Insights into Stability Aspects of Novel Negative Electrodes for Li-ion Batteries

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Abstract

Demands for high energy-density batteries have sharpened with the increased use of portable electronic devices, as has the focus global warming is now placing on the need for electric and electric-hybrid vehicles. Li-ion battery technology is superior to other rechargeable battery technologies in both energy- and power-density. A remaining challenge, however, is to find an alternative candidate to graphite as the commercial anode. Several metals can store more lithium than graphite, e.g., Al, Sn, Si and Sb. The main problem is the large volume changes that these metals undergo during the lithiation process, leading to degradation and pulverization of the anode with resulting limitations in cycle-life.

The Li-ion battery is studied in this thesis with the goal of better understanding the critical parameters determining high and stable electrochemical performance when using a metal or a metal-alloy anode. Various antimony-containing systems will be presented. These represent different routes to circumvent the problems caused by volume change. Sb-compounds exhibit a high lithium storage capability. At most, three Li-ions can be stored per Sb atom, leading to a theoretical gravimetric capacity of 660 mAh/g. Model systems with stepwise increasing complexity have been designed to better understand the factors influencing lithium insertion/extraction.

It is demonstrated that the microstructure of the anode material is crucial to stable cycling performance and high reversibility. The relative importance of the various factors controlling stability, such as particle-size, oxide content and morphology, varies strongly with the type of system studied. The cycling performance of pure Sb is improved dramatically by incorporating a second component, Sb$_2$O$_3$. With a critical oxide concentration of ~25%, a stable capacity close to the theoretical value of 770 mAh/g is obtained for over 50 cycles. Cu$_x$Sb shows stable cycling performance in the absence of oxide. Cu$_x$Sb has been presented for the first time as an anode material in a Li-ion battery context. Studies of the Solid Electrolyte Interphase (SEI) formed on AlSb composite electrodes show an SEI layer thinner than graphite, and with a clearly dynamic character.

Keywords: Li-ion batteries, anode materials, Sb, Cu2Sb, electrodeposition

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List of papers

This thesis comprises a summary based on the following papers, referred to in the text by their Roman numerals:


**III** Thin films of Cu$_2$Sb and Cu$_6$Sb$_2$ as anode materials in Li-ion batteries, H. Bryngelsson, J. Eskhult, L. Nyholm and K. Edström, submitted to Electrochimica Acta.


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Comments on my own contributions to the papers in the thesis:

I  Major part of the experimental work and the writing.

II Major part of the experimental work and the writing.

III Major part of the experimental work and the writing.

IV Synthesis and characterisation of the material. Electrochemical characterisation. Participation in the surface analysis. *In situ* XRD measurements. Discussion and interpretation of the results. Part of the writing.

V Characterisation and synthesis of the material. Electrochemical characterisation. Participation in the surface analysis. Discussion and interpretation of the results. Major part of the writing.
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<tr>
<td>NiCd</td>
<td>Nickel cadmium</td>
</tr>
<tr>
<td>NiMH</td>
<td>Nickel metal hydride</td>
</tr>
<tr>
<td>LiPF₆</td>
<td>Lithium hexafluorophosphate</td>
</tr>
<tr>
<td>EC</td>
<td>Ethylene carbonate</td>
</tr>
<tr>
<td>DEC</td>
<td>Diethyl carbonate</td>
</tr>
<tr>
<td>DMC</td>
<td>Dimethyl carbonate</td>
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<tr>
<td>PC</td>
<td>Propylene carbonate</td>
</tr>
<tr>
<td>PVDF</td>
<td>Polyvinylidene difluoride</td>
</tr>
<tr>
<td>EPDM</td>
<td>Ethylene propylene diene terpolymer</td>
</tr>
<tr>
<td>SEI</td>
<td>Solid electrolyte interphase</td>
</tr>
<tr>
<td>EQCM</td>
<td>Electrochemical quartz crystal microbalance</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscopy</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
</tr>
<tr>
<td>CB</td>
<td>Carbon black</td>
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</table>
1. Introduction

1.1 The Li-ion battery

The increased use of portable electronic devices has raised the demands on batteries and the importance of smaller size and lower weight has sharpened the requirements for high energy-density and efficiency. Additionally, attention to global warming has placed a focus on the need for electric and electric-hybrid vehicles, where the battery is one key technology. A lot has happened since Alexander Volta 1800 introduced his “Volta pile”, which began the development of modern batteries; the most promising battery on the market today is the Li-ion battery, which surpasses other rechargeable battery technologies (like lead acid, NiCd, NiMH) in both energy- and power-density\(^1\) (Figure 1.1).

![Figure 1.1 Comparison of energy densities for different battery concepts.](image-url)
The commercial Li-ion battery consists of carbonaceous materials\(^2\) (for example, graphite) as anode and a lithium-containing transition-metal oxide as cathode\(^3\) (e.g., LiCoO\(_2\), LiMn\(_2\)O\(_4\), LiFePO\(_4\)). The most common electrolytes used are liquid electrolytes, which consist of a lithium salt in an aprotic organic solvent or a solvent mixture. Lithium hexafluorophosphate (LiPF\(_6\)) is commonly used as salt and the most important organic solvents used are Ethylene Carbonate (EC), Diethyl Carbonate (DEC), Dimethyl Carbonate (DMC) and Propylene Carbonate (PC). Additives can be used to control the reactions at the interface between the electrolyte and the electrode material, or flame retardants to improve battery safety.

When charging the battery, Li-ions are extracted from the transition-metal oxide and intercalated into the graphite (Figure 1.2); when using the battery, the opposite reaction takes place. The electrons move in the outer circuit in opposite direction to the Li-ions\(^4\).

![Figure 1.2](image-url) A schematic representation of the Li-ion battery.

Li-ion battery cells can deliver >5V. The capacity of the battery is often expressed as the charge involved in the cell reaction per mass unit, \(i.e., \text{the gravimetric capacity (mAh/g). The theoretical gravimetric capacity (T}_{\text{cap}}\) of an electrode material (insertion of lithium according to eq. 1.1) is given by eq. 1.2.

\[
A + n\text{Li}^+ + ne^- \leftrightarrow \text{Li}_nA \tag{1.1}
\]

\[
T_{\text{cap}} = \frac{(1/M) \times nF}{3.6} \tag{1.2}
\]
where M is the molar mass of the electrode material (A) and F is Faraday’s constant. Another frequently used term is the volumetric capacity (mAh/l), which relates to the density of the material.

1.2 Li-ion battery development

In the 1970’s and 1980’s, secondary Li-ion batteries with intercalation compounds as the cathode and Li-metal as anode were studied intensively and products were developed. One of the most sophisticated was the Molicel\textsuperscript{5}, Li/MnS\textsubscript{2}, which was presented in the late 1980’s. It was soon discovered, however, that using Li-metal as anode led to both safety risks and poor stability. The Li-metal was soon replaced by an intercalation compound\textsuperscript{6}, and already in the early 1990’s Sanyo introduced a graphite/LiCoO\textsubscript{2} prototype cell yielding capacities in the same range as the Molicel\textsuperscript{7}. The safety risks associated with the Li-metal are related to the increase in surface area of the Li metal anode when Li is electroplated onto the metal surface on recharging. This increases the contact between the Li-metal and the electrolyte and leads to an increase in thermodynamically instable electrolyte degradation products, which make the cell sensitive to mechanical, thermal and electrical abuse. It also gives rise to dendrite formation which could lead to short-circuiting when the dendrites pierce the anode/cathode separator. Dendrite formation is avoided by the use of intercalation compounds like graphite\textsuperscript{2}, and both safety and cycle lifetime is improved. Although theoretical capacity is lost, the practical capacity remains in the same range. The search for compounds exhibiting higher capacity than graphite is, however, extensive and today intensive studies are made on metals and semimetals that alloy with lithium, e.g., Al, Sn, Si and Sb.

LiCoO\textsubscript{2} is the current dominant cathode material. However, it is expensive, has a limited practical capacity (<140 mAh/g) and has stability problems at elevated temperatures in the common electrolyte solutions. The cathode is the major factor determining the energy density and rate capability of the Li-ion battery, and extensive studies are made in finding new materials\textsuperscript{3,13}. LiCoO\textsubscript{2}, LiNiO\textsubscript{2}, LiMnO\textsubscript{2}, LiMn\textsubscript{2}O\textsubscript{4} spinel and mixed metal analogues of Li(Mn, Ni, Co)O\textsubscript{2} are studied, as well as LiFePO\textsubscript{4}\textsuperscript{12} which has recently reached the market. Nytén et al.\textsuperscript{14} have also demonstrated the electrochemical performance of a new cathode material, Li\textsubscript{2}FeSiO\textsubscript{4}; this is promising in terms of cost and environment.

The active material is not the only component of the electrode. A composite electrode also comprises a carbon material with high electronic conductivity (e.g., carbon black) and a binder (e.g., polyvinylidene difluoride (PVDF) or ethylene propylene diene terpolymer (EPDM)).
1.3 The Solid Electrolyte Interphase (SEI)

Electrolyte degradation products formed at the interface between the electrolyte and the electrode during discharge is commonly referred to as the Solid Electrolyte Interphase (SEI), a concept which was first introduced by Peled et al.\textsuperscript{15} in 1979. The properties of the SEI are important for performance, temperature stability and safety, since the electrolyte degradation products are thermodynamically instable. The SEI has been studied for graphite, where it is formed during the first cycle below a voltage of 0.8 V (Figure 1.3). This leads to an irreversible loss of capacity, but at the same time it protects the graphite from solvent co-intercalation and exfoliation. It also has a passivity effect on further reduction of the electrolyte during subsequent cycling. The SEI depends mainly on the lithium salt used but also on the type of electrolyte and binder. For the most commonly used organic solvents the main reduction products are lithium alkyl carbonates and lithium carbonates. Polymer-like surface compounds, salt degradation products and LiF are also important reaction products.

![Figure 1.3](image)

*Figure 1.3* The first chronopotentiometric cycle for a graphite/Li cell cycled in a 1 M LiPF\textsubscript{6}, EC:DEC 2:1 electrolyte and a PVDF binder.
Although several models for the morphological structure of SEI layers have been proposed\textsuperscript{15-17}, a more detailed understanding of these complex layers is still lacking. In this respect, a greater appreciation for the need to use extremely pure electrolytes, dry solvents and electrodes has developed in recent years.

The SEI formation on intermetallic compounds has not been studied as extensively as for graphite. SEI studies made on Sn-containing anodes have, however, shown that the electrolyte degradation products are different from those formed on graphite\textsuperscript{18,19}. A model in which the SEI is repeatedly formed, disintegrated and reformed during cycling has been presented. This successive disintegration and reformation of the SEI has been shown to result in a thinner SEI-layer for Sn than for graphite.
2. The scope of this thesis

In this thesis, the Li-ion battery is studied with the goal of better understanding the crucial factors underlying a high and stable electrochemical performance using a metal or a metal alloy as anode. However, these metals undergo large volume expansion during lithiation\(^\text{20}\), leading to degradation and pulverization of the anode, with consequent limited cycle-life. Significant work is currently under way to circumvent this problem. In this thesis, various antimony-containing systems will be presented, representing different routes for circumventing the problems related to this volume change. The influence of particle size, oxide content and morphology on electrochemical performance will be discussed.

Sb-compounds exhibit a high capability for storing lithium\(^\text{21-25}\) and are therefore potential anode materials for Li-ion batteries. Their toxicity\(^\text{26}\) should be noted, however. At most, three Li-ions can be stored per antimony atom (eq. 2.1), leading to a theoretical gravimetric capacity of 660 mAh/g.

\[
3\text{Li}^+ + 3\text{e}^- + \text{Sb} \leftrightarrow \text{Li}_3\text{Sb} \quad (2.1)
\]

However, the volume expansion of ca. 150% during the lithiation process leads generally to a dramatic capacity loss during cycling.

To better understand the parameters influencing lithium insertion-extraction, model systems are here designed in which as few interfering reactions take place as possible. This means that the electrode materials are studied in the absence of additives such as binders and carbon black. The model compounds are made by electrodeposition, which offers precise control of the reactions involved in the deposition. Likewise, the structure, phase composition and thickness of the films can readily be controlled. The thesis starts with a study of electrodeposited Sb in order to explore the parameters influencing the electrochemical performance of a simple system. This is followed by a similar study of electrodeposited Cu\(_2\)Sb, a more complex material. A study of a composite electrode is then made to increase the complexity further. Since Cu\(_2\)Sb is already well studied in composite electrodes, we have chosen the more unexplored AlSb-system.

The study of AlSb focuses on SEI-formation and the lithiation mechanism, and will be discussed in the context of battery life-time. The SEI plays a significant role for the stability and safety of the battery. Several
questions must be answered relating how the intermetallic material itself as well as its volume change influence the SEI.
3. Anode materials for Li-ion batteries

The most commonly used anode material in commercial Li-ion batteries is graphite. The first synthesis of lithium-graphite intercalation compounds was reported by Herold in 1955\textsuperscript{27}. Graphite has gravimetric and volumetric capacities of 372 mAh/g and 820 mAh/cm\textsuperscript{3}, respectively. A lot of effort has been made to find new anode materials with higher capacity than graphite. Metals which alloy with lithium\textsuperscript{1,20,21,25,28-31}, such as Al, Sn, Si, Sb\textsuperscript{22-24}, In and Pb, yield higher gravimetric and volumetric capacities than graphite, and have been investigated extensively. Another aspect of using these metals is their alloying potential (\textit{vs.} Li), which is higher than that of graphite, thereby lowering the risk for Li-plating on the anode, giving a battery with greater safety. As stated, these metals undergo large volume expansion during lithiation\textsuperscript{20}. The gravimetric capacity, volume expansion and alloying potential for some systems are shown in Figure 3.1.

![Figure 3.1](image)

\textbf{Figure 3.1} Gravimetric capacity and volume expansion for different intermetallic compounds (Li\textsubscript{i}M). The insertion voltage is given in the table.

| Material (\textit{z}) | Insertion Voltage vs. Li\textsubscript{||}mv |
|----------------------|--------------------------------------------|
| C                    | 10                                         |
| Al                   | 400                                        |
| Sn                   | 660-180                                    |
| Sb                   | 950                                        |
| Si                   | 330-50                                     |

General routes have been suggested to minimize the problems related to the drastic volume expansion during lithiation: the use of an active material in a composite matrix, intermetallic compounds which have a strong structural
relationship with their lithiated product (with either one active and one inactive metal vs. Li or with both metals active vs. Li), metal oxides or nano-materials. These different approaches are described in this section.

3.1 Active material in a composite matrix

The mechanical stress that the alloy systems experiences as a result of the dramatic volume changes occurring on lithiation can be circumvented if the alloy is finely dispersed in a composite matrix \(^{20,32}\). The volume expansion of this composite is buffered by the matrix. For good electrochemical performance, the matrix should have a high electronic conductivity and high diffusion constant for Li. Boukamp \textit{et al.} \(^{32}\) first introduced the concept in 1981 for a Li-Sn-Si system. In 1999, Mao \textit{et al.} presented a Sn-Fe-C system, where the importance of small grains was stressed \(^{33}\). Mixing metal alloys into an inactive matrix is a common approach to prevent the problems related to volume change and has been shown to be an effective way to achieve stable cycling performance. However, inactive material in a composite matrix reduces the capacity of the electrode \(^{33}\).

3.2 Intermetallic systems

Another way to reduce volume expansion during lithiation is to use intermetallic compounds (A\(_x\)B\(_y\)), which have a strong structural relationship with their lithiated product, with either one active and one inactive metal vs. Li or with both metals active vs. Li.

Cu\(_6\)Sn\(_5\) was the first system, presented by Thackeray \textit{et al.} in 1999 \(^{34}\), in which Sn alone alloys with Li; Cu is extruded from the structure during lithiation to form an intermediate phase, Li\(_2\)CuSn, which has a CuSn framework structure of zinc-blende type. Upon further lithiation, the remaining Cu is extruded, and Li\(_{4.4}\)Sn is formed. The extruded Cu is readmitted into the structure on charging via the same route. The volume expansion on lithiation is reduced to 59% compared to 680% for pure Sn. The work on Cu\(_6\)Sn\(_5\) led to a search for other intermetallic anode candidates with a stable zinc-blende type structure, such as, InSb \(^{37-39}\), GaSb \(^{39}\) and AlSb \(^{39}\); MnSb, Mn\(_2\)Sb \(^{40,41}\), NiSn \(^{42}\) and Cu\(_2\)Sb \(^{43}\) are other examples of system with one metal active and the other inactive to Li.

Cu\(_2\)Sb, which has been studied in this thesis, has a tetragonal structure consisting of Cu layers with alternating layers of Cu and Sb. It was first published in 2001 by Fransson \textit{et al.} \(^{43}\), as anode materials for Li-on batteries. It alloys with Li in a reaction similar to Cu\(_6\)Sn\(_5\). Fransson \textit{et al.} proposed a two-step mechanism, where the first step (eq. 3.1) involves the replacement of Cu for Li in the octahedral sites. Cu is extruded from the structure via a
solid-solution reaction to form Li$_2$CuSb, which has a zinc-blende structure with the retention of a face-centred-cubic (fcc) Sb-array. In the second step, Li is inserted into the vacant interstitial sites of the cubic structure:

\[
\text{Cu}_2\text{Sb} + 2\text{Li}^+ + 2e^- \rightarrow \text{Li}_2\text{CuSb} + \text{Cu} \quad (3.1)
\]

\[
\text{Li}_2\text{CuSb} + \text{Li}^+ + e^- \rightarrow \text{Li}_3\text{Sb} + \text{Cu} \quad (3.2)
\]

Cu$_2$Sb has a gravimetric capacity of 323 mAh/g and a volumetric capacity of 2749 mAh/cm$^3$. The total volume expansion on lithiation is 42% compared to 150% for pure Sb.

InSb$^{37-39}$, AlSb$^{39}$, SnSb$^{35,36,44,45}$ are examples of intermetallic compounds with both metals active to lithium. AlSb, which has been studied in this thesis, has a zinc-blende type structure comprising two elements with clearly different alloying potentials with lithium; Sb alloys with Li at around 0.8 V, and with Al below 0.4 V. Honda et al.$^{46}$ have studied the lithiation process by *ex situ* X-ray diffraction. However, the process is complex and not yet fully understood.

### 3.3 Metal oxides

Metal-oxide anode materials are widely used since the volume changes occurring during cycling are buffered by lithium oxide formed. The metal oxide (M$_x$O$_y$) electrode forms a M/Li$_2$O nanocomposite electrode during the first lithiation step. After Li$_2$O formation, the metal (M) is alloyed with Li to form Li$_x$M$_y$. The latter reaction is reversible, but the reversibility of Li$_2$O depends on the system.

In 1997, Fuji demonstrated electrochemical activity in tin composite oxide glasses$^{47}$. This also led to several independent investigations of tin oxide composites, such as SnO and SnO$_2$$^{48-51}$. During the first lithiation step, tin(II)(IV) in SnO and SnO$_2$ is reduced to metallic Sn, while forming Li$_2$O. The second lithiation step involves the formation of Li$_{4.4}$Sn from metallic Sn.

For these types of compound, Li$_2$O is formed irreversibly. However, in CoO-based electrodes, the Li$_2$O is formed reversibly on cycling, according to investigations by Poizot *et al.*$^{52}$ The M$^{n+} \rightarrow$ M$^0$ conversion reactions can involve as many as 2e$^-$ (CoO)$^{52}$ or 4e$^-$ (RuO$_2$)$^{53}$ per formula unit, compared to the one-electron reactions for classical insertion/deinsertion.
3.4 Nano-size materials

The negative effects of the volume expansion have been reported to decrease using nano-materials\textsuperscript{54-57}. Nano-size materials provide better strain accommodation related to the insertion and removal of Li ions, leading to improved cycle life. Other electrochemical properties are also improved. Scaling down the particle size increases the electrolyte/electrode interface, which improves reaction kinetics and leads to short electronic and ionic path lengths\textsuperscript{58}. This means that the size of the particles is important, irrespective of the approach used to minimize the volume change.

There are, however, also disadvantages associated with the use of nano-materials; the most serious is the added instability related to the increase in unwanted electrolyte degradation products as the electrolyte/electrode interface grows. This can lead to self-discharge, poor cycling and hence shorter life-time. Another disadvantage is that nano-material synthesis often requires advanced synthesis methods.
4. Experimental

4.1 Material synthesis

4.1.1 Electrochemical deposition

Electrochemical deposition\textsuperscript{59} of metals or metal oxides is achieved by oxidation or reduction of species in a solution at the surface of a working electrode. The electrolysis of these species can be performed by applying either a constant current (galvanostatic mode) or a constant potential (potentiostatic mode) across the cell. In this thesis, all deposition has been done galvanostatically. The mass of the deposited material is proportional to the charge transferred during the electrolysis, according to Faraday’s law:

\[
m = \frac{QM}{nF}
\]

Electrochemical deposition is a straightforward and inexpensive method which is generally carried out at ambient temperature. The technique facilitates large-scale production of coatings, which makes it interesting for industrial applications. Since electrochemical deposition also offers precise control of the deposition reactions, the structure, phase composition and thickness of the deposited coatings can therefore be controlled by controlling either the potential or the current density. The absence of binders, etc. results in a higher density of active material in the electrodes.

The electrodeposition reactions were studied using chronopotentiometric and electrochemical quartz crystal microbalance (EQCM) measurements. EQCM has been used to study the mass increase of the working electrode during the electrodeposition, where 9 MHz AT-cut gold-coated quartz crystals (Seiko EG&G model QA-A9M-Au-50) were used as working electrodes. Changes in the frequency were monitored with a quartz crystal analyzer (Seiko EG&G model QCA 922), and data were sampled under computer control using the program WinEchem (EG&G). Prior to antimony electrodepositions, the gold-coated quartz crystals were coated with either metallic nickel or copper to mimic the substrate used during the electrodeposition procedure used for the electrodes.
4.1.2 Bulk material
A high-frequency furnace was used for the drop synthesis\textsuperscript{60} of AlSb. An aluminium ingot was heated to its melting point (660°C) under argon and at a pressure of 300 mbar. Pieces of antimony were dropped into the melt until a 1:1 Sb:Al ratio was attained. The AlSb ingot was cooled and ground by hand before ball-milling. The powder was mixed with 3 wt% graphite as a solid lubricant in a glove-box with an argon atmosphere (< 3 ppm H\textsubscript{2}O and O\textsubscript{2}), and placed in a SPEX (CertiPrep) stainless-steel vessel. The vessel was sealed with an O-ring to maintain the inert atmosphere. High energy ball-milling was performed for 16h at room temperature.

4.2 Electrode preparation, battery assembly and electrochemical characterisation
Both bulk material and electrodeposited thin films have been studied in this thesis. The bulk material was prepared by mixing of 80 wt% AlSb powder, 10 wt% acetylene black (Chevron) carbon powder and 10 wt% binder (PVDF). The electrodeposited films were studied without binder or carbon black. Prior to cell preparation, the electrodes were dried overnight at 120°C in a vacuum furnace in an argon-filled glove-box (<3 ppm H\textsubscript{2}O and O\textsubscript{2}). The typical area of the electrode was 3.14 cm\textsuperscript{2}. The electrolyte used was 1 M LiPF\textsubscript{6} dissolved in a 2:1 solution of ethyl carbonate (EC): diethyl carbonate (DEC) (Merck, battery grade). The LiPF\textsubscript{6} salt was dried overnight at 80°C under vacuum prior to use. The water content of the electrolyte was found by Karl Fischer titration to be <10 ppm. The electrochemical test cells (manufactured in the argon-filled glove-box) comprised a working electrode, a 38 μm thick glass-wool separator soaked in electrolyte and a lithium foil counter electrode; the whole was vacuum-packed in a polymer-coated aluminium pouch fitted with nickel contacts.

The electrochemical performance of the electrodes was tested either galvanostatically using a Digatron BTS-600 system, or potentiostatically using Bio-Logic VMP2 or MacPile II battery-testing units.
4.3 Characterisation of the electrodes

The structure and composition of the electrodes were investigated with X-ray diffraction\textsuperscript{61} (T2T Siemens D5000 diffractometer with CuKα radiation). The preycled electrodes were studied in transmission mode, either at the I711 beam-line at the Swedish synchrotron radiation laboratory MAX in Lund, Sweden, or in-house using an automatic STOE powder diffractometer, equipped with a position-sensitive detector (PSD) with Co-radiation. Extra care was taken to avoid exposure to air (Papers III and IV). The amorphous oxide was identified by Raman spectroscopy using a Renishaw 2000 Raman spectrometer equipped with a near-infrared diode laser (783 nm, 20 mW). The morphology of the coatings was studied by scanning electron microscopy (SEM)(LEO 1550). Transmission electron microscopy (TEM) micrographs of powders scraped from the deposited coatings were also obtained using a JEOL 2000 FXII instrument. X-ray photoelectron spectroscopy (XPS) was used to ascertain the oxidation state of the antimony, and to obtain a depth-profile for the oxide content. These experiments were performed with a PHI 5500 system using monochromatic Al Kα (1486.6 eV) radiation.

4.4 Characterisation of the SEI

The SEI was studied by XPS\textsuperscript{62} on a PHI 5500 system, using monochromatized AlKα at 1486.6 eV. The electrodes were dried overnight at 120°C prior to cell preparation to remove water from the electrodes. Prior to surface analysis, all electrodes were removed from the battery and immersed in DEC for 30 minutes in a glove-box. This DEC rinse was used to remove electrolyte salt residues not inherent to the SEI. The electrodes were then dried at room temperature for 1h under reduced pressure, mounted on a sample-holder in the glove-box, and transported to the XPS analysis chamber using a specially-designed transport vessel to avoid contact with air. The spectra were calibrated and normalized as described in Papers IV and V.
5. Control of electrode composition and microstructure by electrochemical deposition

Coatings of the model compounds (Sb and the more complex Cu$_2$Sb) have been prepared by electrodeposition. One advantage of using electrochemical deposition for synthesis of electrode materials is that it can be deposited directly on a metallic substrate which can later serve as current collector. There is therefore no need to use binders and electronically conducting additives (e.g., carbon black), the presence of which can complicate interpretation of the results.

Coatings with different amounts of oxide (and without oxide) have been prepared and tested as negative electrode in a Li-ion battery. The dependence of the composition and morphology of the coatings on electrolyte composition will be presented in this chapter. The morphology and composition of the coatings is discussed based on X-ray diffraction, Raman spectroscopy, EQCM, XPS, SEM and TEM measurements. All depositions were made in electrolytes containing 75 mM potassium antimony tartrate.

5.1 Tuning the oxide content in Sb/Sb$_2$O$_3$ coatings

Co-deposition of Sb and Sb$_2$O$_3$ was carried out using a local pH increase at the substrate surface during electrodeposition of Sb to facilitate precipitation of Sb$_2$O$_3$. Coatings with different oxide content were obtained by adjusting the buffer capacity in the electrolyte. The deposition is first carried out on a Ni substrate; the resulting coatings will later be compared with deposition on Cu.

Comparing coatings deposited in an unbuffered solution (pH 4.1) with coatings deposited in a solution containing a mixture of 0.090 M KCl and 0.110 M HCl (pH 1.3), it is clear that two different morphologies are obtained (Figure 5.1).
In the unbuffered solution, with a pH of 4.1 to allow precipitation of Sb$_2$O$_3$, uniform smooth black deposits comprising agglomerated particles were obtained; a pH of 1.3 gave silvery-white brittle coatings made up of large well-defined crystals. The SEM micrographs also indicated smaller particles for the coating deposited in the unbuffered solution. This was further verified by XRD measurements (Paper I), from which a crystallite size of 260 nm was determined for the coating deposited at pH 1.3. The deposit obtained in the unbuffered solution gave two different crystallite sizes: 95 and 16 nm. The coatings had a thickness of around 300 nm (Figure 5.2).
The nucleation of Sb was more difficult in the pH 1.3 solution compared to the unbuffered solution. This indicates that Sb$_2$O$_3$ provides nucleation sites, facilitating deposition of antimony and consequently influencing the Sb grain-size.

As depicted in the TEM micrographs (Figure 5.3) of the coatings deposited in the unbuffered solution, the deposit contained Sb with a particle-size down to 20 nm (the larger, darker particles in Figure 5.3a) surrounded by a matrix of smaller Sb$_2$O$_3$ particles (<2 nm). The electron diffraction pattern exhibited rings from nanocrystalline Sb$_2$O$_3$ and a polycrystalline Sb pattern.

Figure 5.3 TEM micrographs showing larger, darker and slightly faceted nanoparticles of Sb surrounded by a matrix of smaller Sb$_2$O$_3$ particles (a), and small (<2 nm) nanoparticles agglomerated on the surface of larger particles (b).

The mass of the deposited Sb/Sb$_2$O$_3$ coatings is larger than that expected on the basis of a 3 e$^-$ reduction of Sb(III) to Sb, which indicates that the co-deposition of Sb$_2$O$_3$ does not involve an electrochemical reaction. This is further supported by EQCM measurements (Figure 5.4), where the mass increase was found to be 1.23 times higher than expected. From the constant slope of the frequency versus time plot, it is also clear that the co-deposition rate of Sb$_2$O$_3$ was constant throughout the entire deposition process (except during nucleation: t < 10s). This means that the necessary increase in pH occurred within the first 10s of deposition. The constant co-deposition of Sb$_2$O$_3$ throughout the procedure is also supported by XPS depth profiles (Paper I).
There is a large difference in the deposition potential between the two solutions (Figure 5.5). This is due to the iR drop and that different complexes are involved in the deposition procedure.

Although we have not been able to find the relevant stability constants for the antimony tartrate system and hence predict the precise nature of the
species present in the solution, it is clear that the dimer Sb$_2$(H$_2$L)$_2^{2-}$ is one possible species in the unbuffered solution$^{63}$. In this case, H$_2$L denotes tartrate having lost not only its two carboxyl protons but also its two hydroxyl protons. The deposition reactions for Sb-deposition in an unbuffered electrolyte can be written:

\[
\text{Sb}_2\text{(H}_2\text{L})_2^{2-} + 6 \text{e}^- \leftrightarrow 2 \text{Sb} + 2 \text{H}_2\text{L}^4^+ \quad (5.1)
\]

\[
2 \text{H}_2\text{L}^{4+} + 4 \text{H}^+ \leftrightarrow 2 \text{L}^{2-} \quad (5.2)
\]

\[
\text{Sb}_2\text{(H}_2\text{L})_2^{2-} + 4 \text{H}^+ + 6 \text{e}^- \leftrightarrow 2 \text{Sb} + 2 \text{L}^{2-} \quad (5.3)
\]

From reaction (5.3), obtained by combining reactions (5.1) and (5.2), it is clear that protons are consumed in the reduction of the antimony tartrate, which will result in a local pH increase at the substrate surface. As a result, Sb$_2$O$_3$ begins to precipitate in the solution (eq. 5.4) in the vicinity of the substrate surface, and Sb$_2$O$_3$ can become incorporated into the coatings according to:

\[
\text{Sb}_2\text{(H}_2\text{L})_2^{2-} + 2 \text{OH}^- + \text{H}_2\text{O} \leftrightarrow \text{Sb}_2\text{O}_3 + 2 \text{L}^{2-} \quad (5.4)
\]

Reaction (5.2) and (5.3) are, in fact, better written as:

\[
2 \text{H}_2\text{L}^{4+} + 4 \text{H}_2\text{O} \leftrightarrow 2 \text{L}^{2-} + 4 \text{OH}^- \quad (5.5)
\]

and

\[
\text{Sb}_2\text{(H}_2\text{L})_2^{2-} + 4 \text{H}_2\text{O} + 6 \text{e}^- \leftrightarrow 2 \text{Sb} + 2 \text{L}^{2-} + 4 \text{OH}^- \quad (5.6)
\]

due to the rapid pH increase during electrodeposition. The electrodeposition procedure in the unbuffered solution is presented schematically in Figure 5.6.
Since the precipitation of $\text{Sb}_2\text{O}_3$ is the result of an increase in pH during the electrodeposition process, the results of the depositions are expected to depend on the buffer capacity of the electrolyte. At pH 1.3, a significant increase in pH at the electrode surface is not expected since the buffer capacity of this solution is significantly higher than that of the pH 4.1 solution; Sb is thus expected to be deposited without precipitation of $\text{Sb}_2\text{O}_3$. As indicated by the different deposition potentials (after correction of the iR drop), the speciation is also different in the pH 1.3 and 4.1 solutions: in the pH 1.3 solution, the Sb(III) is most likely to be present as chloride complexes$^{64}$ (and not $\text{Sb}_2(\text{H}_2\text{L})_2^{2-}$), for which a local pH change should not occur on reduction (see Paper II for the reaction mechanism).

Coatings were also made in electrolytes with pH 2, pH 2.5 and pH 3, to study the influence of pH and buffer capacity on composition. The influence of current density on oxide contents was also studied.

Since the precipitation of $\text{Sb}_2\text{O}_3$ takes place in a reducing environment, it could be expected to be reduced to Sb. However, the significant amount of $\text{Sb}_2\text{O}_3$ found in the deposited layer suggests that the reduction process is incomplete. This could be because the $\text{Sb}_2\text{O}_3$ particles are coated with an ever-growing protective layer of Sb, thereby suppressing the reduction. A crucial question is then whether this process can be utilized to obtain Sb/$\text{Sb}_2\text{O}_3$ coatings thicker than 300 nm.

---

**Figure 5.6** A schematic representation of the deposition process of Sb/$\text{Sb}_2\text{O}_3$ on Ni in the unbuffered solution.
5.2 Deposition of Sb/Sb2O3 coatings thicker than 300 nm

It was found that thicker coatings of pure Sb could be prepared in the pH 1.3 solution merely by increasing deposition time. However, the corresponding deposition of thicker Sb/Sb2O3 coatings was found to be less straightforward. Simply increasing deposition time resulted in coatings with less oxide content than in the thin films. The dissolution rate of Sb2O3 from the electrode into the solution increases with time, as a result of an increase in local concentration of the liberated tartrate as the complex dissociates during the deposition. Various attempts have been made to obtain thicker films with high oxide content (paper II). A thick coating with morphology and oxide concentration similar to that deposited in an unbuffered solution with a current density of 1.92 mA/cm² has not so far been obtained, however.

5.3 Deposition of Sb/Sb2O3 on Cu

In Paper III, deposition of Sb was carried out on Cu in order to obtain thin coatings of Cu2Sb. Synthesis of Cu2Sb was performed using the copper in the substrate and the electrodeposited antimony, where the antimony coatings so-obtained were heat-treated at 300°C in a vacuum furnace inside an argon-filled glove-box (O2, H2O < 2 ppm) to increase the rate of Cu diffusion into the deposit. Cu2Sb was found to be the only phase present after 1h of heat-treatment (Figure 5.7a and c). After 48h of heat-treatment, a new phase was observed. According to the phase diagram for antimony and copper65, there are two stable phases at room temperature: Cu2Sb and Cu6Sb2. The new phase can thus be ascribed to the hexagonal incomensurate structure Cu6Sb2, which can be expected to form in the presence of an excess of copper in the system.66 In the coating deposited at pH 1.3, there were only traces of Cu2Sb after 48h of heat-treatment, whereas the coating deposited at pH 4.1 contained a mixture of Cu2Sb and Cu6Sb2.
In accordance with the earlier described deposition of Sb and Sb$_2$O$_3$ on Ni, electrolytes with different pH were used to deposit Sb and Sb$_2$O$_3$ coatings with different microstructure. The chronopotentiograms of the deposition indicate that the mechanisms involved during the deposition were the same as for deposition on Ni. However, the morphology is strongly dependent on the type of substrate used (Figure 5.8).
When Sb$_2$O$_3$ is co-deposited, 100-200 nm long particles with a thickness of around 10 nm were obtained for depositions made in an unbuffered solution. Films deposited on Ni under similar condition contained agglomerated nanoparticles (Figure 5.1a). This is most likely to be a result of the nucleation process, which is affected by oxide covering the Ni surface. Comparing coatings deposited in an unbuffered solution on Cu with a coating deposited on Cu in a pH 1.3 solution it is seen that co-deposition of Sb$_2$O$_3$ also gives rise to smaller particles when Cu is used as a substrate.

The nucleation process seems also to affect the oxide content in the electrode. EQCM measurements show that the amount of codeposited oxide was only 8%, compared to ca. 25% for deposition on Ni under similar conditions (Figure 5.9).
Figure 5.9 EQCM measurements of deposition of Sb/Sb$_2$O$_3$ on Cu with a current density of 4 mA/cm$^2$ in a quiescent solution of 0.075 M antimony tartrate at pH 4.1.

However, the mass increase during the first 14s was in the same range as for deposition on Ni under similar conditions. The lower mass increase during the remaining 86s can be explained by an increase in dissolution of the co-deposited Sb$_2$O$_3$, since the free ligand concentration of the tartrate complex increases with time. As a result of a difference in morphology, the surface area exposed to the electrolyte of the film (where the ligand concentration is high) is larger when deposited on Cu than on Ni. The co-deposited oxide is therefore dissolved more easily, since it is not incorporated into the film and covered by Sb.
6. Cycling stability of anode materials for Li-ion batteries

The electrochemical performance of different Sb-materials, representing different routes to circumvent the effect of the large volume changes involved in the lithiation mechanism, is discussed in this section. The complexity of the system is increased stepwise, starting with the model compound Sb, moving to the more complex model compound Cu₂Sb, and then to an AlSb composite electrode. The way different parameters, such as morphology, particle size, oxide content and electrode composition, influence the electrochemical performance are studied. The parameters giving a stable cycling performance are compared for the different systems. A focus is placed on the SEI formation for the AlSb electrode, which is studied from the viewpoint of electrochemical performance.

6.1 Sb/Sb₂O₃

6.1.1 The influence of oxide content on cycling stability

In the previous section, it was shown that it is possible to obtain coatings composed of Sb and different amounts of Sb₂O₃ by tuning the pH during electrodeposition. Coatings comprising nanoparticles of Sb and Sb₂O₃ with a concentration of ca. 25% Sb₂O₃ were obtained from a pH 4.1 solution prepared by simply dissolving antimony tartrate in deionised water. The presence of oxide is confirmed as a voltage plateau around 1.6 V (Figure 6.1a). Sb₂O₃ reacts with Li to form Li₂O according to eq 6.1:

\[
6 \text{Li}^+ + \text{Sb}_2\text{O}_3 + 6 \text{e}^- \leftrightarrow 3 \text{Li}_2\text{O} + 2 \text{Sb}
\] (6.1)

The electrochemical reactions in the same voltage range on charging indicate that the reaction is to some extent reversible. A further difference between these discharge profiles is a plateau at about 0.4 V, observed for the Sb but not for the Sb/Sb₂O₃ coating. Although this plateau becomes less pronounced on repeated cycling, it is still observable after ten cycles. It would seem that the plateau is visible only on the lithiation of well-defined
Sb (or Sb/Sb\textsubscript{2}O\textsubscript{3}) particles within the coatings. In Paper II, it is shown that this plateau is much less pronounced for thick Sb coatings containing a wider range of particle sizes and thus constituting a less well-ordered system.

**Figure 6.1** a) Chronopotentiograms showing the first three cycles for Sb/Sb\textsubscript{2}O\textsubscript{3} (a) and pure Sb (b) coatings on Ni.

Long-term cycling of the electrodes shows that the cycling stability of the electrode material increases dramatically when the oxide is present (Figure 6.2), where excellent stabilities are exhibited with a reversible capacity of about 640 mAh/g for at least 50 cycles: this is close to the theoretical capacity for a coating containing *ca.* 25% Sb\textsubscript{2}O\textsubscript{3} (770 mAh/g).
Figure 6.2 Cycling stability of an Sb/Sb$_2$O$_3$ coating (grey circles) and a pure Sb coating (black circles). The filled circles represent the discharge capacity and the open circles the charge capacity.

The first chronopotentiometric cycles of electrodes containing amounts of oxide less than 25% are shown in Figure 6.3. The Sb$_2$O$_3$ content in the coatings, which can be estimated from the charge required for reaction to occur (6.1), was found to be ca. 12%, 6% and 7% for coatings prepared in the pH 2, pH 2.5 and pH 3 electrolytes, respectively. Although the electrodes cycle well initially (for about 10 cycles), it is clear that none shows a stable cycling performance under long-term cycling.
Figure 6.3 The first chronopotentiometric cycle for Sb/Sb₂O₃ coatings deposited on Ni at pH 2, pH 2.5 and pH 3. The cycling stabilities for the respective coatings are shown in the inset figure.

The notion, that morphology affects the stability of the coatings is further supported by the electrochemical performance of coatings deposited with a current density of 40 mA/cm² in a pH 1.3 solution, and with a current density of 4.0 mA/cm² in a pH 4.1 solution (Figure 6.4). The coatings have an oxide concentration of ca. 18% and 23%, respectively (based on the Sb₂O₃ reduction plateau). Nevertheless, as seen in the inset in Figure 6.4, the stabilities of the coatings were found to be poor, although the 4.0 mA/cm² coating reaches a stable capacity of about 300 mAh/g after ca. 40 cycles.
Figure 6.4 The first chronopotentiometric cycles for Sb/Sb$_2$O$_3$ coatings deposited on Ni with a current density of 40 mA/cm$^2$ in a pH 1.3 solution (1) and at a current density of 4 mA/cm$^2$ in a pH 4.1 solution (2). The cycling stabilities for the respective coatings are shown in the inset figure.

This result shows that stable cycling behaviour is not reached, although the electrodes have an oxide concentration in the same range as the well-performing electrodes deposited on Ni (Figure 6.2). It can thus be concluded that the stability of the electrodeposited Sb/Sb$_2$O$_3$ coatings, when used as anodes in Li-ion batteries, depends both on the concentration of Sb$_2$O$_3$ in the coatings as well as on the size of the Sb and Sb$_2$O$_3$ particles. The extent to which the oxide and particle-size content influence the electrochemical behaviour can be difficult to assess, since the precipitation of Sb$_2$O$_3$ influences particle size.

6.2 Cu$_2$Sb

6.2.1 Cycling stability
Coatings deposited in an unbuffered solution on a Cu surface contained, according to EQCM, a smaller amount of oxide than those deposited on a Ni surface. This is also evident in the first discharge profile when the coatings are tested as negative electrodes in a Li-ion battery (Figure 6.5). The oxide is again reduced at 1.6 V (Figure 6.5a). The charge required for the reaction
given in eq. 6.1 suggests that the amount of co-deposited oxide was ca. 5% rather than 9% as indicated by EQCM data. This value of 5% is an underestimate, however, since the total charge involved in the first discharge includes a contribution from the formation of an SEI layer at potentials close to 0.9 V (Paper I). The capacity of the first discharge significantly exceeds the theoretical capacity of 386 Ah/g for an electrode containing 9% oxide, indicating significant SEI formation within the same voltage range as the lithiation reaction.

![Figure 6.5 Chronopotentiograms showing the first three cycles for an oxide-containing Cu$_2$Sb (a) and a pure Cu$_2$Sb coating (b).](image)

Long-term cycling of the Cu$_2$Sb electrodes (Figure 6.6) shows that the oxide does not improve the cycling stability as it does for Sb. On the contrary, the oxide-containing samples start losing capacity after 25 cycles. The Cu$_2$Sb electrodes not containing oxide show stable cycling for at least 65 cycles with a capacity of around 300 mAh/g, close to the theoretical value of 325 mAh/g. Earlier studies of composite electrodes containing Cu$_2$Sb have shown stable cycling performance with capacities upto 290 mAh/g$^{43}$. However, the capacity has been shown to vary between different studies,
since the reversibility of the first lithiation step is strongly dependent on preparation procedure\textsuperscript{43,67-69}. The fact that the oxide-containing samples cycle well for as long as 25 cycles stresses the importance of a long-term cycling in assessing the stability of a material.

![Figure 6.6 Cycling stability for a pure Cu$_2$Sb (black circles) and an oxide-containing Cu$_2$Sb (grey circles) coating. The filled circles represent the discharge capacity and the open circles the charge capacity.](image)

It is not surprising that the oxide is not needed to secure stable cycling of Cu$_2$Sb. The compound is formed \textit{via} the intermediate phase Li$_2$CuSb, and is structurally related to the final product Li$_3$Sb (Figure 6.7). Moreover, the volume expansion on lithiation is only \textit{ca.} 42\%, compared to \textit{ca.} 150\% for pure Sb. The Sb$_2$O$_3$ buffering effect should thus be much less for Cu$_2$Sb than for Sb.
Figure 6.7 Cu<sub>2</sub>Sb (a) is lithiated via the intermediate phase Li<sub>2</sub>CuSb (b) to form the end product Li<sub>3</sub>Sb (c).

These results clearly show that stable cycling can be obtained for Cu<sub>2</sub>Sb films with particle sizes in the range 200-300 nm. The poor cycling behaviour of the oxide-containing samples, can be attributed to loss of contact between an increasing fraction of the material. Disassembling the cycled batteries reveal that parts of the oxide-containing material have lost contact with the Cu electrode, whereas no such effect is seen for the pure Cu<sub>2</sub>Sb material.

6.2.2 The lithiation process

The first discharge curves for the Cu<sub>2</sub>Sb samples (Figure 6.5) exhibit two plateaus (at about 0.85 and 0.66 V) ascribable to a combination of SEI layer formation and stepwise lithiation of Sb. Since three discrete plateaus are seen in the corresponding second-cycle discharge curves, it is likely that the SEI formation cycle masks the lithiation plateaus during the first cycle, and that the lithiation, in fact, involves three different reactions. This means that step one in eq. 3.2 should be divided into two, steps yielding either:

\[ \text{Cu}_2\text{Sb} + \text{Li}^+ + \text{e}^- \leftrightarrow \text{LiCu}_2\text{Sb} \] (6.2)

\[ \text{LiCu}_2\text{Sb} + \text{Li}^+ + \text{e}^- \leftrightarrow \text{Li}_2\text{CuSb} + \text{Cu} \] (6.3)

according to the suggestion of Morcrette et al.\textsuperscript{67} or:

\[ \text{Cu}_2\text{Sb} + \text{Li}^+ + \text{e}^- \leftrightarrow \text{LiCuSb} + \text{Cu} \] (6.4)

\[ \text{LiCuSb} + \text{Li}^+ + \text{e}^- \leftrightarrow \text{Li}_2\text{CuSb} \] (6.5)

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based on the reactions proposed by Matsuno et al. 70. This is further supported by the three plateaus observed during the delithiation on the first cycles in Figure 6.5, and the fact that XRD data confirm the reformation of Cu₂Sb during the delithiation step (see below). However, three discrete alloying potentials have yet to be seen for composite electrodes, where the presence of binder and carbon black makes the discharge profiles more indistinct43.

The capacity associated with the plateau at 1.05 V, where Cu₂Sb reformation is expected, is higher for the coating deposited at pH 4.1 than at pH 1.3. This could suggest that the reformation of Cu₂Sb benefits from the presence of smaller particles in the pH 4.1 sample. The larger capacity for the pH 4.1 material may, however, also be due to Sb₂O₃ reformation, as discussed above.

It is also evident that the irreversible first-cycle capacity is smaller for the oxide-containing samples than for the deposition made at pH 1.3. A particle-size effect was recently described by Morcrette et al.67, who showed that the reformation of Cu₂Sb only takes place within materials containing sufficiently small particles. The reformation of Cu₂Sb has also been studied by XRD (Figure 6.8), which shows Cu₂Sb reformation for both samples after one cycle.

Figure 6.8 XRD for patterns for a pure Cu₂Sb (a) and an oxide-containing Cu₂Sb (b) coating after the first chronopotentiometric cycle, recorded at C/10 rate for one cycle.
From the cycling performance, it can be concluded that the presence of oxide (which chiefly influences particle size) seems to improve structural reversibility. However, the cycling of pure Cu$_2$Sb is also to some extent reversible, showing a stable capacity close to its theoretical value on long-term cycling (for 65 cycles), whereas the oxide seems to contribute to contact problems. The oxide does not have the same stabilising effect on Cu$_2$Sb as on Sb, which undergoes large volume changes during cycling.

### 6.3 Cu$_9$Sb$_2$

Electrochemical performance of electrodes containing Cu$_9$Sb$_2$ was tested for the first time in a Li-ion battery context. It was shown that the lithiation process takes place at 0.4 V, which is lower than for the lithiation of Cu$_2$Sb (Figure 6.5a). However, the delithiation process occurs over the same voltage range as Cu$_2$Sb. On the second discharge, the chronopotentiogram is more similar to that of Cu$_2$Sb (Figure 6.9a), although the plateaus are less pronounced and, upon further cycling, more discrete plateaus are formed (Figure 6.9b). The chronopotentiogram indicates that Cu$_2$Sb (with an excess of surrounding Cu) is formed on delithiation rather than Cu$_9$Sb$_2$. However, the detailed lithiation process must be studied further with *in situ* XRD.

![Figure 6.9](image)

**Figure 6.9** Chronopotentiograms showing the first and second cycle (a) and the 15$^{th}$ cycle after ca. 260h (b) for pure Cu$_9$Sb$_2$.  

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The Cu$_9$Sb$_2$ electrodes show a stable capacity on long-term cycling (Figure 6.10), but with a higher initial irreversible capacity than Cu$_2$Sb resulting in a lower capacity. The oxide-containing coatings, which involved a mixture of Cu$_2$Sb and Cu$_9$Sb$_2$ after 48h of heat-treatment, exhibit unstable cycling, analogous to the oxide-containing Cu$_2$Sb coatings in Figure 6.6.

![Figure 6.10](image)

**Figure 6.10** Cycling stability of pure Cu$_9$Sb$_2$ (black circles) and oxide-containing Cu$_9$Sb$_2$ (grey circles) coatings. The filled circles represent the discharge capacity and the open circles the charge capacity.

### 6.4 AlSb

The surface chemistry and the lithiation mechanism of AlSb are studied in Papers IV and V to get a deeper understanding of the reactions involved. AlSb has shown stable cycling with a capacity of 250 mAh/g when cycled over a 1.2-0.5 V voltage window, while it loses capacity with every cycle when cycled down to 0.01 V (Figure 6.11). The study focuses on the low-potential region, since cycling to this lower potential influences electrochemical performance negatively.
Figure 6.11 The cycling stability of ball-milled AlSb electrodes cycled over a voltage window of 1.2-0.5 V (grey circles) and 1.2-0.01 V (black circles).

The surface has been studied at various lithiation stages (Figure 6.12) during the first discharge, as well as after galvanostatic cycling for shorter (3 cycles) and longer (50 cycles) periods.
Figure 6.12 The first chronopotentiometric cycle of ball-milled AlSb electrodes cycled over a voltage window of 1.2-0.5 V (grey line) and 1.2-0.01 V (black line); A-G indicate surface characterized lithiation stages.

6.4.1 SEI formation during the first cycles

XPS studies of the SEI were made on ball-milled electrodes that had been equilibrated potentiostatically to 0.9 V, 0.75 V, 0.5 V and 0.01 V, as indicated in Figure 6.12. The thickness of the SEI-layer is related to the intensity of the carbon black (CB) peak at 284.4 eV. The increase in SEI-thickness during subsequent discharge is seen as a decrease in the intensity of the CB peak in the C1s spectra (Figure 6.13). The most significant increase in SEI-thickness occurs between 0.5 V and 0.01 V.

The C-F bonds in the PVDF binder appear at 290.7 eV in the C1s spectra of an uncycled electrode. Since the SEI-layer is growing during discharge, the intensity of the PVDF peak decreases, and a shoulder appears at higher binding energies (above 292 eV). This peak is believed to originate from degradation of the PVDF through reactions with electrolyte.
Figure 6.13 XPS C1s spectra for AlSb electrodes before discharge (A) and potentiostatically equilibrated to 0.9 V (B), 0.75 V (C), 0.5 V (D) and 0.01 V (E) (a); and enlargement of the CB peak at 284.6 eV (b).

The influence of voltage window on SEI-thickness is further verified by studies of electrodes cycled galvanostatically to their delithiated state after 3 cycles (Figure 6.14). The carbon-black peak for the electrode cycled over a 1.2-0.5 V voltage window has a slightly higher intensity relative to the 286 eV peak than for the electrode cycled down to 0.01 V. The difference is subtle, but becomes more pronounced after sputtering for 30s and 60s. The carbon-black peak increases more quickly with sputtering time for the electrode cycled over a 1.2-0.5 V voltage window, implying that a thinner SEI layer has been formed.
6.14 XPS C1s spectra for AlSb electrodes in their delithiated state after three cycles using a voltage window of 1.2-0.5 V (a) and 1.2-0.01 V (b). The XPS spectra are recorded after 0s, 30s and 60s of sputtering.

The surfaces of AlSb electrodes cycled galvanostatically are compared in Figure 6.15 to those for a graphite electrode. All electrodes are in their delithiated state and have been cycled with a current density of C/10 for three cycles. The composition of the surface species for AlSb is similar to that on the graphite surface, but the ratio between the different functional groups is different. Smaller amounts of alkyl carbonates (at ~287.9 eV and ~289.7 eV) and/or Li alcoxides (at ~287.9 eV) are found on the AlSb surface. The peak at ~292 eV is also present for the graphite electrode. This indicates that the origin of this peak is dependent on the type of electrolyte and binder used rather than on the anode material. This result supports the suggested electrolyte-binder reactions and PVDF degradation.
Figure 6.15 XPS C1s spectra for AlSb electrodes using a voltage window of 1.2-0.5 V (a) and 1.2-0.01 V (b) and graphite (c). The electrodes are in their delithiated state after three cycles.

6.4.2 SEI after long-term cycling

There is an obvious difference in SEI-thickness between AlSb and graphite after 50 cycles compared to after only 3 cycles (Figure 6.16). The SEI is thinner for AlSb than for graphite, where the carbon-black peak now is completely hidden by electrolyte degradation products. There is also still a difference in SEI-thickness between the AlSb electrodes cycled over different voltage windows. The carbon-black peak is more intense for the electrodes cycled over a 1.2-0.5 V voltage window. There is also a difference in the SEI formed between the lithiated and the delithiated state. The functional groups are the same, but the ratio between them differs, and the SEI appears to have a dynamic character. This is more pronounced for the electrode cycled down to 0.01 V. This is consistent with the notion of repeated SEI formation, disintegration and reformation. The disintegration of the SEI is brought about by the volume changes occurring during lithiation and delithiation. The volume changes are almost certainly larger for the electrode cycled down to 0.01 V, since it is expected to be fully lithiated. A more dynamic character can hence be expected. The disintegration and reformation of the SEI layer can also be expected to contribute to a thinner SEI layer for intermetallics than for graphite. It has already been shown that
the SEI layers on Sn-containing anodes are different from those on graphite\textsuperscript{18,19}.

![Figure 6.16 XPS C1s spectra for AlSb electrodes after 50 cycles using a voltage window of 1.2-0.5 V (a) and 1.2-0.01 V (b) and graphite (c), in their delithiated (thin line) and lithiated (thick line) states.](image)

That the capacity decreases with every cycle using a 1.2-0.01 V voltage window could be a result of increased SEI formation on successive cycling.

6.4.3 The lithiation process

The lithiation mechanism is here discussed based on \textit{in situ} XRD measurements made in transmission mode, in combination with the surface studies and electrochemical cycling. The alloying scheme of Li with AlSb is complex and is not yet fully understood. This complexity is increased by reversible reactions occurring between the intermetallic and the electrolyte at potentials below 0.5 V (see above).

The first chronopotentiometric cycle of ball-milled AlSb electrodes shows the presence of oxide formed during the synthesis around 1.5 V. There is a gently sloping plateau between 0.9 V and 0.5 V, which is suggested to correspond to the insertion of lithium into the interstitial sites of the AlSb zinc-blende framework to form a metastable $\text{Li}_x\text{AlSb}$ phase:

\[\text{AlSb} + x\text{Li}^+ + xe^- \rightarrow \text{Li}_x\text{AlSb}\]

The sloping nature of this plateau indicates that Li forms a solid-solution in AlSb. Additional electrochemical processes are seen in the discharge curve for potentials below 0.5 V. For pure Sb, the formation of $\text{Li}_3\text{Sb}$ occurs at
0.8 V (Figure 6.1). The XRD pattern for the ball-milled AlSb contains large amorphous regions (see Paper IV). XRD studies were made on crystalline hand-ground AlSb to get some picture of the lithiation mechanism. In situ XRD of electrodes equilibrated potentiostatically to 0.5 V and 0.01 V show, however, that the concomitant main extrusion process of aluminium, which ultimately yields a Li₃Sb discharge product (eq. 6.7), occurs first below 0.5 V (Figure 6.17).

\[ \text{Li}_x\text{AlSb} + x\text{Li}^+ + xe^- \rightarrow \text{Li}_3\text{Sb} + \text{Al} \]  \hspace{1cm} (6.7)

![XRD profiles of AlSb electrodes made from hand-ground powder equilibrated potentiostatically to 0.5V and 0.01V.](image)

**Figure 6.17** XRD profiles of AlSb electrodes made from hand-ground powder equilibrated potentiostatically to 0.5V and 0.01V.

The electrochemical reactions between 0.5 and 0.01 V are hence not attributed to lithiation of the extruded aluminium to form LiAl, which is suppressed in carbonate-based electrolytes, but rather to the overpotential required to continue the reaction from AlSb to Li₃Sb towards the end of discharge. SEM micrographs of electrodes made from ball-milled powder as well as from hand-ground powder are shown in Figure 6.18.
Figure 6.18 SEM micrographs of AlSb electrodes made from ball-milled powder (a) and hand-ground powder (b).

The first chronopotentiometric cycle of an electrode made from hand-ground powder shows a high irreversible capacity (Figure 6.19a). It also shows a smaller amount of oxide than ball-milled samples. The plateau at lower potentials (<0.5 V) is also more pronounced. For the electrode cycled over a 1.2-0.01 V voltage window, it is shown that the capacity decreases dramatically during the first 5 cycles, until stable cycling is reached with a capacity lower than 50 mAh/g (Figure 6.19b). This is similar to the electrode cycled over 1.2-0.5 V a voltage window.

Figure 6.19 The first chronopotentiometric cycle of hand-ground AlSb electrodes cycled over a voltage window of 1.2-0.5 V (grey line) and 1.2-0.01 V (black line) (a); and cycling stability of hand-ground AlSb electrodes cycled over a voltage window of 1.2-0.5 V (grey circles) and 1.2-0.01 V (black circles) (b).
Particle size most certainly plays a significant role in determining the electrochemical performance of AlSb.
7. Concluding remarks

7.1 Parameters influencing electrochemical performance

The microstructure of the anode material is crucial for obtaining a battery with stable cycling performance and with high reversibility. The importance of the different properties controlling the stability, such as particle size, oxide content and morphology has been studied in this thesis. It has been demonstrated using a stepwise increase in the complexity of the system studied, that these parameters vary strongly with the type of system.

The cycling performance of pure Sb, which undergoes severe volume changes, is improved dramatically by incorporating a second component, Sb$_2$O$_3$ (optimally ca. 25%). Electrochemical performance has also been shown to be strongly dependent on particle size and morphology for these Sb/Sb$_2$O$_3$ compounds. The extent to which these parameters influence cycling stability is so far difficult to assess, since the oxide concentration affects the size of the particles formed during the deposition process.

Cu has a buffering effect for Cu$_2$Sb. Oxide is not required to achieve a stable cycling performance. The cycling stability of Cu$_2$Sb does not show the same dependence on particle size as Sb/Sb$_2$O$_3$. Particle size and oxide content appear, however, to influence the structural reversibility of Cu$_2$Sb, which is improved when the oxide is incorporated into the electrode and the particles become smaller. Cu$_9$Sb$_2$ has been presented for the first time as an anode material in a Li-ion battery context. Stable but lower cycling capacities were found compared to Cu$_2$Sb; and a transformation of Cu$_9$Sb$_2$ into Cu$_2$Sb occurred during cycling.

For AlSb, it has been shown that cycling stability is strongly dependent on the voltage window used during cycling. AlSb has been studied as a composite electrode, in the presence of carbon black and binder, thus further increasing the complexity. It is here demonstrated that the formation of electrolyte species on the electrode surface is influenced by the voltage window, and that the SEI layer has a dynamic character. It is also shown that the cycling stability of the material decreases enormously when it consists of particles in the micron range, compared to particles ball-milled down to the nm range. Ball-milled materials often contain impurity oxides in the final
product. As for Sb/Sb$_2$O$_3$, it is also here difficult to ascertain the extent to which the oxide and the size of the particles improve cycling performance.

7.2 Synthesis of model compounds

It is relatively simple to control the microstructure of the anode material and to study different parameters separately by preparing the anode by electrodeposition. The technique is cheap, quick and readily applicable in to an industrial context.

It has been demonstrated that it is possible to obtain a nanomaterial of Sb and Sb$_2$O$_3$ using a local increase in pH at the electrode surface. The oxide content in the electrode, as well as the size of the particles, can be controlled by varying the pH or the current density in the deposition step. It has also been shown that Cu$_2$Sb films can be synthesized by heat-treating coatings of Sb or Sb/Sb$_2$O$_3$ electrodeposited on copper substrates. The concentration of Sb$_2$O$_3$ in the films was found to be significantly lower for deposition on Cu than on nickel. Deposition on Cu also resulted in larger particles. Cu$_6$Sb$_2$ was obtained by increasing the duration of the heat treatment. The synthesis method is versatile and particularly promising for preparing anode materials for microbatteries, since the current collector is used as the substrate in the synthesis step. Preliminary results for Sb electrodeposited on Cu nano current-collectors open up exciting perspectives for its potential use in future three-dimensional microbatteries (3D-MBs).
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[Signature]
Användandet av bärbara elektroniska apparater som mobiltelefoner och datorer har ökat dramatiskt under det senaste årtiondet. Utvecklingen går hela tiden mot mindre och lättare apparater vilket naturligtvis ställer samma krav på batteriet. I och med att den globala uppvärmningen har fått ökad uppmärksamhet har också fokus på el- och hybridbilar ökat, i vilka batteriet är en nyckelkomponent. I dagsläget använder man en rad olika uppladdningsbara batterier så som blysyra-, nickeldiamond- nickelmetallhydrid- och litiumjonbatterier. Litiumjonbatterier är den grupp av batterier som idag utvecklas snabbast och det är dem som vi hittar i de flesta av dagens mobiltelefoner och bärbara datorer. De har hög energitäthet (kan lagra mycket energi per volym och vikt), vilket gör dem små och lätta.


**Figur 1** En schematisk bild av ett litiumjonbatteri under urladdning.

Figur 2 Elektrodeponering av antimon och nanopartiklar av antimonoxid.


Figur 3. SEM-bilder av elektrodeponerade elektroder bestående av a) antimon och antimonoxid och b) antimon.

Alla mina exempel visar att elektrodkemin i ett litiumjonbatteri är komplex och att varje material måste optimeras allt efter sina unika elektrokemiska egenskaper. Ett hybridbilsbatteri kommer att kräva en viss kemi som är skild från kemin i ett batteri som används för en mobiltelefon och ett mikrobatteri kommer i sin tur kräva sin optimala kombination av material. Mina resultat visar att det går att renodla systemen på ett sådant sätt att resultaten går att använda för att förstå hur vilka egenskaper som är viktigast. Det gör det möjligt att optimera materialen i ett litiumjonbatteri.
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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”.)