Fundamental Insights into the Electrochemistry of Tin Oxide in Lithium-Ion Batteries

SOLVEIG BÖHME
Abstract

This thesis aims to provide insight into the fundamental electrochemical processes taking place when cycling SnO\(_2\) in lithium-ion batteries (LIBs). Special attention was paid to the partial reversibility of the tin oxide conversion reaction and how to enhance its reversibility. Another main effort was to pinpoint which limitations play a role in tin based electrodes besides the well-known volume change effect in order to develop new strategies for their improvement.

In this aspect, Li\(^+\) mass transport within the electrode particles and the large first cycle charge transfer resistance were studied. Li\(^+\) diffusion was proven to be an important issue regarding the electrochemical cycling of SnO\(_2\). It was also shown that it is the Li\(^+\) transport inside the SnO\(_2\) particles which represents the largest limitation. In addition, the overlap between the potential regions of the tin oxide conversion and the alloying reaction was investigated with photoelectron spectroscopy (PES) to better understand if and how the reactions influence each other's reversibility.

The fundamental insights described above were subsequently used to develop strategies for the improvement of the performance and the cycle life for SnO\(_2\) electrodes in LIBs. For instance, elevated temperature cycling at 60 °C was employed to alleviate the Li\(^+\) diffusion limitation effects and, thus, significantly improved capacities could be obtained. Furthermore, an ionic liquid electrolyte was tested as an alternative electrolyte to cycle at higher temperatures than 60 °C which is the thermal stability limit for the conventional LP40 electrolyte. In addition, cycled SnO\(_2\) nanoparticles were characterized with transmission electron microscopy (TEM) to determine the effects of long term high temperature cycling. Also, the effect of vinylene carbonate (VC) as an electrolyte additive on the cycling behavior of SnO\(_2\) nanoparticles was studied in an effort to improve the capacity retention. In this context, a recently introduced intermittent current interruption (ICI) technique was employed to measure and compare the development of internal cell resistances with and without VC additive.

**Keywords:** Tin, Tin oxide, Lithium-ion batteries, Electrochemistry, High temperature cycling, Conversion reaction, XPS, SEM

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List of papers

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

I  On the electrochemistry of tin oxide coated tin electrodes in lithium-ion batteries  

II Overlapping and Rate Controlling Electrochemical Reactions for Tin(IV) Oxide Electrodes in Lithium-Ion Batteries  
S. Böhme; K. Edström and L. Nyholm, *Submitted Manuscript*.

III Elevated temperature lithium-ion batteries containing SnO$_2$ electrodes and LiTFSI – Pip$_{14}$TFSI ionic liquid electrolyte  

IV Photoelectron Spectroscopic Evidence for Overlapping Redox reactions for SnO$_2$ Electrodes in Lithium-ion Batteries  

V The Influence of Al$_2$O$_3$ and Diamond as Additives on the Cycling Performance of SnO$_2$ Electrodes in Lithium-Ion Batteries  
S. Böhme; K. Edström and L. Nyholm, *In Manuscript*.

VI Effects of Elevated Temperature and Vinylene Carbonate on the Electrochemical Performance of SnO$_2$ Nanoparticles in Lithium-Ion Batteries  
S. Böhme; C.-W. Tai; K. Edström; G.A. Seisenbaeva and L. Nyholm, *In Manuscript*.

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My contributions to the appended papers

• **Paper I**
  I was involved in planning the study and conducted all of the experimental work. I wrote part of the manuscript and was involved in all discussions.

• **Paper II**
  I was involved in planning the study and conducted all of the experimental work. I wrote part of the manuscript and was involved in all discussions.

• **Paper III**
  I was involved in planning the study. I also conducted all of the electrochemical experiments as well as the SEM and XPS analysis in this work. I wrote part of the manuscript and was involved in all discussions.

• **Paper IV**
  I was involved in planning the study and conducted all of the experimental work. I wrote part of the manuscript and was involved in all discussions.

• **Paper V**
  I was involved in planning the study and conducted all of the experimental work. I wrote part of the manuscript and was involved in all discussions.

• **Paper VI**
  I was involved in planning the study. I also conducted the electrochemical experiments as well as the SEM and XPS analysis in this work. I wrote the main part of the manuscript and was involved in all discussions.

• **Disclaimer:** Part of this thesis is based on my licenciate thesis entitled *On the electrochemical behavior of tin oxides in lithium-ion batteries* (Uppsala University, 2015).
The author also contributed to the following publications that are not included in this thesis:

i  **Elemental Lithium Trapping in Alloy forming Electrode Materials and Current Collectors for Lithium based Batteries**
   D. Rehnlund; F. Lindgren; S. Böhme; T. Nordh; Y. Zou; J. Pettersson; U. Bexell; M. Boman; K. Edström and L. Nyholm, *Submitted Manuscript*.

ii **Substrate with doped diamond layer for lithium-based systems**
   D. Rehnlund; S. Böhme and L. Nyholm, *Filed patent*.

iii **The Influence of Particle Size and Temperature on the Electrochemistry of SnO₂ Electrodes in Sodium-Ion Batteries**

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For science must breathe the oxygen of freedom.

JOHN C. POLANYI
1. Introduction

The main energy sources currently used in our society are based on fossil fuels like oil, gas and coal. These are, however, finite resources and emit the climate affecting gas carbon dioxide ($CO_2$). Therefore, alternative energy sources have to be explored. Renewable sources like solar and wind energy are attractive, however, dependent on the development of better energy storage systems. Therefore, rechargeable battery systems are of increasing importance as they can replace combustion engines in cars and store excess energy produced in power plants. Lithium-ion batteries (LIBs) are on the way to becoming the main system for rechargeable batteries since they can store more energy per unit volume and weight than other battery types, e.g., nickel-metal hydride or nickel-cadmium batteries. Nowadays, LIBs are normally used in portable electronics like cell phones and computers. In these cases graphite is the most commonly used anode material, but other materials with higher energy and power densities are required for use in power plants and cars. Alloying materials like silicon, tin or lead can store much more energy than graphite but they also have much shorter cycle lives, an effect traditionally assigned to large volumetric changes associated with lithium incorporation. This is, in fact, the main problem to be tackled in research concerning alloying anode materials for high power and energy applications. [1–5]

1.1 Lithium-ion batteries (LIBs)

In batteries electricity is generated via redox reactions where oxidation and reduction are taking place at different electrodes and thus are locally separated. Upon discharge the oxidation takes place at the anode (negative electrode) while the reduction takes place at the cathode (positive electrode). The electrons move from the anode to the cathode through an electric conductor outside the cell and can be used to power an electronic device. At the same time ions migrate through the electrolyte. Secondary batteries can be recharged when an outer current is applied which results in movement of electrons and ions in the opposite direction. One example of secondary batteries is LIBs. Their mode of operation is schematically depicted in Figure 1.1. Upon discharge the anode is oxidized and lithium ions ($Li^+$) are released into the electrolyte. $Li^+$ migrate through the electrolyte to the cathode where they are incorporated while anions from the electrolyte salt move in the opposite direction. The electrons run to the cathode via an outer wire and reduce the cathode material.
During charging of the LIB an external current is applied and the processes are reversed. [3–5]

Typical electrolytes for LIBs consist of an organic solvent, usually a combination of ethylene carbonate, dimethyl carbonate and diethyl carbonate, in which a lithium salt, such as $\text{LiPF}_6$, $\text{LiBF}_4$, $\text{LiBOB}$ (lithium bis(oxalato)borate), or $\text{LiClO}_4$, has been dissolved. Cathode materials are, for example, layered oxides like $\text{LiCoO}_2$, spinels like $\text{LiMn}_2\text{O}_4$ and olivines like $\text{LiFePO}_4$, i.e., lithium containing oxides comprising metals that are able to adopt different oxidation states and incorporate $\text{Li}^+$. [3–5]

The first possible anode material that comes to mind is metallic lithium but there are several problems associated with its use. One issue is that lithium reacts strongly with commonly used electrolytes leading to safety problems. In addition, lithium grows dendrites when it is deposited on the anode during charge. These dendrites can eventually short-circuit the cell when they reach the cathode. In commercial LIBs graphite is currently used as the anode material. However, graphite has a rather low volumetric and gravimetric capacity (372 $\text{mAh/g}$ and 850 $\text{mAh/cm}^3$, respectively, for full lithiation, i.e., when $\text{C}_6\text{Li}$ is formed). This is a drawback when higher energy and power densities are required as for instance in electric vehicles (EVs) or power plants. Therefore, a lot of research is focussing on the development of new anode materials for LIBs with higher capacities. [3–5]

![Figure 1.1. Schematic figure showing a LIB.](image)

### 1.2 Anode materials for LIBs

Anode materials can be divided into three different categories. The first is insertion materials where lithium (Li) is incorporated into spaces in a structure
that were empty before. This process can be either heterogeneous meaning that the filling of the structure takes place randomly or homogeneous implying a systematic filling. Typical insertion materials are carbon-based compounds and some transition metal oxides like $TiO_2$ (anatase). In graphite $Li$ is stored between the graphene layers. The second category consists of materials that react with $Li$, i.e., where an actual chemical conversion takes place. They show large capacities but also large voltage hysteresis effects. Examples are transition metal oxides like $Fe_2O_3$ and $Co_3O_4$ as well as transition metal phosphides like $CoP_3$ and $NiP_2$. [6, 7] The last category comprises compounds that form alloys with $Li$. Examples are elements like tin ($Sn$) and silicon ($Si$) which show high capacities, but for which large volume expansions occur upon alloying. [3, 4, 7, 8]

1.2.1 Carbon based materials

Graphite is the most important carbon based anode material and can store up to one $Li$ per six carbon atoms. There are different graphitic carbon structures that can be used as anode materials which generally can be divided into graphite, disordered (hard and soft) carbons as well as nanostructured carbons. Graphite is a crystalline material where graphene layers are stacked in an ABAB-structure and lithium can be incorporated between the layers. Carbon atoms in disordered carbons are also arranged in graphene sheets, but not stacked into an ABAB-structure. Random rotational and translational disorders between the layers can be found instead. Other widely researched carbon structures are single and multi-walled carbon tubes (SWCNTs and MWCNTs), which are graphene sheets rolled into the shape of a cylinder. [6, 9]

1.2.2 Transition metal oxides

Other anode material candidates are transition metal oxides that can be classified based on the reaction type they undergo during $Li$ incorporation. There are certain oxides that undergo an intercalation reaction similar to graphite, e.g., spinel structures like $Fe_3O_4$ and $Mn_3O_4$ or the above mentioned $TiO_2$ (anatase). The other possibility is that the oxide is consumed by a conversion reaction where $Li_2O$ and the corresponding metal are formed reversibly according to reaction $MO_x + 2xLi + 2xe^- \rightleftharpoons xLi_2O + M$. Examples are $\alpha - Fe_2O_3$ and $Co_3O_4$. [6] Upon the first cycle the structures undergo irreversible amorphization after which they cycle reversibly. There are also some mixed oxides which can react with $Li$ in conversion reactions, e.g., vanadates $FeV_4O_4$ or $MnMoO_4$. [10]
1.2.3 Metals alloying with lithium

There are several metals which are suitable alloying materials for anodes in LiBs. They react reversibly according to the reaction \( M + xLi + xe^- \rightleftharpoons Li_xM \) and display much higher capacities than carbons as seen in Figure 1.2. The most promising alloying materials have so far proven to be tin (Sn), silicon (Si), germanium (Ge), arsenic (As) and lead (Pb). Due to the low abundance as well as the toxicity of Ge, As and Pb, Sn and Si have attracted the most interest. [4, 7, 8]

![Gravimetric and volumetric capacities of several Li hosting elements. The values were taken from the literature. [7, 8]](image)

All alloying materials show a high degree of volume expansion when incorporating Li. This is due to the density differences between Li and the electrode materials as Li has a much lower density than the latter. In a battery cell this leads to cracking, pulverization and eventually loss of the electric contact to the material during extended cycling. Therefore, the main goal in the development of new Sn and Si compounds for anode materials has so far been to minimize the volume change effects in order to prolong the cycle life. There are different strategies to achieve this based on the use of amorphous materials, nanoparticles, porous materials, thin films, active binders and a limited degree of reduction. [6, 7] However, limited volume change effects also result in limited energy densities. As a consequence, there is always a trade-off between cycle life and energy density for alloying materials. [11, 12]

There have also been efforts to incorporate metals into alloys or composites to decrease the volume expansion effects. There are two different types of alloys. The first consists of compounds containing one element which alloys with Li and one which does not, e.g., \( Cu_6Sn_5 \). An example of the second type...
is SnSb where both elements are reactive towards Li. In addition, composites with oxides and carbon have received much interest as these can act as inert matrices buffering towards volume changes. [6–8, 11, 12]

1.2.4 Tin and tin oxides

The reasons for the present research interest in tin based compounds are the high energy density of metallic tin (Sn) (theoretical specific capacity: 991 mAh/g) and the possibility of obtaining high power densities from these materials. [7, 8] However, tin based electrodes show fast capacity fading upon cycling generally ascribed to the large volume changes associated with the alloying between Sn and Li. This gives rise to cracks and, thus, the loss of active electrode material. In addition, the reactions with the electrolyte at the Sn interface have received a lot of scientific interest as an understanding of these processes can help to improve the performance of tin based electrodes too. [4, 11–13] Especially, SnO and SnO₂ are of importance as they show theoretical specific capacities of 1491 mAh/g and 1270 mAh/g, respectively. This is due to a combination of the tin oxide conversion reaction yielding Sn (see the conversion reaction of metal oxides) and the following alloying reaction between Sn and Li (see Reactions 1.1 and 1.2 below with x = 1; 2 and y = 4.4 for full lithiation). [12, 14, 15]

\[
2xLi^+ + 2xe^- + SnO_x \rightleftharpoons xLi_2O + Sn \quad (1.1)
\]

\[
yLi^+ + ye^- + Sn \rightleftharpoons Li_ySn \quad (1.2)
\]

During the alloy formation on the first cycle, the solid electrolyte interphase (SEI) layer is formed as well. This SEI is formed on the electrode surface by the electrochemical reduction of thermodynamically unstable electrolyte components below 1.0 V vs. Li⁺/Li and protects it from further electrolyte reactions after the initial cycle. [16–19] It has, however, been reported that the SEI could also be formed at potentials between 1.2 V and 1.5 V vs. Li⁺/Li on tin based anodes. [20, 21] Earlier reports have, in contrast, proposed that the electrochemical reaction taking place at about 1.2 V vs. Li⁺/Li represents the irreversible conversion of SnOₓ to Sn and Li₂O as described by Reaction 1.1. [14, 22, 23] A Li₂O matrix is thereby formed which encloses Sn particles. At potentials below 0.9 V vs. Li⁺/Li, the alloy formation, as described in Reaction 1.2, can subsequently be observed. [14, 22–28] It is, thus, still unclear at which potential exactly the SEI is formed in tin oxide electrodes during the first reduction. Furthermore, the formation of an unstable SEI is part of the reason for continued capacity fading due to reactions between electrode material and electrolyte. For this reason, vinyle carbonate (VC) and fluoroethylene carbonate (FEC) have been tested as electrolyte additives in order to form a more stable SEI and enable better capacity retention. [29–33]
The conversion reaction is generally assumed to be irreversible occurring only on the first cycle. This results in a large capacity loss already after the initial cycle which is one of the main problems for the application of tin oxides in LIBs. Nonetheless, there have recently been studies investigating the possible reversibility of this conversion reaction in which different techniques, e.g., $^{119}\text{Sn}$-Mössbauer; X-ray absorption and X-ray tomography, could detect a reversibility of the tin oxide conversion reaction. [24–26, 34–36] A partial conversion reversibility has even been observed in studies using diverse nanosized $\text{SnO}_x$ based structures and has mainly been explained by either the small particle size or the use of additives, e.g., carbon or copper. [26,36–42] The improved cycling behavior in these cases can to some part be due to an enhanced reversibility of the conversion reaction, but also to better buffering of the large volume changes that happen during alloying and dealloying. [37–42]

Many articles in the literature relate the $\text{SnO}_2$ particle size to improved capacity retention. These studies have shown that smaller particles lead to better capacity retention, an observation which can at least partially be explained by kinetic or mass transport limitations. [43–49] In these reports, it can also be seen that the theoretical capacity of $\text{SnO}_2$ (1491 mAh/g) is normally only reached during the first reduction (i.e., discharge in a half-cell) when using nanoparticles of 10 nm or smaller with conventional cycling rates. When using larger particles the initial capacity is normally lower than 1491 mAh/g since this capacity is only obtained if the $\text{Li}_{4.4}\text{Sn}$ state is reached. Therefore, the $\text{SnO}_2$ reduction must be complete and the alloying reaction must give rise to $\text{Li}_{4.4}\text{Sn}$. However, in larger $\text{SnO}_2$ particles not all of the active material is used for cycling indicating slow electronic or mass transport within the material. [43–49] Some reports even describe a limitation due to slow electron conduction or $\text{Li}^+$ mass transport as possible reasons for the low capacity retention of $\text{SnO}_2$ electrodes. [15, 27, 35, 50–53]

The extent of the capacity loss and irreversible conversion of tin oxide have also been found to strongly depend on the potential window employed for electrochemical cycling. The capacity loss or irreversibility seemed more pronounced when decreasing the lower potential window or increasing the upper potential window. [14, 22–25] A significant agglomeration of Sn to larger particles within the $\text{Li}_2\text{O}$ matrix upon extended cycling has also been reported which could at least partially explain the capacity losses seen for tin oxide based electrodes. This agglomeration into larger Sn particles can limit the alloying reaction between Sn and Li. [14, 22, 23] It is still not clear if the $\text{Li}_y\text{Sn}$ formation (alloying) is completed to $y = 4.4$ and if the alloying and dealloying are fully reversible as is often assumed to be the case. Additionally, an overlap between the conversion and alloying reactions, during reduction and oxidation has been observed in literature. This overlap could affect the reversibility of both reactions. [54, 55]
The scope of this thesis

I The aim of the initial study was to gain more insight into the reversibility and the mechanisms of the tin oxide conversion reaction as well as the electrochemistry of the native tin oxide layer formed on tin in air. Therefore, different potential windows were applied for electrochemical cycling of nanometer thin tin oxide layers.

II The influence of high temperature cycling commercial, μm sized SnO$_2$ was studied as well. In these experiments, special attention was paid to the effect of the elevated temperature on the reversibility of the conversion reaction and the alloying reaction. Another goal was to test if an enhanced reversibility at elevated temperature could lead to improved capacities for SnO$_2$ electrodes.

III As the high temperature cycling in Paper II led to improved capacities for SnO$_2$ electrodes, an ionic liquid (IL) based electrolyte (0.5 M LiTFSI in Pip$_{1,4}$TFSI) was tested too. The reason for this study was that ILs have a much better thermal stability than conventional electrolytes that only are stable up to 60 °C. SnO$_2$ could, thus, be cycled at an even higher temperatures with the IL based electrolyte.

IV An overlap between the potential regions of the tin oxide conversion and the alloying reaction had been observed in Paper II. This phenomenon and its mechanism were studied more elaborately afterwards. The intention was to determine if and how this overlap influences the reversibility of the conversion reaction and the alloying reaction.

V The impact of Li$^+$ diffusion on the electrochemical reactions and the performance of SnO$_2$ electrodes was investigated as well. In this aspect, two phenomena were studied, which were the Li$^+$ transport between the SnO$_2$ particles and the Li$^+$ transport inside the SnO$_2$ particles. The aim was to determine which of these two is the greater limiting factor.

VI Finally, the effects of elevated temperature and the vinylene carbonate (VC) electrolyte additive on the cycling behavior of SnO$_2$ nanoparticles were tested. The high temperature cycling was supposed to supply increased capacities based on Paper II while the VC additive should provide enhanced capacity retention. Thus, the goal of these experiments was to combine the benefits of both approaches. Another aim was to study the long term effects of high temperature cycling on the SnO$_2$ nanoparticles to determine the feasibility of this strategy.
2. Methods

2.1 Electrodeposition

Electrodeposition is a method with several advantages compared to other deposition synthesis routes as it can be carried out at ambient pressure and temperature unlike chemical vapour deposition (CVD) and atomic layer deposition (ALD). The technique also enables precise control of the reaction products and their properties, e.g., coating thickness and composition. [56,57] Metals are deposited on a working electrode (substrate) via reduction or oxidation of dissolved compounds in a solution by the application of either a controlled current (galvanostatic deposition) or a controlled potential (potentiostatic deposition). [56, 57] Thus, electrode materials can be directly deposited on a metallic substrate that later can serve as a current collector. [58, 59] The deposited material mass can be calculated with the help of Faraday's law seen in Equation 2.1 with $Q$ as the applied charge, $M$ the molar mass, $n$ the valency number of the deposited ions and $F$ the Faraday constant. [56, 57]

$$m = \frac{Q \cdot M}{n \cdot F}$$  \hspace{1cm} (2.1)

In Paper I, a $SnCl_2$ solution containing trisodium citrate was employed. The pH of the electrolyte was adjusted to 4 using concentrated hydrochloric acid. [60–64] The first step was the oxidation of tin(II) to tin(IV) by blowing air through the solution at 85 °C. [65] The tin(IV) solution was then used for galvanostatic deposition of metallic tin on gold substrates by the application of a cathodic current, i.e., 5 mA/cm$^2$. Some of the tin films were later anodized in the same solution employing linear sweep voltammetry from 0 to +0.8 and +1 V vs. Ag/AgCl, respectively. Thus, tin oxide coatings of different thickness were obtained. An Ag/AgCl electrode served as the reference electrode and a platinum wire was used as the counter electrode. Electrodepositions were carried out with a VersaSTAT 4 potentiostat from Princeton Applied Research.

2.2 Structural and elemental characterization

2.2.1 Photoelectron spectroscopy (PES)

Photoelectron spectroscopy (PES) is a highly surface sensitive technique in which the photoelectric effect is exploited. X-rays are used to excite electrons which leave their atom shells as a consequence. The incoming X-rays have
a defined energy and the kinetic energy of the electrons leaving the sample is measured in ultra-high vacuum. The energy difference between the initial X-ray radiation \((h\nu)\) and the measured kinetic energy \((E_{\text{kinetic}})\) of the electrons is the binding energy \((E_{\text{binding}})\) which is unique for a certain shell in a specific element. The material’s work function \((\Phi)\), i.e., the energy necessary to move an electron from a shell to a point in vacuum immediately outside the surface, has to be deducted too. This calculation is represented in Equation 2.2. The binding energy is usually subject to a chemical shift depending of the atom’s chemical environment, i.e., its oxidation state and neighbouring elements, which allows conclusions to be drawn regarding a sample’s chemical composition. [66–68]

\[
E_{\text{binding}} = h\nu - (E_{\text{kinetic}} - \Phi)
\]  

(2.2)

The in-house X-ray photoelectron spectroscopy (XPS) was performed with a PHI 5500 Multi-Technique system (Perkin Elmer) using a monochromatic Al K\(_\alpha\) X-ray source and a pass energy of 23.5 eV. The pressure in the analysis chamber was about \(3 \cdot 10^{-9}\) bar. The excitation energy in this case was \(h\nu = 1487\,\text{eV}\). Additional hard X-ray photoelectron specotroscopy (HAXPES) measurements in Paper IV were carried out at the Bessy II synchrotron facility (HIKE end station [69], KMC-1 beamline [70], Helmholtzzentrum Berlin, Germany) where two different fixed excitation energies, i.e., \(h\nu = 2005\,\text{eV}\) (corresponding to an analysis depth of about 14 nm [71,72]) and \(h\nu = 6015\,\text{eV}\) (corresponding to an analysis depth of about 40 nm [71,72]), respectively, were used. The goal was to obtain information about different analysis depths.

Calibration of the binding energy scale was carried out based on the hydrocarbon C\(_1s\) peak at 285.0 eV and the peaks were analyzed using a non-linear Shirley-type background. [73] Fingerprint spectra were recorded at the beginning and at the end to determine that there was no damage to the samples due to the X-ray radiation during the measurements. The software Casa XPS was used to fit curves to the obtained spectra. For post-cycling studies of the tin oxide electrodes the batteries were dismantled in an argon filled glove box (M-Braun) and the electrodes were rinsed with DMC (dimethyl carbonate) prior to transfer to the PES chamber using a special built transfer system to avoid contact with air which otherwise can react with the electrode surface and alter it. [68, 74, 75]

2.2.2 Scanning electron microscopy (SEM) and Energy dispersive spectroscopy (EDX)

In this technique an electron beam is used to scan the sample surface. Different responses of the sample can be used to create a topographic image of the surface. One possibility is to use the backscattered electrons of the beam and the other is to use electrons emitted from the sample due to the beam impact
(secondary electrons). The first provides better topographic information while
the latter mode gives more insight into the composition of the sample. For the
electron beam and the detection a high vacuum is required. [76]

Energy dispersive spectroscopy (EDX) can also be carried out to determine
the elements contained in a sample through the detection of characteristic X-
ray radiation. When hitting the atoms of the sample the electron beam excites
the atoms by dislodging electrons from inner shells. Electrons of outer shells
then de-excite to the empty states in inner shells and emit characteristic X-ray
radiation which has a certain wavelength for every element, corresponding to
the energy difference between the shells. All elements with a higher atomic
number than three can be analysed. EDX can even be used for elemental
mapping of the sample surface. In this case the electron beams scans the
surface and the response by the detector can be related to a certain spot on the
sample. [76]

In this work backscattered electrons were used and SEM micrographs were
recorded using a SEM LEO 1550 instrument from Zeiss. EDX and EDX map-
ning were carried out in Paper V using an EDX analyser from Oxford Instru-
ments as well as the software AZtec from Oxford Instruments.

2.2.3 Transmission electron microscopy (TEM) and Energy
electron loss spectroscopy (EELS)

TEM operates analogous to optical microscopy. The difference is that it uses
the wave properties of electrons instead of visible light waves. Electrons have
a much shorter wavelength than visible light which makes it possible to ob-
serve a lot smaller structures. The resulting resolution is about a thousand
times higher compared to a regular light microscope and makes it possible to
resolve image features on an Ångström scale. The mechanism can be under-
stood with simple optical ray diagrams. Thus, it is a good technique for the
analysis of very small nanoparticles regarding size and morphology, which
was done in Paper VI. [76, 77]

Energy electron loss spectroscopy (EELS) can be carried out in TEM instru-
ments and was used in Paper VI. As the primary electron beam with a known
kinetic energy passes through a TEM specimen, it can dislodge electrons from
their shells. This results in characteristic X-rays or Auger electrons which re-
quire specific energies from the primary electron beam for each element and
shell, as well as different compositions and oxidation states. The kinetic en-
ergy of the primary beam electrons leaving the specimen can be measured and
the energy loss determined. [76]

TEM images were collected using a Schottky field emission electron micro-
scope (JEOL JEM-2100F) operated at 200 kV equipped with a Gatan Ultra-
scan 1000 CCD camera, Gatan Orius 200D camera and a post-column imaging
filter (Gatan Tridiem 863). TEM grids were prepared in an argon filled glove
box and transferred to the microscope using a JEOL vacuum transfer holder. The material was supported by a TEM copper grid with holey carbon supporting films. EELS was performed to investigate the oxidation states of the tin oxides, by studying the oxygen $K$ edges. [78, 79] The analysis and processing of the EELS spectra were performed with a Gatan Digital Micrograph. As tin oxides are sensitive to the electron beam, the acquisition time of the EELS spectra taken in diffraction mode was not longer than 30 seconds. [78, 79]

2.3 Electrochemical characterization

2.3.1 Electrode preparation

The tin oxide coated tin crystals in Paper I could be used as synthesized electrodes in electrochemical cells. In Paper II, conversely, slurry electrodes were prepared using commercially available, $\mu$m sized $SnO_2$ particles (Sigma Aldrich) representing 85 wt% of the solid slurry components. In addition, 10 wt% carbon black as well as 5 wt% binder consisting of CMC/SBR (carboxymethyl cellulose/styrene butadiene) in a ratio of 3:1 were added. After suspending the mixture in water it was ball-milled for several hours. The suspension was then cast on a copper foil. After drying for 24 hours at room temperature, circular electrodes with a diameter of 20 mm and a total mass loading of about 5.6 mg were cut from the foil. Slurries containing $SnO_2$ nanoparticles (35 to 55 nm, US Nano Research Inc.) or 9 nm $SnO_2$ particles according to [51]) (Paper III-VI) were stirred in a glass vial for one week before being cast on a copper foil. All other treatments were the same as for the electrode preparation in Paper II. In Paper V, 25 wt% $Al_2O_3$ (5 nm, US Nano Research Inc.) or diamond (3 to 10 nm, US Nano Research Inc.) were added to the slurries where the $SnO_2$ mass fraction was lowered to 60 wt %, resulting in a weight ratio of 7:3 ($SnO_2$:additive).

2.3.2 Battery cell assembly

Prior to electrochemical testing all electrodes were dried at 120 $^\circ$C (tin oxide coated tin electrodes in Paper I) or 90 $^\circ$C ($SnO_2$ slurry electrodes in Paper II-VI) in a vacuum furnace (Büchi). The electrochemical behavior of the tin oxide electrodes was analyzed in two-electrode pouch cells employing lithium foil as the counter electrode and glass fibre as the separator. The only exception was Paper III where a solupor separator was used. The battery assembly was carried out in an argon filled glove box (M-Braun) to prevent side reactions caused by oxygen and water. In the process the tin oxide electrodes, the separator soaked with electrolyte and the lithium foil were stacked and a nickel current collector was attached to each electrode. The assembly was then sealed to yield a pouch cell. As the electrolyte, 1 M $LiPF_6$ dissolved in
ethyl carbonate/diethyl carbonate (EC/DEC) (1:1), i.e., LP40 was employed. 0.5 M LiTFSI in Pip$_{1,4}$TFSI (ionic liquid) was used in Paper III. In Paper VI, 2 wt% vinylene carbonate (VC) was added to the LP40 electrolyte for some experiments. A schematic figure of the pouch cell assembly can be seen in Figure 2.1. For studies at elevated temperature some electrochemical cells were maintained at 60 °C or 80 °C, respectively, in an oven (Nüve) while cycling.

![Figure 2.1. Schematic figure of the pouch cell assembly.](image)

2.3.3 Cyclic voltammetry (CV)

In CV, the potential applied to an electrode is scanned back and forth within a predefined interval. This causes oxidation and reduction of electroactive species in the sample at certain potentials which can be detected by plotting the current as a function of the potential. The shape of the CVs and the peak positions thus provide information about the oxidation and reduction processes as well as the reversibility of the redox system. By varying the potential scan rate, insights into mass transport processes and electron kinetics can be obtained. [80,81]
The CVs in this work were recorded with a BioLogic SA VMP2 instrument using the EC-Lab software. Each CV was recorded with a new, fresh electrode, starting with a reduction from the open circuit voltage (OCV).

2.3.4 Galvanostatic cycling
During galvanostatic cycling, a constant current is generally applied and the potential monitored as a function of time. The cell will take on the potential required for an electrochemical reaction that can sustain the applied current. Ideally, these potentials are visible as potential plateaus for distinct reactions in contrast to the peaks obtained in the CV mode. However, due to sluggish kinetics or mass transport often slopes are observed rather than plateaus. The process is repeated many times, i.e., cycles, where a negative current and a positive current are applied alternately. This method is often used to estimate the capacities of electrochemical systems like batteries or supercapacitors over many cycles. [80, 82]

The galvanostatic cycling in this work was carried out with an Arbin BT-2043 battery cycler and a Digatron MBT. Each experiment was carried out with a fresh, new sample, starting with a reduction from the OCV. The cut-off potentials used in this work were 0.05 V vs. \( \text{Li}^+ / \text{Li} \) for discharge (reduction) and 2.5 V vs. \( \text{Li}^+ / \text{Li} \) for charge (oxidation).

2.3.5 Electrochemical impedance spectroscopy (EIS)
Impedance spectroscopy is widely used to estimate resistances and capacitances in electrochemical systems. For this the impedance, i.e., the resistance of an alternating current (AC), is measured over a range of frequencies. This method can be a useful tool for the in-situ characterization of battery systems. [80, 81, 83]

The impedance spectra for Papers II and VI were recorded with a BioLogic SA VMP2 instrument using the EC-Lab software. Prior to the measurements the system was given ten minutes time to relax to the OCV. EIS data before cycling was measured after lowering the cell potential to 1.2 V vs. \( \text{Li}^+ / \text{Li} \) while the measurements after the cycling were carried out at the new OCV of 1.4 V vs. \( \text{Li}^+ / \text{Li} \). For the EIS measurements three-electrode pouch cells were used where a second lithium foil was added as a reference electrode between the lithium counter electrode and the tin oxide electrode.

2.3.6 Intermittent current interruption method (ICI)
Intermittent current interruption (ICI) is a technique for the quantification and visualization of the internal resistance of batteries recently introduced by Lacey et al. [84] It was used in Paper VI to follow the development of the
internal cell resistance during long term cycling. Galvanostatic cycling was carried out at a rate of C/10 as described above, but current interruptions of 0.5 seconds were inserted every five minutes. The internal resistance could then be estimated from these interruptions assuming an ohmic voltage drop, i.e., \( R = \frac{dE}{dI} \), where \( dE \) is the difference between \( E_{t=0} \) which is obtained from a plot of \( E \) vs. \( \sqrt{t} \) and \( E_{t \neq 0} \) which is measured right before the interruption. [84] The data was processed with the programming language R using the "tidyverse" add-on packages. [85] One advantage is that the internal resistance can be visualized as a function of both capacity and cycle number. [84]

The galvanostatic cycling with current interruptions was carried out with an Arbin BT-2043 battery cycler. Each experiment was carried out with a fresh, new sample, starting with a reduction from the OCV.
3. Electrochemical behavior of tin oxide coated tin films in LIBs

3.1 Electrochemical cycling of the tin oxide coated tin electrodes

In Paper I, electrodepositions were carried out in \( \text{SnCl}_2 \) solutions containing citrate anions as chelating agents. Tin(II) was oxidized to tin(IV) by blowing air through the solution at elevated temperatures.\[65\] Metallic \( \text{Sn} \) was deposited on gold substrates by employing a cathodic current of \( 5 \text{ mA/cm}^2 \). After electrodeposition, the \( \text{Sn} \) films reacted with oxygen dissolved in water to form native tin oxide layers which were only a few nanometers thick.\[86, 87\] Certain samples were additionally oxidized electrochemically employing linear voltammetric scans from 0 to +0.8 and +1 V vs. \( \text{Ag/AgCl} \), respectively, yielding tin oxide layers of different thicknesses.

The electrochemical behavior of the tin oxide coated tin electrodes was investigated using CV in different potential windows. The goal was to study electrochemical reactions during the cycling in the presence and in the absence of the alloying reaction, i.e., down to 0.05 V vs. \( \text{Li}^+/\text{Li} \) (with alloying) and down to 0.9 V vs. \( \text{Li}^+/\text{Li} \) (without alloying), to gain information about the reversibility of the conversion reaction and the influence of the alloying reaction on it. Furthermore, cycling was carried out at relatively high potentials, i.e., up to 3.5 V vs. \( \text{Li}^+/\text{Li} \) to obtain information about the electrochemical processes at high potentials. In Figure 3.1, CVs for the native tin oxide coated samples are displayed. Reduction peaks for the alloying between \( \text{Sn} \) and \( \text{Li} \) could be observed between 0.8 and 0.2 V vs. \( \text{Li}^+/\text{Li} \) while the reduction peaks below 0.2 V vs. \( \text{Li}^+/\text{Li} \) most likely were due to an alloying reaction between lithium and gold (Figure 3.1b).\[88, 89\] The corresponding dealloying could be observed in the form of the subsequent oxidation peaks between 0.2 and 1.4 V vs. \( \text{Li}^+/\text{Li} \). In the first cycle, there was even a very small reduction peak at about 1.7 V vs. \( \text{Li}^+/\text{Li} \) corresponding to the reduction of the native tin oxide. The latter did, however, not reappear in the following cycles since its current was too small to be detected when compared to the large currents of the alloying reactions. Therefore, cycling was carried out only down to 0.9 V vs. \( \text{Li}^+/\text{Li} \) as is seen in Figure 3.1a. In this case the conversion was observed to be reversible, as is indicated by the oxidation peaks for the reoxidation of \( \text{Sn} \) to \( \text{SnO}_x \) and the recurring \( \text{SnO}_x \) reduction peaks. Nonetheless, the capacities of the reduction peaks decreased with cycle number and the second cycle
reduction only showed about half the capacity compared to the one for the initial reduction. These observations concerning the reduction peak capacities proved to be scalable with increasing tin oxide layer thickness. The reduction peak capacity of the second cycle was about half of the value of the first cycle for all three different tin oxide layer thicknesses. [14, 22]

As seen in Figure 3.2 CVs were also recorded up to a potential of 3.5 V vs. \( \text{Li}^+/\text{Li} \). For all samples (even those with thicker tin oxide layers) merging oxidation peaks were observed between 3.0 V and 3.5 V vs. \( \text{Li}^+/\text{Li} \) on the first cycle. However, the reactions appeared to be irreversible since there were no corresponding reduction peaks on the reverse scan. The oxidation observed above 3.0 V vs. \( \text{Li}^+/\text{Li} \) did hence not contribute to a better reversibility of the conversion as can be seen in Figure 3.2a. The oxidation peaks above 3.0 V vs.
$Li^+/Li$ showed large peak currents and were, therefore, ascribed to an irreversible reaction between metallic $Sn$ and the electrolyte. The currents of the merged oxidation peaks were large and thus unlikely to stem from an oxidation of metallic $Sn$ to $SnO_x$ as there were only small amounts of oxygen present in the system. Surface analysis employing XPS showed that tin(II) fluoride ($SnF_2$) was formed at 3.5 V vs. $Li^+/Li$ indicating a reaction between metallic $Sn$ and fluorine containing species in the electrolyte at potentials above 3.0 V vs. $Li^+/Li$.

*Figure 3.2.* Cyclic voltammograms recorded with 1 mV/s for native tin oxide coated tin electrodes between a) 0.9 and 3.5 V vs. $Li^+/Li$ and b) 0.05 and 3.5 V vs. $Li^+/Li$. 

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3.2 Characterization of cycling products

Electrodes stopped at potentials of 2.5 and 3.5 V vs. \( \text{Li}^+/\text{Li} \), respectively, after one full cycle were characterized using XPS and SEM. The \( \text{Sn}3d_{5/2} \) XPS peaks are depicted in Figure 3.3 for different tin oxide layer thicknesses at different potentials. The presence of SEI compounds like \( \text{LiF} \), carbonates, \( P - F \) and organic \( C - O \) could be observed in the \( O1s, F1s \) and \( C1s \) spectra in Paper I. [74, 90–95] The \( \text{Sn}3d_{5/2} \) XPS peaks showed that \( \text{SnO}_x \) was the dominating tin species at 2.5 V vs. \( \text{Li}^+/\text{Li} \) for all samples. [92, 96, 97] A small amount of metallic \( \text{Sn} \) was always present as well. [19, 97, 98] The presence of \( \text{SnO}_x \) species on the surface of the cycled electrodes at a potential of 2.5 V vs. \( \text{Li}^+/\text{Li} \) additionally implied the reversibility of the conversion reaction.

![Figure 3.3](image)

*Figure 3.3.* In-house XPS spectra \( (h\nu = 1487 \text{ eV}) \) with curves fitted to the \( \text{Sn}3d_{5/2} \) peaks after one cycle at 2.5 V vs. \( \text{Li}^+/\text{Li} \) and after one cycle at 3.5 V vs. \( \text{Li}^+/\text{Li} \) for different tin oxide layer thicknesses.

At 3.5 V vs. \( \text{Li}^+/\text{Li} \), \( \text{SnF}_2 \) could be observed in the \( \text{Sn}3d_{5/2} \) spectra for the samples with the native tin oxide layer and the one anodized to +0.8 V vs. \( \text{Ag}/\text{AgCl} \). [97, 99] This indicated that metallic \( \text{Sn} \) was oxidized to \( \text{SnF}_2 \) at potentials above 3.0 V vs. \( \text{Li}^+/\text{Li} \). The reaction probably included fluorine containing species originating from the electrolyte. The tin oxide layer on the samples anodized to +1.0 V vs. \( \text{Ag}/\text{AgCl} \) might have been too thick to observe the formation of \( \text{SnF}_2 \) underneath the tin oxide layer.
SEM micrographs are shown in Figure 3.4 including a pristine electrode, i.e., an electrode that had not been built into a battery, and samples stopped at 2.5 and 3.5 V vs. Li$^+$/Li, respectively. It is clear that the surface morphology did not change upon the reversible cycling of SnO$_x$ between 0.9 and 2.5 V vs. Li$^+$/Li as Sn crystals were still visible. The SnF$_2$ formation above 3.0 V vs. Li$^+$/Li, however, resulted in an obvious change in the surface morphology.

![Figure 3.4](image)

*Figure 3.4. SEM images of the native oxide coated electrodes, i.e., tin oxide layer of about 6 nm, for a pristine sample; an electrode after one cycle at 2.5 V vs. Li$^+$/Li and an electrode after one cycle at 3.5 V vs. Li$^+$/Li.*

All observations and interpretations described above are summarized in Figure 3.5. The pristine samples were covered by nanometer thick layers of SnO$_x$ on the Sn crystals. At 2.5 V vs. Li$^+$/Li typical SEI species were detected at the surface (i.e., LiF, LiPF$_6$, Li$_2$CO$_3$ and organic C−O). [74,90–95] In addition, tin oxide (SnO$_x$) was present which proved that the electrode cycled reversibly to a certain extent between 0.9 and 2.5 V vs. Li$^+$/Li. At 3.5 V vs. Li$^+$/Li the same SEI species were observed at the very top of the surface. Furthermore, signals for tin(II) fluoride (SnF$_2$) were found at 3.5 V vs. Li$^+$/Li.
Figure 3.5. Schematic figure depicting the tin oxide electrode surface at different potentials.
4. Electrochemical behavior of SnO₂ electrodes at elevated temperatures

Following the study about the tin oxide coated tin electrodes in Paper I, we decided to look at a more conventional system based on electrodes containing commercially available, μm sized SnO₂ particles, binders as well as Carbon Black. Again, different potential windows were applied to study the conversion reaction and its reversibility. Especially, the cycling behavior at an elevated temperature 60 °C was of interest in order to learn about possible mass transport limitations of the alloying and the conversion reactions.

4.1 High temperature cycling of commercial SnO₂

4.1.1 Cyclic voltammetry

Cyclic voltammograms were recorded in different potential windows to investigate the influence of the alloying reaction on the conversion reaction and electrode degradation at high potentials. In Figure 4.1 CVs of the fifth cycle at room temperature and 60 °C, respectively, are displayed for different potential windows. In Figure 4.1a the alloying reaction is included, in Figure 4.1b it is excluded as well as in Figure 4.1c where the cycling was instead extended to over 3.0 V vs. Li⁺/Li. The reduction peaks below 1.8 V vs. Li⁺/Li stemmed from the reduction of SnOₓ while the oxidation peak at about 2.0 V vs. Li⁺/Li corresponded to the reoxidation of Sn to SnOₓ. [14,22] In the CV including the alloying reaction (Figure 4.1a) the reduction peak at 0.7 V vs. Li⁺/Li could be assigned to the conversion of SnO₂ to Sn. The reduction peak below 0.4 V vs. Li⁺/Li corresponds to the alloying reaction between Sn and Li. The oxidation peak at 0.6 V vs. Li⁺/Li originates from the dealloying reaction while at least a part of the broad, merging oxidation peaks between 1.1 and 2.5 V vs. Li⁺/Li could be assigned to the reoxidation of Sn to SnOₓ. It is also evident from Figure 4.1a that the peaks of the conversion and the alloying reaction are merging. It is a sign that both reactions are overlapping to some extent.

Reversible cycling for SnOₓ, and hence a reoxidation of Sn to SnOₓ, between 0.9 and 2.5 V vs. Li⁺/Li could again be seen when excluding the alloying reaction (see Figure 4.1b). Reduction peaks with corresponding oxidation peaks of the same charge magnitude could be observed. These findings are in good agreement with the results for the model system based on SnOₓ coated Sn
Figure 4.1. Cyclic voltammograms of the SnO$_2$ electrodes obtained at different temperatures for a) 0.05 to 2.5 V vs. Li$^+/\text{Li}$ (including alloying); b) 0.9 to 2.5 V vs. Li$^+/\text{Li}$ (excluding alloying) and c) 0.9 V to > 3 V vs. Li$^+/\text{Li}$ (excluding alloying, but including electrolyte decomposition).
electrodes studied in Paper I. When comparing the CVs obtained at room temperature with those at 60 °C, it can be seen that the obtained current densities were significantly higher at the elevated temperature. This could be due to the fact that either the $Li^+$ mass transport or the electron kinetics were enhanced for the conversion and the alloying reaction when raising the temperature to 60 °C. When cycling only the conversion reaction in Figure 4.1b, the peaks observed at 60 °C were also narrower and displayed smaller overpotentials. The latter means that the reduction peak moved to higher potentials and the oxidation peak to lower potentials which resulted in a smaller peak separation $\Delta E$. Thus, the peak separation $\Delta E$ between the oxidation and reduction peaks was decreased from about 0.7 V at room temperature to 0.5 V at 60 °C. These observations imply improved mass transport or electron kinetics. Larger current densities were also obtained for both the reduction and oxidation reactions. When looking at Figure 4.1b, it can further be seen that the potentials of the oxidation and the reduction peaks have shifted differently compared to each other. The oxidation peak clearly shows a larger peak shift as than the reduction peak. This observation indicates that the limitation in the present system is not due to an ohmic drop effect since these phenomena should cause the same shift for the oxidation and the reduction peak. For this reason, a $Li^+$ mass transport limitation is more likely. Furthermore, "diffusion tails" can be observed following the oxidation peak, especially at room temperature which again implies that the present system is mainly limited by slow $Li^+$ transport.

Figure 4.1c shows the cycling behavior between 0.9 V and 3.7 V as well as 3.5 V vs. $Li^+/Li$ at room temperature and 60 °C, respectively. Above 3.0 V vs. $Li^+/Li$ irreversible oxidation peaks could be observed in both CVs. The potential window had to be extended to 3.7 V vs. $Li^+/Li$ at room temperature to be able to observe these irreversible oxidation peaks. At 60 °C, however, a window up to 3.5 V vs. $Li^+/Li$ was sufficient since the oxidation peaks were visible at lower potentials. Furthermore, potential windows extending above 3.5 V vs. $Li^+/Li$ led to battery failure at 60 °C. An explanation for these observations could be improved kinetics for oxidative degradation reactions of electrolyte components on the electrode surface at higher temperatures. As no elemental Sn was present in the pristine $SnO_2$ electrodes, it is unlikely that the observed oxidation peaks originated from an oxidation of $Sn$ to $SnF_2$ as was the case in Paper I. It is more likely that oxidative degradation reactions involving electrolyte components, especially organic compounds, gave rise to the irreversible oxidation peaks above 3.0 V vs. $Li^+/Li$ in this study. This assumption is supported by the $Sn3d_{5/2}$ XPS spectra in Figure 4.2, that do not show any $SnF_2$, which was also the case for the $F1s$ spectra in Paper II. In the $F1s$, $C1s$ and $O1s$ spectra of Paper II, the formation of a thick layer of organic compounds could be seen instead on the electrode surface at 3.7 and 3.5 V vs. $Li^+/Li$. 

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4.1.2 Characterization of cycling products

The products formed at certain potentials were investigated using XPS. The objective was mainly to gain a better understanding of the electrochemical processes occurring at relatively high potentials, i.e., 2.5, 3.7 and 3.5 V vs. \( \text{Li}^+ / \text{Li} \). The in-house XPS spectra of the \( \text{Sn}3d_{5/2} \) peaks are presented in Figure 4.2.

![In-house XPS spectra](image)

**Figure 4.2.** In-house XPS spectra \((h\nu = 1487 \text{ eV})\) with curves fitted to the \( \text{Sn}3d_{5/2} \) peaks obtained after one cycle at room temperature and 60 °C, respectively, for cells stopped at 2.5; 3.7 and 3.5 V vs. \( \text{Li}^+ / \text{Li} \).

Analogously to the results for the system studied in Paper I, it was found that \( \text{SnO}_x \) was the dominating species at 2.5 V vs. \( \text{Li}^+ / \text{Li} \), besides a small amount of Sn. [19, 92, 97, 98] It is unclear from the XPS data if \( \text{SnO} \) or \( \text{SnO}_2 \) is reformed upon oxidation, most likely a mixture of both is present. [78, 97, 100] These findings confirmed that \( \text{SnO}_x \) can be cycled partially reversibly under certain conditions. This behavior was observed for both the electrodes cycled at room temperature and at 60 °C. When increasing the potential to 3.7 V vs. \( \text{Li}^+ / \text{Li} \) at room temperature or 3.5 V vs. \( \text{Li}^+ / \text{Li} \) at 60 °C, only one peak corresponding to \( \text{SnO}_x \) could be detected in the \( \text{Sn}3d_{5/2} \) spectrum (Figure 4.2). Furthermore, the \( \text{Sn}3d_{5/2} \) peak showed much weaker intensities and are noisier in both cases (i.e., at room temperature and 60 °C). The reason for these weaker \( \text{Sn} \) signals was found to be the oxidation reactions taking place above 3.0 V vs. \( \text{Li}^+ / \text{Li} \). As mentioned above, it is most likely that electrolyte components were oxidized above 3.0 V vs. \( \text{Li}^+ / \text{Li} \) and formed a layer of oxidized organic compounds on the electrodes which as a consequence decreased the intensity of the \( \text{Sn} \) signal. Thus, the organic electrolyte decomposition prod-
uct layer made the detection of the $Sn3d_{5/2}$ peak more difficult and resulted in very weak $Sn$ signals. This result was also supported by the the $C1s$, $F1s$ and $O1s$ XPS peaks in Paper II. [74, 90–95] These observations are, hence, different from that of Paper I.

4.1.3 Electrochemical impedance spectroscopy

In Figure 4.3 EIS are shown for the $SnO_2$ electrodes, before cycling (black triangles), after one cycle (red triangles) and after two cycles (blue triangles), respectively. Before the first cycle a large charge transfer resistance could be observed. [15, 51, 52] Nonetheless, after one and two cycles only a mass transport dependence of the impedance could be detected. Both contributions to the impedance, the charge transfer resistance before the first cycle and the mass transport limitation after cycles one and two, hinder the electrochemical reactions of the $SnO_2$ electrodes during electrochemical cycling and can be overcome easier when cycling at higher temperatures as is shown by the CVs in Figure 4.1. The EIS spectra, hence, likewise indicate that the reason for the improved cycling behavior at higher temperatures mainly is of a mass transport nature, i.e., there is indeed a limitation due to slow $Li^+$ transport.

![Figure 4.3](image)

*Figure 4.3. EIS spectra measured for the $SnO_2$ electrodes before cycling (obtained at 1.2 V vs. $Li^+/Li$) as well as after one cycle and two cycles (both obtained at 1.4 V vs. $Li^+/Li$).*

4.1.4 Galvanostatic cycling

The capacities obtained from galvanostatic cycling at a rate of C/10 at both room temperature and 60 °C are displayed in Figure 4.4 where 0.05 V and 2.5 V vs. $Li^+/Li$ were used as the cut-off potentials (i.e., including the alloying
reaction). It is evident that the capacities obtained at 60 °C are significantly higher than those at room temperature. The differences vary and are about 200 mAh/g for the initial five cycles and about 150 mAh/g for cycles 30 to 60. The capacity improvement can be explained by the enhancement of Li$^+$ mass transport at the elevated cycling temperature. These results show that the observations made for the CVs and EIS (Figures 4.1 and 4.3) have strong implications for the practical use of tin oxide based electrodes in LIBs. It is shown that high temperature cycling can significantly increase the capacities for SnO$_2$ electrodes over many cycles.

![Figure 4.4](image)

*Figure 4.4. Capacities obtained from galvanostatic cycling of the SnO$_2$ electrodes at rate of C/10 at different operating temperatures, i.e., room temperature (RT) and 60 °C, using 0.05 V and 2.5 V vs. Li$^+$/Li as the cut-off potentials (i.e., including the alloying reaction).*

4.2 High temperature cycling of SnO$_2$ nanoparticles with an ionic liquid based electrolyte

The standard LP40 electrolyte as well as other commonly used electrolytes with organic solvents can only be used up to a temperature of 60 °C. [101] Ionic liquid (IL) based electrolytes have much higher thermal stabilities and can therefore be used at higher temperatures. [101–104] As SnO$_2$ electrodes showed improved cycling performance at higher temperatures in Paper II (Figure 4.4), SnO$_2$ nanoparticles of 35 - 55 nm were tested with the IL based electrolyte 0.5 M LiTFSI in Pip$_{1.4}$TFSI in Paper III. [104] Electrochemical cycling of similar ionic liquids with Si electrodes at room temperature have previously been reported in the literature. [105] The aim of these experiments was to test SnO$_2$ electrodes at higher temperatures than would be possible with LP40 and, thus, to reach higher capacities. The CVs depicting the first and fifth
cycle when cycling with the IL based electrolyte at a rate of 0.1 mV/s and a temperature of 80 °C can be observed in Figure 4.5a. They can be compared to the first and fifth cycle CVs at the same rate using the LP40 electrolyte at room temperature presented in Figure 4.5b. Even though the CV shapes are slightly different for the two electrolytes, it can be seen that the same electrochemical reactions are taking place when using the IL based electrolyte as in the LP40 electrolyte. These reactions include the conversion of $SnO_2$ to $Sn$ (between 1.0 and 0.7 V vs. $Li^+/Li$) and the alloying reaction (between 0.7 and 0.05 V vs. $Li^+/Li$) during the reductive scan as well as the dealloying (between 0.2 and 1.1 V vs. $Li^+/Li$) and the conversion back to $SnO_x$ (between 1.1 and 2.0 V vs. $Li^+/Li$) during the oxidative scan.

![Cyclic voltammograms obtained for SnO$_2$ electrodes (35 - 55 nm) cycled with a) LP40 electrolyte at room temperature (RT) and b) the 0.5 LiTFSI in Pip$_{1,4}$TFSI electrolyte at 80 °C. Both CVs were recorded at a rate of 0.1 mV/s.](image-url)
In Figures 4.6a and b the capacities obtained from galvanostatic cycling are shown for the IL based electrolyte at 80 °C (red squares) and the conventional LP40 electrolyte at room temperature (black squares). It can be seen that the initial discharge capacity is much higher for the IL based electrolyte (942 mAh/g) than for LP40 (754 mAh/g). However, the first charge capacities are of the same magnitude for both electrolytes and show no increase for the IL based electrolyte (447 mAh/g for the IL based electrolyte and 486 mAh/g for LP40). Furthermore, irreversible capacity losses could be observed up to cycle 15 for the IL based electrolyte which was not the case for LP40. These results imply that the high discharge capacity in the first cycle does not originate from the use of more SnO$_2$ material. It rather appears to involve irreversible reduction reactions of the IL based electrolyte.

![Figure 4.6](image.png)

**Figure 4.6.** Capacities for SnO$_2$ electrodes (35 - 55 nm) obtained from galvanostatic cycling at a rate of C/10 for SnO$_2$ (35 - 55 nm) with LP40 at room temperature and the 0.5 LiTFSI in Pip$_{1,4}$TFSI electrolyte at 80 °C with 0.05 V and 2.5 V vs. Li$^+$/Li as the cut-off potentials.

Figure 4.7 shows SEM micrographs of an uncycled SnO$_2$ electrode (a), i.e., an electrode stored in a battery at OCV for four days, as well as an electrode cycled galvanostatically for 60 cycles at 80 °C and a rate of C/10. The SnO$_2$ particles are clearly visible in Figure 4.7a while an electronically insulating layer was formed on the cycled electrode in Figure 4.7b. The latter obscured the SnO$_2$ particles. This suggests that the large initial capacity losses for the IL based electrolyte during the first 15 cycles originated from the reduction of the IL based electrolyte which resulted in the formation of a thick SEI layer. These findings were further supported by the XPS spectra in Paper III which also showed that the SEI layer thickness increased throughout cycling. These observations indicate that a stable SEI layer was more difficult to obtain with the IL based electrolyte. This could be due to the formation of SEI species that are soluble in the IL based electrolyte. [106–108] Thus, a mixture of more and
less soluble SEI compounds could be obtained during electrolyte reduction. Partial SEI dissolution would enable the continuous reduction of the IL based electrolyte by the exposure of new electrode surface. In addition, the XPS spectra in Paper III indicated that the SEI species were chemically very similar to and mainly originated from the IL solvent. This chemical similarity between the electrolyte reduction products and the IL solvent probably facilitated their extensive dissolution. Nonetheless, the IL based electrolyte shows capacities of the same magnitude at 80 °C as LP40 at room temperature from cycle 15 onwards.

*Figure 4.7.* SEM images for a) an uncycled electrode and b) an electrode cycled galvanostatically with $0.5 \text{LiTFSI}$ in $\text{Pip}_{1,4}\text{TFSI}$ as the electrolyte at a rate of C/10 and 80 °C for 60 cycles.
5. Tracking the first cycle of SnO$_2$ electrodes in LIBs with photoelectron spectroscopy

In Paper IV, the overlap seen between conversion and alloying reaction observed in Paper II and other reports was investigated in more detail employing SnO$_2$ nanoparticles (35 - 55 nm). [54, 55] In this study batteries were stopped at different potentials before and after the peaks observed in the CV. PES was carried out both with in-house equipment for XPS and synchrotron based HAXPES to determine which species were present at these potentials in Paper IV. [68] Although for simplicity, not all excitation energies and analysis depths are shown in this thesis and the reader is hence referred to Paper IV for details. The first CV cycle is displayed in Figure 5.1 where red circles mark at which potentials the cells were stopped to perform measurements. In addition, the C$_{1s}$ and F$_{1s}$ HAXPES peaks were used to track the SEI evolution during the first cycle in the CV mode. [68]

![Figure 5.1. Cyclic voltammogram of the first cycle for a SnO$_2$ electrode (35 - 55 nm) cycled between 0.05 V and 2.5 V vs. Li$^+$/Li at a scan rate of 1 mV/s. The red circles indicate the potentials at which the PES spectra were measured.](image)

In Figure 5.2 the Sn$_3$d$_{5/2}$ HAXPES peaks ($h\nu = 2005$ eV) are displayed which are of interest to investigate the overlap between the conversion and alloying reactions. Only SnO$_2$ is detected by the HAXPES spectra at 1.2 V vs. Li$^+$/Li as no electrochemical reactions take place during the scan to this potential. [92,97,98] Sn alone should be detected at 0.4 V vs. Li$^+$/Li after the
first reduction peak, if exclusively the conversion reaction were to take place between 1.2 V and 0.4 V vs. Li⁺/Li. However, both Sn and Li₄Sn can be observed for all analysis depths at 0.4 V vs. Li⁺/Li. [19, 92, 97, 98] This finding suggests that the conversion and alloying reaction overlap within this potential range. The reason could be the initial formation of an Sn layer on the particle surface with SnO₂ still left inside the particles. If the Li⁺ transport through the Sn layer is slow, LiₓSn can start to form at the surface before all SnO₂ is converted inside the particles when the appropriate potential region is reached. The alloying reaction continues afterwards down to 0.05 V vs. Li⁺/Li where both Sn and LiₓSn can still be observed at all analysis depths. [19, 92, 97, 98] This result indicates that the alloying reaction is not completed at the end of the reductive scan.

During the oxidative scan, LiₓSn and Sn can both be observed at 1.0 V vs. Li⁺/Li which implies that the dealloying is not completed during the first oxidation peak. Therefore, dealloying and conversion also overlap during the oxidative scan. [19, 92, 97, 98] The reason could be slow Li diffusion through an Sn layer on the particle surface, which initially forms on the particle upon dealloying. As a consequence, dealloying cannot be completed and it can in turn hinder a complete conversion of Sn to SnOₓ. It is difficult to determine if SnO, SnO₂ or intermediates are reformed upon oxidation as mentioned under section 4.1.2, and because of this tin oxide is generally denoted SnOₓ in this work. [78, 100] At 2.5 V vs. Li⁺/Li, mainly SnOₓ and a smaller amount of Sn

Figure 5.2. HAXPES spectra (hν = 2005 eV) fitted to the Sn₃d₅/₂ peaks at different potentials, i.e., discharge (reduction): 1.2 V, 0.4 V and 0.05 V vs. Li⁺/Li and charge (oxidation): 1.0 V and 2.5 V vs. Li⁺/Li as well as for a pristine sample.
are visible. [19, 92, 97, 98] Generally, it is difficult to assign currents or peaks in CVs of SnO$_2$ exclusively to one electrochemical reaction as the alloying and conversion reactions overlap to some extent. These observations were supported by the Sn3d PES peaks obtained at excitation energies of 1487 eV and 6015 eV as well as the O1s PES peaks in Paper IV.

![Figure 5.3. Schematic illustration of the mechanism of the overlapping alloying and conversion reactions. The model is derived from the observations in the Sn3d$_{5/2}$ PES spectra.](image)

The above described mechanisms concerning the overlap between alloying and conversion reaction are summarized in Figure 5.3. It shows the Sn layer (grey with Li$_2$O) that is formed during reduction and which blocks Li$^+$ diffusion, with SnO$_2$ (violet) remaining underneath. Alloying is therefore confined to the exterior parts of the particle. The crack formation caused by volume changes during alloying accounts for the observation of small SnO$_2$ (violet) amounts at low potentials. Upon oxidation, dealloying takes place, at first forming another passivating Sn layer (grey) on top of the Li$_x$Sn alloy (green). This could lead to Li$_x$Sn (green) still being present inside the particles while oxidation of Sn (grey) to SnO$_x$ (red) takes place on the particle surface.

The C1s HAXPES peaks ($n\nu = 2005$ eV) can be seen in Figure 5.4. In Paper IV C1s PES spectra are presented for excitation energies of 1487 eV and 6015 eV where the varying excitation energies also enable the investigation of different depths of the SEI. [71, 72] For the pristine sample and at 1.2 V vs. Li$^+$/Li, Carbon Black (CB) is the dominating species with the highest peak area in Figure 5.4. [71, 72, 74, 90, 91, 93, 94] The remaining peaks, i.e., C − H, C − O and CO$_2$ originate from the CMC and SBR binders as well as surface contaminants. The growth of the latter three peak areas as well as the emerging CO$_3$ peak at potentials below 1.2 V vs. Li$^+$/Li are proof of SEI formation. CO$_3$, i.e., carbonates like Li$_2$CO$_3$ and C − H as well as P − F
species and \( LiF \) (see \( F1s \) peaks in Figure 5.5b) are major SEI components on \( SnO_2 \) electrodes. [71, 72, 74, 90] While the SEI peak areas are growing, the CB peak area is declining. Its evolution is depicted in Figure 5.5a for the in-house XPS data (\( h\nu = 1487 \) eV, see Paper IV for spectra) and the HAXPES data (\( h\nu = 2005 \) eV) at shallower analysis depths which allows conclusions to be drawn about the SEI thickness. In Figure 5.5a, it can be seen that the CB peak area already declines to a small extent between the pristine \( C1s \) spectra and the ones taken at 1.2 V vs. \( Li^+/Li \). This implies that a small amount of SEI is already formed at these high potentials. [20, 21] The CB peak area further decreases when continuing the reductive scan to 0.4 V vs. \( Li^+/Li \) and then to 0.05 V vs. \( Li^+/Li \). This continued decline shows that the SEI is formed over almost the entire first reductive scan that is not confined to one potential region. Nonetheless, this is most likely a time dependent effect in the CV mode rather than a potential dependent effect which implies that the SEI formation rate could be diffusion controlled.

![Figure 5.4. HAXPES spectra \((h\nu = 2005 \) eV\) fitted to the \( C1s \) peaks at different potentials, i.e., discharge (reduction): 1.2 V, 0.4 V and 0.05 V vs. \( Li^+/Li \) and charge (oxidation): 1.0 V and 2.5 V vs. \( Li^+/Li \) as well as for a pristine sample.](image)

Throughout the oxidative scan, the CB peak area increases towards 1.0 V vs. \( Li^+/Li \) and then again to 2.5 V vs. \( Li^+/Li \) (Figure 5.5a). However, it does not reach the same peak area as observed before cycling to 1.2 V vs. \( Li^+/Li \). This observation indicates a partial dissolution of the SEI during the oxidative scan. [106, 109, 110] These results confirm that the SEI formation on tin based electrodes is a dynamic process, including several formation and dissolution
processes. [17, 109, 110] These observations are further supported by the O1s and F1s PES peaks in Paper IV.

The F1s HAXPES ($h\nu = 2005$ eV) spectra in Figure 5.5b show that no fluorine species are present in the pristine sample. Nonetheless, $C - F$ and $P - F$ species as well as $LiF$ can be observed after the reductive scan at 0.05 V vs. $Li^+/Li$ as SEI compounds. [90, 111] However, after the oxidative scan, i.e., at 2.5 V vs. $Li^+/Li$, the $C - F$ peak has disappeared and the $P - F$ peak area has decreased in size compared to $LiF$. This development can also be seen in the other F1s PES spectra in Paper IV. These observations indicate that the nonpolar, organic $C - F / P - F$ species dissolve to a greater extent during the oxidative scan than more polar, inorganic compounds like $LiF$. This phenomenon has been predicted by some reports based on simulations and solubility experiments. [107, 108]

![Figure 5.5](image.png)

**Figure 5.5.** a) Evolution of the relative CB peak area measured in the C1s spectra during discharge (reduction) and the following charge (oxidation) for both in-house XPS data ($h\nu = 1487$ eV) and synchrotron based HAXPES data ($h\nu = 2005$ eV). b) HAXPES spectra (2005 eV) fitted to the F1s peaks for a pristine electrode, an electrode stopped at 0.05 V vs. $Li^+/Li$ and an electrode stopped at 2.5 V vs. $Li^+/Li$. 

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6. The influence of particle size and additives on the electrochemical performance of SnO₂ in LIBs

6.1 Al₂O₃ and diamond as additives in SnO₂ electrodes

In Paper II, a Li⁺ mass transport limitation was observed which was studied in more detail in Paper V. For that purpose, SnO₂ particles of 35 to 55 nm were used together with 5 nm Al₂O₃ and 3 to 10 nm diamond particles, respectively. The smaller additive particles created a matrix around the larger SnO₂ particles within the cast electrodes. Al₂O₃ is a good Li⁺ conductor, while diamond is a poor Li⁺ conductor and both are poor electronic conductors. [112–116] It was, therefore, expected that the Al₂O₃ additive should improve the performance of the SnO₂ electrodes, while diamond should impair it. Thus, investigating the electrochemical performance of SnO₂ when using these two different additives should give a better understanding on the role of Li⁺ diffusion in SnO₂ electrodes.

In Figure 6.1, the CVs of the fifth cycle are displayed for SnO₂ electrodes containing Al₂O₃ (red line, SnO₂/Al₂O₃), diamond (blue line, SnO₂/diamond) and no additive (black line, SnO₂), respectively. Clear differences can be seen for the SnO₂/diamond electrode (blue line) compared to the SnO₂/Al₂O₃ and SnO₂ electrodes. On the reductive scan, the SnO₂/diamond electrode shows an overpotential of about 0.3 V for the SnO₂ reduction as compared to the other two electrodes. Furthermore, the peaks appear to be merging to a greater extent and the current densities are smaller. In addition, no broad peak for the reoxidation of Sn to SnOₓ can be observed between 1.0 and 2.2 V vs. Li⁺/Li which can be seen for SnO₂/Al₂O₃ and SnO₂ CVs (red and black line). Instead, a "diffusion tail" can be observed following the dealloying reaction visible in the SnO₂/diamond CV (blue line). In consequence, the diamond additive significantly impairs the electrochemical performance of SnO₂ and inhibits the reoxidation of Sn to SnOₓ. When looking at the CVs of the SnO₂/Al₂O₃ and SnO₂ electrodes (red and black line), no significant differences can be observed which implies that the differences observed for SnO₂/diamond should be due to poor Li⁺ diffusion. In conclusion, uninhibited Li⁺ mass transport is vital for reduced overpotentials, larger currents and even an enhanced reversibility of the conversion in SnO₂ electrodes.

In Figures 6.2a to c, the discharge and charge capacities obtained from galvanostatic cycling at C/10 are shown for SnO₂/Al₂O₃ (red dots), SnO₂/dia—
Figure 6.1. Cyclic voltammograms of the fifth cycle recorded for SnO$_2$ electrodes containing Al$_2$O$_3$, diamond or no additive between 0.05 V and 2.5 V vs. Li$^+$/Li at a rate of 1 mV/s.

$\text{SnO}_2$ (blue triangles) and $\text{SnO}_2$ (black squares) electrodes. The capacity fades much faster for the $\text{SnO}_2$/diamond electrode than for the other two samples. This could be due to the hardness of diamond, rather than poor Li$^+$ mass transport. [117] The diamond additive increases the stiffness and inflexibility of the electrode which leads to extended pulverization due to the volume changes during alloying. This finding was confirmed by increased crack formation observed in the SEM images of the $\text{SnO}_2$/diamond electrodes in Paper V. Furthermore, a lot of the electrode material was detached from the $\text{SnO}_2$/diamond electrodes when opening the batteries after cycling.

Nonetheless, it can also be seen that Al$_2$O$_3$ does not improve the electrochemical performance as expected when comparing the $\text{SnO}_2$/Al$_2$O$_3$ and $\text{SnO}_2$ electrodes. In the CVs (Figure 6.1), no significant differences are visible between the two samples (red and black line). The capacities obtained from galvanostatic cycling (Figures 6.2) initially display similar slow capacity fading. The $\text{SnO}_2$/Al$_2$O$_3$ electrode shows worse capacity retention than the pure $\text{SnO}_2$ electrode. This can be seen when looking at Figure 6.2 where the $\text{SnO}_2$/Al$_2$O$_3$ electrode (red dots) starts to show lower capacities than the $\text{SnO}_2$ electrode (black squares) from about cycle 30 onwards. These results show that it is the Li$^+$ mass transport inside the particles that is the main limitation for $\text{SnO}_2$ electrodes, if the mass transport between the particles is not additionally hindered. [113] Furthermore, worse capacity retention has earlier been reported for $\text{SnO}_2$/Al$_2$O$_3$ compared to pure $\text{SnO}_2$ electrodes. This observation had then been assigned to a possible agglomeration of the material into Al rich and Sn rich areas during cycling. [113] This explanation could be confirmed by EDX mapping which can be found in Paper V. The phase separation of Al and Sn regions is likely to lead to a faster agglomeration of Sn into larger
particles, which has previously been described as source of capacity fading in SnO$_2$ electrodes. [14, 22, 23]

As it seems to be mainly the Li$^+$ transport inside the electrode particles that is limiting, an agglomeration of Sn into larger particles with smaller surface areas could increasingly slow down Li$^+$ diffusion. Thus, the amount of electrode material reached by Li$^+$ could be steadily declining if the cycling rate, i.e., the time domain is not changed. This phenomenon is, therefore, a possible explanation for the lower capacities obtained for the SnO$_2$/Al$_2$O$_3$ electrode as compared to the SnO$_2$ electrode after extended cycling. This finding is also in accordance with the results from Paper IV, where the initially formed Sn layer appeared to hinder Li$^+$ transport further into the particles.

6.2 Comparison of initial discharge capacities for different SnO$_2$ particle sizes

In order to investigate the role of Li$^+$ diffusion inside SnO$_2$ particles in more detail, initial discharge capacities for different particle sizes, i.e., diameter, of pure SnO$_2$ particles were compared in Paper V. The results are presented in Table 6.1 for pure SnO$_2$ particles where some values are taken from our own work, and others from literature. [14, 43, 49, 118, 119] For visualization, the initial discharge capacities are also plotted versus the average diameter in Figure 6.3. When looking at Table 6.1 and Figure 6.3, it can be seen that the initial discharge capacities decrease rapidly with growing particle size. Only for SnO$_2$ particles under 10 nm in diameter can values close to the theoretical value of 1491 mAh/g be reached, i.e., 1480 mAh/g for 2 nm and 1400 mAh/g
for 6 nm. [43, 118] This confirms the assumption that the $Li^+$ mass transport inside the $SnO_2$ particles plays a crucial role for their electrochemical performance. As a consequence, a complete reaction of the active material and, thus, the full theoretical capacity can only be obtained for $SnO_2$ particles that are smaller than 10 nm in diameter when using conventional cycling rates. Extremely low rates would have to be applied in order to reach the theoretical capacity of larger particles.

**Table 6.1.** Initial discharge capacities obtained from galvanostatic cycling for different $SnO_2$ particle sizes in diameter. The values were taken from the literature and our own work.

<table>
<thead>
<tr>
<th>Form</th>
<th>Diameter [nm]</th>
<th>Capacity [mAh/g]</th>
<th>Rate</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>spherical</td>
<td>&gt;400</td>
<td>500</td>
<td>C/5</td>
<td>[14]</td>
</tr>
<tr>
<td>spherical</td>
<td>60</td>
<td>550</td>
<td>C/5</td>
<td>[14]</td>
</tr>
<tr>
<td>hierarchical nanobaskets</td>
<td>2</td>
<td>1480</td>
<td>C/2</td>
<td>[43]</td>
</tr>
<tr>
<td>nanobaskets</td>
<td>300</td>
<td>560</td>
<td>C/2</td>
<td>[43]</td>
</tr>
<tr>
<td>hollow shells</td>
<td>12-15</td>
<td>829</td>
<td>1C</td>
<td>[49]</td>
</tr>
<tr>
<td>nanotubes</td>
<td>6</td>
<td>1400</td>
<td>C/5</td>
<td>[118]</td>
</tr>
<tr>
<td>nanotubes</td>
<td>10-15</td>
<td>940</td>
<td>C/8</td>
<td>[119]</td>
</tr>
<tr>
<td>spherical</td>
<td>35-55</td>
<td>754</td>
<td>C/10</td>
<td>this work</td>
</tr>
<tr>
<td>spherical</td>
<td>&gt;1000</td>
<td>686</td>
<td>C/10</td>
<td>this work</td>
</tr>
</tbody>
</table>

**Figure 6.3.** Initial discharge capacities obtained from galvanostatic cycling as a function of the average $SnO_2$ particle size in diameter. The values were taken from the literature and our own work. See Table 6.1 for the references and the respective cycling rates.
6.3 Electrochemical performance of SnO$_2$ nanoparticles at high temperature and with VC as an electrolyte additive

As the results in Table 6.1 and Figure 6.3 had shown that it is very difficult to extract the full theoretical capacity from SnO$_2$ particles larger than 10 nm, SnO$_2$ nanoparticles of 9 nm were used for the experiments in Paper VI. The aim was to alleviate any Li$^+$ mass transport limitations within the active material and obtain the highest possible capacities from SnO$_2$. Furthermore, experiments including VC (vinylene carbonate) as an electrolyte additive were carried out to optimize not only the initial capacities, but also the capacity retention. The SnO$_2$ nanoparticles were synthesized according to a modified procedure described in the literature. [51]

6.3.1 Galvanostatic cycling

Figures 6.4a to c feature the capacities obtained for the SnO$_2$ nanoparticles over 120 cycles under different cycling conditions, i.e., a) at room temperature; b) at 60 °C and c) at room temperature with a 2 wt% VC additive. For each condition three cycling rates, 1C (black squares); C/5 (red dots) and C/10 (blue triangles) in Figure 6.4, were tested. The corresponding cycling curves and CVs can be found in Paper VI and its supporting information. It can be seen that in these experiments all the initial discharge capacities significantly exceed the theoretical value of 1491 mAh/g which shows that the particles are now small enough to extract the full theoretical capacity. However, the values are up to 500 mAh/g larger than the theoretical capacity. Therefore, it is reasonable to assume that part of these large first discharge capacities are due to the reduction of electrolyte components instead of SnO$_2$. It should be noted that this initial electrolyte reduction can also lead to the formation of soluble products besides the SEI layer which would explain the large discrepancy between the theoretical capacity and the present results. [106–108] Despite the extended electrolyte reduction in the initial cycle, larger capacities can be observed over many cycles as compared to for the larger SnO$_2$ particles in Chapters 4.1 and 6.1. An interesting feature is that the capacities do not differ significantly between Figure 6.4a and b, but are of the same magnitude for both, room temperature and 60 °C. An obvious increase of the capacity values had been observed when cycling at elevated temperature for the μm sized SnO$_2$ particles in Chapter 4.1. An explanation for this phenomenon could be the extremely small size of the 9 nm SnO$_2$ particles. They are small enough for Li$^+$ diffusion to occur rapidly and do not need any high temperature activation which was the case for the larger particles in Chapter 4.1. In addition, it is surprising that the best capacity retention at 60 °C (Figure 6.4b) is obtained at the fastest cycling rate of 1C. A possible explanation for this behavior could be that the reversibility of the conversion reaction is enhanced when high rates...
Figure 6.4. Capacities of the SnO$_2$ electrodes (9 nm) obtained from galvanostatic cycling with different rates at a) room temperature, b) 60°C and c) at room temperature with 2 wt% VC additive. The cut-off potentials were 0.05 V and 2.5 V vs. Li$^+$/Li.
and elevated temperatures are employed, i.e., more Sn can be reoxidized to SnO\textsubscript{x}. Enhanced reversibility of the conversion reaction had been observed in Paper II for elevated temperature cycling and in Paper V for high cycling rates.

In Figure 6.4c capacities obtained from cycling the 9 nm SnO\textsubscript{2} particles at room temperature with 2 wt % VC electrolyte additive are presented. The goal of these experiments was to improve capacity retention of the 9 nm SnO\textsubscript{2} electrodes. It can be seen that VC indeed provides a very good capacity retention and high capacities over 120 cycles for all cycling rates (i.e., 1C; C/5 and C/10). The reason for this behavior is the formation of a thicker, more stable SEI layer by VC, that protects the electrode from further electrolyte reduction and can help to protect the integrity of the electrode material from the volume changes experienced during cycling which has been reported earlier in the literature. [29–33] Evidence for these SEI properties can also be found in the SEM images and XPS spectra shown in Paper VI. Further experiments employing the VC additive at 60 °C were carried out in an effort to combine the benefits of electrolyte additives and cycling at elevated temperature. However, the VC additive lead to large charge currents at 60 °C which were up to 500 mAh/g higher than the corresponding discharge currents from cycle 25 onwards. Therefore, VC was not used for further tests at elevated temperature. Evidence for this can be seen in the galvanostatic cycling data of Paper VI. We refrained from the use of FEC (fluoroethyl carbonate) as an alternative electrolyte additive as concerns about its high temperature stability have earlier been reported in the literature. [120] Therefore, one future challenge is clearly to find electrolyte additives that can be used for cycling at elevated temperatures.

6.3.2 Electrochemical impedance spectroscopy
Figures 6.5a and b show EIS spectra obtained at room temperature a) without additive and b) with 2 wt % VC additive. In general, the same features as described in 4.1.3 can be observed in both spectra, i.e., a high charge transfer resistance before cycling (black triangles) and only a mass transport limitation after cycles one (red triangles) and two (blue triangles). [15, 51, 52] Nonetheless, the impedance including the VC additive (Figure 6.5b) is much larger than without VC additive (Figure 6.5a). This result indicates a higher resistance in the electrochemical cell caused by the VC additive. [30,33]

6.3.3 Intermittent current interruption (ICI)
Figure 6.6 features graphs obtained from the intermittent current interruption (ICI) experiments described in Chapter 2.3.6, showing a) the median resistance plotted versus cycle number and b) the resistance plotted versus potential for cycles 1, 5 and 30. [84] In these graphs, the 9 nm SnO\textsubscript{2} electrodes
Figure 6.5. EIS spectra measured for the SnO$_2$ electrodes (9 nm) before cycling (obtained at 1.2 V vs. Li$^+$/Li) as well as after one cycle and two cycles (both obtained at 1.4 V vs. Li$^+$/Li) with a) LP40 electrolyte at room temperature and b) LP40 electrolyte with 2 wt % VC additive at room temperature.
were cycled at room temperature in the LP40 electrolyte. It can be seen in Figure 6.6a that the resistance for the initial discharge (150 Ohm) is significantly higher than for the following cycles. This is a consequence of the large charge transfer resistance that was also observed in the EIS spectra prior to cycling (Figure 6.5a). The charge transfer resistance disappears after the first cycle which is why the median resistances are significantly lower afterwards. Following the initial discharge, the median resistances increase steadily with cycle number up to cycle 60 (Figure 6.6a). This resistance growth could either be related to the agglomeration into bigger particles as seen in the transmission electron microscopy (TEM) images under 6.3.4 or it could be due to the crack formation that originates from the volume changes during alloying and dealloying. [3, 4, 13]

In Figure 6.6b, the resistance is plotted versus potential which shows that the resistances are generally high at the beginning and end of both discharge and charge. The high resistances at the beginning of discharge and charge could be related to the overpotentials of the electrochemical reactions (i.e., conversion, alloying and dealloying). Similar observations, regarding high resistances at the beginning and end of the discharge and charge, have previously been reported for Si electrodes through EIS measurements. [121–123] Nonetheless, the first discharge in Figure 6.6b (red dots) behaves quite differently from the other cycles, i.e., the resistance grows slowly in the beginning, shows a maximum at about 1.0 V vs. Li$^+$/Li and decreases subsequently. This behavior could be related to the SEI formation, which should begin around 1.0 V vs. Li$^+$/Li and continue below this potential. [98, 124, 125] The charge transfer resistance of the SEI formation process is high in the beginning, i.e., at 1.0 V vs. Li$^+$/Li, and decreases continuously when lowering the potential as the electroactive area grows at the same time. Thus, the high charge transfer resistance observed before cycling (see Figure 6.5a) declines during the first discharge. Another possible explanation could be that the access to unreacted SnO$_2$ is increased by crack formation in the electrode material below 1.0 V vs. Li$^+$/Li which could decrease the resistance as well.

In Figure 6.6b, the resistance at the end of charge above 1.0 V vs. Li$^+$/Li grows progressively with increasing cycle number. This phenomenon could be explained by the partial irreversibility of the conversion reaction. During the initial cycles (e.g., cycles 1 and 5) a larger fraction of SnO$_x$ is reformed and the currents at higher potentials are converted into the conversion reaction of Sn to SnO$_x$. Eventually, smaller amounts of SnO$_x$ are reformed, as the oxidation becomes increasingly limited by the polarization resistance which grows continuously above 1.0 V vs. Li$^+$/Li (e.g., cycle 30).

Short resistance plateaus can be seen at the end of discharge below 0.2 V vs. Li$^+$/Li for cycles 5 and 30 in Figure 6.6b (blue and green dots). Similar observations have been reported in the literature for Si electrodes with the help of EIS measurements. In these cases the reason for the resistances below 0.2 V vs. Li$^+$/Li was said to be extended SEI formation. [121–123] This was
Figure 6.6. a) Median resistances and b) the resistance plotted versus the potential for cycles 1, 5 and 30. The data and plots were both obtained from the ICI method for the SnO$_2$ electrodes (9 nm) at room temperature without VC additive. C denotes the charge (oxidation) and D denotes the discharge (reduction).
explained by damage to the SEI that could occur when the particles expand during the alloy formation. [121–123] Similar processes could be responsible for the resistance plateaus observed below 0.2 V vs. $Li^+/Li$ in Figure 6.6b. Another possible explanation for these features could be the formation of a new $Li-Sn$ alloy phase with a different charge transfer resistance at this potential.

In Figure 6.7 the ICI plots are presented for a cell that has been cycled with 2 wt % VC at room temperature with a) the median resistance plotted versus cycle number and b) the resistance plotted versus potential for cycles 1, 5 and 30. [84] In Figure 6.7a, it can be seen that the median resistances are generally higher with the VC additive than without which could already be deduced from the EIS data in Figure 6.5b. However, it can also be observed that, following the drop after the initial discharge, the median resistances increase significantly slower than without the VC additive (compare Figure 6.6a). The reason for this behavior could be that the VC formed SEI is more stable and flexible. Thus, it could protect the $SnO_2$ electrode better from crack formation and help to maintain its integrity during cycling, which is further supported by the SEM images in Paper VI. These effects could result in the preservation of a higher electronic conductivity as it has been stated in previous reports. [32, 126] Another difference between Figures 6.7 and 6.6 can be found when looking at the first discharge in Figure 6.7b where the resistance is plotted versus potential (red dots). There is a slow increase in resistance down to 1.0 V vs. $Li^+/Li$, but no pronounced maximum can be seen. This observation is different from Figure 6.6b where no VC additive was used and a clear resistance maximum at 1.0 V vs. $Li^+/Li$ is visible during the first discharge. Unlike the plots obtained without VC (red dots in Figure 6.6b), the resistance shows a rather stable behavior below 1.0 V vs. $Li^+/Li$ when VC is added (red dots in Figure 6.7b). These findings indicate that the SEI formation with VC starts around 1.0 V vs. $Li^+/Li$ too, but that its mechanism is different depending on if VC is included or not. The resistance plateaus below 0.2 V vs. $Li^+/Li$ during discharge in cycle 5 and 30 are missing in Figure 6.7b (blue and green dots). This could indicate that these features in Figure 6.6b are indeed SEI related since it is only the SEI properties that should be dependent on the use of the VC additive. The alloying processes and $Li-Sn$ alloy phases should be independent of the VC additive and identical in both $SnO_2$ electrodes. Nonetheless, there is too little evidence in the data to draw any definite conclusions.

Generally, the VC formed SEI seems to be more stable and able to better protect the electrode from pulverization and helps to maintain its integrity. These factors could explain the excellent capacity retention obtained from cycling with VC (Figure 6.4c). [32, 126] Otherwise, the resistances in Figure 6.7 are quite similar to the ones obtained without VC in Figure 6.6. The results presented here are further supported by the SEM images and XPS spectra in Paper VI where a denser electrode morphology as well as a more continuous
Figure 6.7. a) Median resistances and b) the resistance plotted versus the potential for cycles 1, 5 and 30. The data and plots were both obtained from the ICI method for the SnO$_2$ electrodes (9 nm) at room temperature with 2 wt% VC additive. C denotes the charge (oxidation) and D denotes the discharge (reduction).
and thicker SEI layer was found after employing the VC additive for electrochemical cycling.

6.3.4 Characterization of cycling products

**Transmission electron microscopy (TEM)**

Figure 6.8 represents the TEM images collected for the 9 nm $SnO_2$ electrodes, i.e., a) a pristine electrode, b) an electrode cycled for 60 cycles at room temperature and c) an electrode cycled for 60 cycles at 60 °C.

In Figure 6.8a, the particles are spread out evenly and show a homogeneous particle size distribution. After 60 cycles at room temperature in galvanostatic mode an accumulation of particles on the right side of the image can be seen in Figure 6.8b. In addition, the particles are generally larger, show a more heterogeneous size distribution and their boundaries seem less clear and blurred (Figure 6.8b). These results show that an increase in particle size takes place during electrochemical cycling in conjunction with an accumulation of particles in certain places.

After cycling for 60 cycles in galvanostatic mode at 60 °C in Figure 6.8c, the particles have changed even more as compared to room temperature cycling (Figure 6.8b). The particles appear to have accumulated at the bottom right part of the image. Also, they are even larger than after cycling at room temperature and the particle boundaries have been blurred even more.

It should be noted that the batteries were stopped in the charged, i.e., delithiated, state before disassembly. This means that the observed particle growth cannot stem from the volume expansion experienced by $Sn$ during alloying. An explanation for these observations could be the agglomeration of nanoparticles into larger particles during electrochemical cycling which has previously been discussed in literature. [14,22,23] As the effects seem more severe on the electrode cycled at 60 °C (Figure 6.8c), it can be concluded that the particle agglomeration is accelerated at higher temperatures. This result indicates that even though cycling at elevated temperature leads to improved capacities for larger $SnO_2$ particles (see Chapter 4.1), it might also shorten their cycle life due to the enhanced particle agglomeration.

**Energy electron loss spectra (EELS)**

Figure 6.9 features the normalized EELS spectra for 9 nm $SnO_2$ particles cycled galvanostatically at room temperature (RT) over 10 (red line) and 60 cycles (yellow line), respectively, as well as particles cycled at 60 °C over 10 (violet line) and 60 cycles (blue line), respectively. The batteries were stopped and disassembled in the charged (oxidized) state at 2.5 V vs. $Li^+$/Li. The spectra also include data from one pristine sample (black line). Represented in Figure 6.9 are the oxygen K-edges. The red and blue dashed guide lines indicate the theoretical position of the $SnO$ (about 553 eV, red) and $SnO_2$ (about 558 eV, blue) peaks. [78, 79]
Figure 6.8. TEM images of one pristine electrode and electrodes cycled galvanostatically over 60 cycles at C/5: a) pristine electrode, b) electrode cycled with LP40 at room temperature for 60 cycles and c) electrode cycled with LP40 at 60 °C for 60 cycles.
These experiments were carried out in an effort to determine if SnO, SnO$_2$ or a mixture of both is formed upon charge (oxidation), since this is very difficult to determine by XPS, as mentioned in Chapters 4 and 5. [78, 100] In the EELS data, one sharp peak at about 532 eV can be observed in all spectra which is caused by all oxygen containing electrode species together, i.e., SnO$_2$, SnO, CMC and possibly SEI or electrolyte residues. One signal originating solely from SnO$_2$ can be observed at about 558 eV. However, it can be seen that features related to SnO, i.e., a signal at about 553 eV, seem to be present in the pristine sample (black line), even though this sample only consisted of SnO$_2$. [78, 79] These apparent SnO features are probably caused by interferences from the Carbon Black, the CMC/SBR binder as well as SEI and electrolyte residues which render these spectra much noisier than the bulk data reported in the literature. [78, 79] Nonetheless, some qualitative conclusions can still be drawn from the EELS data. For example, it can be seen that SnO$_2$ signals (about 558 eV) are still dominating the spectrum after 10 cycles at room temperature (red line). When looking at the particles cycled for 60 cycles at room temperature, in contrast, the SnO$_2$ feature at about 558 eV has decreased and a smaller signal at about 553 eV is visible, which indicates the presence of a mixture between SnO and SnO$_2$, or possibly intermediate tin oxides such as Sn$_3$O$_4$ or Sn$_5$O$_6$. [78, 79, 127, 128] This observation implies that

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*Figure 6.9.* Energy electron loss spectra of the oxygen $K$-edges for a pristine electrode (black), an electrode after 10 cycles at room temperature (red), an electrode after 60 cycles at room temperature (yellow), an electrode after 10 cycles at 60 °C (violet) and an electrode after 60 cycles at 60 °C (clue).
there is an increase of $SnO$ and a decrease of $SnO_2$ with growing cycle number as a result of the conversion reaction's partial irreversibility.

Similar observations can be made for the $SnO_2$ nanoparticles cycled at 60 °C. After 10 cycles (yellow line), the spectrum looks very similar to the one after 60 cycles at room temperature, with a signal at about 553 eV, revealing a mixture of $SnO$ and $SnO_2$ or intermediate oxides. This feature at 553 eV has almost disappeared completely after 60 cycles at 60 °C (violet line) leaving only fingerprint peaks for $SnO$.

In general, there seems to be a decrease in the amount of $SnO_2$ and an increase in the amount of $SnO$ with growing cycle number due to the partial irreversibility of the conversion reaction. Furthermore, intermediate oxides like $Sn_3O_4$ or $Sn_5O_6$ could be present as well on the cycled electrodes.
7. Conclusions

This work's main goal was to gain a deeper understanding about the fundamental electrochemical processes taking place when cycling tin oxide in LIBs. Therefore, a model system containing tin oxide coated tin films was studied in the first part of this thesis. These experiments showed a partial reversibility of the tin oxide conversion reaction when excluding the alloying reaction. Raising the potential above 3.0 V vs. $Li^+/Li$ did not lead to an increased reversibility of the conversion reaction. Instead, the XPS results at 3.5 V vs. $Li^+/Li$ showed evidence for the formation of $SnF_2$ on the electrode surface of metallic $Sn$ due to oxidation reactions with the electrolyte. This sensitivity towards electrochemical oxidation and fluoride formation can be of importance for applications of oxygen deficient tin based anodes, such as metallic $Sn$.

In the second part of this thesis, it was shown that electrochemical cycling of $SnO_2$ particles at elevated temperatures (i.e., 60 °C) resulted in a better cycling performance. Galvanostatic cycling at 60 °C resulted in a capacity increase of about 30 % over 60 cycles. These benefits of high temperature cycling are probably due to improved $Li^+$ mass transport. As conventional electrolytes like LP40 are only stable up to about 60 °C, an IL based electrolyte (0.5 M $LiTFSI$ in $Pip_{1.4}TFSI$) was used to cycle $SnO_2$ particles at 80 °C in another study. The aim was to reach even higher capacities for the $SnO_2$ particles. However, the IL based electrolyte proved to be very sensitive to electrochemical reduction which resulted in large capacity losses during the first 15 cycles. Thus, much research is still required to develop IL based electrolytes that are more stable towards reduction. The results presented in this thesis regarding high temperature cycling are of interest for hybrid electric vehicle (HEV) battery systems where it could lead to the reduction of the cooling systems.

The following section focussed on the overlap observed in CVs between the potential regions of the $SnO_2$ conversion and the alloying reaction. This work could confirm an overlap during both reduction (discharge) and oxidation (charge). A reason for this could be the formation of a passivating $Sn$ layer on the particle surface that inhibits $Li^+$ from reaching $SnO_2$ still left underneath. An $Sn$ layer can likewise cause the overlap of dealloying and conversion reaction during oxidation. Furthermore, a continuous SEI formation over the entire reductive scan and a partial SEI dissolution during the oxidative scan could be observed. The data showed that mainly unpolar, organic SEI compounds like $P−F$ and $C−F$ species were dissolved during oxidation while the more polar, inorganic salt $LiF$ remained on the surface.
Another study focussed on the $Li^+$ mass transport limitations in $SnO_2$ electrodes. Experiments including $Al_2O_3$ (good $Li^+$ conductor) and diamond (poor $Li^+$ conductor), respectively, as additives showed that it is mainly the $Li^+$ transport within the $SnO_2$ particles that is of importance and not in between them. In addition, the comparison of initial discharge capacities for pure $SnO_2$ particles with regard to their particle size indicated that it is extremely difficult to reach the full theoretical capacity of 1491 mAh/g with particles larger than 10 nm in diameter using conventional cycling rates.

The last part dealt with the influences of high temperature cycling (i.e., at 60 °C) and the VC electrolyte additive on the electrode performance of 9 nm $SnO_2$ particles. Very good capacity retention was obtained when employing the VC additive at room temperature. An intermittent current interruption method (ICI) was used to investigate the development of the internal cell resistance during cycling with and without VC, respectively. The resistances grew steadily with cycle number due to either agglomeration into larger particles or crack formation. This steady resistance increase was slowed down when VC was added. The VC formed SEI layer hence seems to be more stable and flexible and can efficiently protect the $SnO_2$ electrode against volume change effects such as loss of electrical contact. Finally, TEM characterization of the 9 nm $SnO_2$ particles showed particle agglomeration caused by extended cycling which was accelerated at elevated temperature. This result implies that, although high temperature cycling can improve the capacities of $SnO_2$ electrodes, it might also shorten their cycle lives.
8. Svensk sammanfattning

För drygt 25 år sedan införde Sony de första litiumjonbatterierna vilka snabbt erövrade världen. Fördelen med litiumjonbatterier jämfört med andra uppladdningsbara batterier som nickel-metallhydrid, nickel-kadmium eller blybatterier är att de kan lagra mycket mer energi i förhållande till sin vikt och volym. Därför används de i stort sett i all bärbar elektronik idag.


Det kan även vara interessant att använda sig av en tennoxid istället för metalliskt tenn. I tennoxider kombineras en konverteringsreaktion där tennoxiden reagerar med litium och bildar litiumoxid och elementärt tenn (se reaktionsformel 8.2) med legeringsreaktionen mellan litium och tenn (se reaktionsformel 8.1). Tenn(IV)oxid (SnO₂) har alltså en total teoretisk kapacitet på 1491 mAh/g medan tenn(II)oxid (SnO) kan ge 1270 mAh/g. Det stora problemet med tennoxiderna är dock att reduktion av oxidten (både tenn(IV)oxid och tenn(II)oxid) vanligtvis är irreversibel och leder till en stor kapacitetsförlust efter första cykeln. Det har dock nyligen visats att en viss reversibilitet för tennoxidens konverteringsreaktion kan uppnås genom att använda nanopartiklar eller genom att begränsa potentialfönstret.

\[ yLi^+ + ye^- + Sn \rightleftharpoons Li_ySn \] (8.1)
Huvudsyftet av detta arbete är att undersöka de elektrokemiska reaktionerna och mekanismerna mellan tennoxid och litium i detalj. Med hjälp av dessa resultat kan tennoxiders användning som anodmaterial i litiumjonbatterier förbättras. Figur 8.1 visar en schematisk bild av batterier som användes i detta arbete (a) och ett foto av ett sådant batteri inkopplad i en miniräknare (b).

\[
2xLi^+ + 2xe^- + SnO_x \rightleftharpoons xLi_2O + Sn
\]  

Figure 8.1. a) Schematic bild av ett batteri som användes i detta arbete. b) Foto av ett sådant batteri som är kopplat till en miniräknare.

I de första experimenten kunde vi konstatera att tennoxids konverteringsreaktion med litium är reversibel när legeringsbildningen utesluts från cyklingen. Senare visade sig konverteringsreaktionen vara partiellt reversibel även när legeringsbildningen inkluderades. Dessutom ledde svep upp till höga potentialer (> 3.0 V vs. Li^+ / Li) till degraderingsreaktioner med elektrolyten (LiPF_6 i etylenkarbonat och dietylkarbonat), dvs. den vätska som placeras mellan de två elektroderna (här: arbetselektrod och motelektrod i Figur 8.1a).

Andra experiment vid olika cyklingshastigheter och högre temperatur (dvs. 60 °C) tydde på att tennoxids elektrokemiska reaktioner med litium begränsas genom långsam diffusion av litijjoner. På grund av detta kunde energitätheten av tenn(IV)oxid ökas med ca. 30 % när den användes vid 60 °C
istället för rumstemperatur då litiumjondiffusionen accelererades. Detta resultat är av stort intresse för en möjlig användning inom batterisystem för hybridbilar där man gärna vill reducera antalet nödvändiga kylsystem. Då vanliga elektrolyter som $\text{LiPF}_6$ i etylenkarbonat och dietylkarbonat enbart är stabila upp till 60 °C, testades även en jonvåtskebaserad elektrolyt (0.5 M $\text{LiTFSI}$ i $\text{Pip}_1\text{,4TFSI}$). En jonvåtska är ett salt som är flytande vid rumstemperatur. Ten(IV)oxid testades så vid 80 °C. Tyvärr visade sig den jonvåtskebaserade elektrolyten vara instabil mot elektrokemisk reduktion vid låga potentialer vilket ledde till stora kapacitetsförluster inom de första 15 cyklar. Sökandet efter mer stabila jonvåtskebaserade elektrolyter kommer därför att vara en stor utmaning i framtiden.

Fotoelektronspektroskopisk data (photoelectron spectroscopy, PES) visade att potentialregionerna för ten(IV)oxidens konverteringsreaktion och legeringsbildning överlappar inom cyklovoltammetriska mätningar. Anledningen är mest sannolikt den långsamma litiumjondiffusionen genom ett passiverande tennskikt som bildas först under konverteringen (när ten(IV)oxid reduceras) och delegeringen (när legeringen oxideras).

Vidare kunde detta arbete påvisa att det är litiumjondiffusionen inom tennoxidpartiklarna och ej mellan dem som begränsar reaktionshastigheten. Det syntes också att ten(IV)oxidens fulla teoretiska kapacitet av 1491 mAh/g bara kan unnyttjas om partiklarna är mindre än 10 nm i diameter.

I den sista studien testades därför ten(IV)oxid med en partikelstorlek av 9 nm och den fulla teoretiska kapaciteten kunde uppnås på detta sätt i den första cykeln. Vidare testades vinylenkarbonat (VC) som additiv till elektrolyten ($\text{LiPF}_6$ i etylenkarbonat och dietylkarbonat) vilket gav ett mycket stabiltare SEI-skikt (solid electrolyte interphase). SEI-skiktet bildas på ten(IV)oxidelektroder ytor genom elektrokemisk reduktion av elektrolytkomponenter under den första cykeln och skyddar elektroden mot liknande reaktioner i fortsättningen. Ett SEI-lager bildat av VC inhägnar elektroden ännu bättre mot dessa reaktioner. Dessutom kan det VC formade SEI-skiktet skydda elektroden mot följderna av de stora volymsförändringar som legeringsbildningen medför. Detta kunde visas med hjälp av en relativt ny periodisk strömavbrytnings-teknik (intermittent current interruption method, ICI) som möjliggör visualiseringen av batteriets interna resistans. Till sist testades de 9 nm stora tenn(IV)oxidpartiklarna även vid 60 °C. Resultatet var att långvarig användning av dessa partiklar leder till agglomerering så att större partiklar växer fram. Denna process påskyndas när partiklarna cyklas vid 60 °C istället för rumstemperatur. Detta betyder att fastän högtemperaturcykling resulterar i högre energitäthet för större ten(IV)oxidpartiklar, så kan det även medföra en förkortad livslängd för batteriet.
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Solveig
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