conductive additive and the LMO active material (Figure 30d) remain essentially unaffected. The common denominator for materials that exhibit peak shifts (LTO and PVdF) as a function of electrode potential is that they are semiconductors or insulating materials while LMO and CB, on the other hand, are good electron conductors. Good electronic conductivity ensures that a material is properly grounded to the spectrometer during the measurement. This means that the material and the spectrometer are on the same potential (or Fermi level ($E_F$)). With insulating components, a different surface potential is achieved when compared to the more conductive parts, similarly to the SEI formation on Au in the previous section.

Thus, the observed binding energy shifts for active and inactive components in composite electrodes should be considered as a function of electrode potential and the electronic conductivity of the specific compound. With these insights, it is again clear that different types of energy calibration are preferable depending on the point of interest and that in some cases; no internal energy calibration is required at all.
Figure 30. a) C1s, b) F1s, c) Ti2p and d) Mn2p spectra for a mixed materials electrode measured at different electrode potentials. From Paper VI.
Conclusions

The SEI that results in better cycling performance is rich in LiF and polycarbonate species from the FEC and VC decomposition. The polycarbonate compounds are located in the outer parts of the SEI while the inner SEI is rich in Li alkyl carbonates. Without additives the SEI is built up by essentially LiF and Li alkyl carbonate compounds in a homogeneous mixture.

The LiTDI salt or its decomposition products does not affect the Si particle surface. It is, however, not suitable to use this salt without electrolyte additives since the SEI formed by the pure electrolyte results in poor cycling performance. A considerable increase in surface oxide is observed with increasing cycling and the increase is more pronounced without electrolyte additives.

Remaining Li in the Si material is a major source of capacity losses during cycling. A self-discharge mechanism is observed that to at least some part is diffusion limited. This mechanism also contributes to a large fraction of the capacity loss in each cycle. The electrochemical methods that are used to identify these processes could easily be applied to different Si materials and also other electrode materials.

HAXPES is a suitable technique to analyze Si electrode materials. It is shown in this work that new peaks emerge from a more lithiated phase and that the overall peak positions from bulk materials are altered as a function of the lithium content. Also, the surface modifications as a function of cycling is possible to probe and a relative increase in surface oxides are observed with increased cycling. HAXPES is thereby one of few techniques that can be used for the analysis of both the bulk Si reactions, the surface oxide and the SEI simultaneously. In addition to this, HAXPES with different excitation energies also allows for a depth profiling of the SEI layer.

This work has encountered and pinpointed several important processes that affect the measured binding energies in PES analysis of battery materials. Most importantly, it is shown that the binding energy of poorly conducting components are affected by the electrode potential and that SEI formation causes a peak position shift with respect to the underlying electrode. The energy scale calibration of PES spectra should be carefully considered, especially when new materials and structures are analyzed. The mapping of these effects should provide a good starting point for future PES analysis on battery materials.
The commercialization of the Si electrode is challenged by several mechanisms that lower the performance and prevents the use of Si electrodes in full-cell batteries. By efficient additives the cycling performance is enhanced but still the continuous SEI formation must be decreased further to obtain a commercially viable alternative.

Remaining Li in the Si electrode is a seldom considered source for capacity losses but as indicated by the results in the present work, this effect should be seriously considered. Further investigations are needed to determine the mechanism behind the Li lost in the Si material and to, if possible, suggest ways to circumvent this problem.

More analysis tools would be helpful to analyze the mechanisms and reactions in the Si during cycling. HAXPES is a technique that can probe changes in the Si material during lithiation and de-lithiation processes, but a complete understanding of the lithiation mechanisms of Si is needed to link PES the spectra to certain phases or transformations of the material.

Finally, PES analysis of battery materials is still a young research area where efforts should be focused on understanding mechanisms and processes affecting the measured binding energies. This could make PES analysis an even more powerful tool in studying aging mechanisms of battery materials.
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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. (Prior to January, 2005, the series was published under the title “Comprehensive Summaries of Uppsala Dissertations from the Faculty of Science and Technology”.)