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„Thermochemical and electrochemical investigation of high capacity SnSx- based anode materials for lithium-ion batteries“

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Abstract

In recent years tin sulfides, particularly SnS and SnS₂, have attracted significant attention in the energy storage research community. Their high theoretical specific capacities (1111 mAh g⁻¹ for SnS and 1209 mAh g⁻¹ for SnS₂) make them promising candidates for anode-active materials for Li-ion batteries. Additionally, they possess the advantages of being cost-effective and environmentally friendly. During the lithiation process, Sn-S-based materials undergo a conversion reaction with Li, forming Li₂S and Sn. Further lithiation triggers the alloying reaction between Sn and Li, forming various Sn-Li intermetallic phases. Notably, these newly formed Sn-Li phases have significantly larger unit cell volumes than their parent phases, causing the active material particles to crack on repeated alloying and dealloying of tin. Ultimately, the continuous cracking usually leads to pulverisation of the anode material and reduced contact between the particles. These mechanisms contribute to cell degradation and capacity fade at higher cycle numbers.

This thesis focuses on assessing and understanding the structure-processing-property relations in Sn-S materials and Sn-S-based electrodes. Such investigations can yield measurable enhancements in the electrochemical performance of this materials class.

Both precipitation and hydrothermal methods were used to synthesise SnS and SnS₂ materials. In all cases, SnCl_x·yH₂O (x= 2; y= 2 for SnS and x= 4; y= 5 for SnS₂) was used as a Sn source and thioacetamide as a S source. The physicochemical properties of the as-synthesised materials were examined by powder X-ray diffraction (PXRD), and structural parameters were extracted using Rietveld analysis of the measured patterns. Furthermore, the sample morphologies were characterised by scanning electron microscopy (SEM), and the crystallinity of the samples was further investigated by transmission electron microscopy (TEM). The presence of surface impurities, which may be formed during material synthesis, was examined by X-ray photoemission spectroscopy (XPS). Furthermore, the as-prepared materials were subjected to drop solution calorimetry to determine the enthalpy of formation.

The electrochemical cycling performance of the as-prepared materials was investigated in half-cell configurations (Sn-S working electrodes vs Li/Li⁺ counter electrodes). In this way, comparisons were drawn

between materials with the same chemical composition but different particle sizes and morphology and materials with different chemical compositions and very similar morphology.

In addition to the above experiments, in-situ dilatometry was performed to quantify the changes in the thickness of SnS and SnS₂ electrodes during cycling. *Ex-situ* XRD and *ex-situ* SEM were utilised to investigate the role of crystal chemistry and particle morphology on electrochemical performance *post-mortem*. The results showed that the electrodes made of partially amorphous SnS₂, which was synthesised via the precipitation, expands the least on alloying. Additionally, the cycling data show that partially amorphous SnS₂ performs better than SnS and well-crystallised SnS₂. Two effects could be attributed to those results. Firstly, it is hypothesized that thicker *in-situ* Li₂S layers are formed via the conversion mechanism on particles with lower specific surface areas. These thicker layers can better restrain the volume changes of Sn during cycling. Secondly, due to the intercalation step prior to the conversion reaction in SnS₂, it is postulated that Li₂S and Sn are homogeneously distributed on the atomic scale after the conversion reaction, which further helps minimise the volume expansion of Sn during cycling.

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This thesis has been prepared as a compilation of research papers and it consists of the following papers:

Paper 1.

Damian M. Cupid, Arlavinda Rezqita, Albina Glibo, Martin Artner, Viktor Bauer, Raad Hamid, Marcus Jahn, Hans Flandorfer, **“Understanding and modelling the thermodynamics and electrochemistry of lithiation of tin (IV) sulfide as an anode active material for lithium-ion batteries”**, Published in *Electrochimica Acta*, 375 (2021), 137936. DOI: [10.1016/j.electacta.2021.137936](https://doi.org/10.1016/j.electacta.2021.137936)

Albina Glibo conducted the literature review and edited the paper.

Paper 2.

Albina Glibo, Nicolas Eshraghi, Andreas Mautner, Marcus Jahn, Hans Flandorfer, Damian M. Cupid, **“Synthesis and comparative performance study of crystalline and partially amorphous nano-sized SnS₂ as anode materials for lithium-ion batteries”**, Published in *Electrochimica Acta*, 428 (2022), 140869. DOI: [10.1016/j.electacta.2022.140869](https://doi.org/10.1016/j.electacta.2022.140869)

Albina Glibo conducted the literature review, designed methodology, conducted experiments, analysed and interpreted results, and wrote paper 2. Nicolas Eshraghi and Andreas Mautner provided support in conducting electrochemical impedance and XPS measurements, respectively. Marcus Jahn, Hans Flandorfer and Damian M. Cupid provided research guidance and edited the paper.

Paper 3.

Albina Glibo, Nicolas Eshraghi, Yuri Surace, Andreas Mautner, Hans Flandorfer, Damian M. Cupid, **“Comparative study of electrochemical properties of SnS and SnS₂ as anode materials in lithium-ion batteries”** Published in *Electrochimica Acta* 441 (2023) 141725. DOI: [10.1016/j.electacta.2022.141725](https://doi.org/10.1016/j.electacta.2022.141725)

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Paper 4.

Albina Glibo, M. Reda, Yuri Surace, Damian M. Cupid, Hans Flandorfer, **“Correlation between microstructure, thermodynamic stability and electric work of tin sulfide active anode materials for Li-ion batteries”**, Submitted on 10th of July 2023 in Journal of Alloys and Compounds with manuscript number: JALCOM-D-23-10054

Albina Glibo conducted the literature review, conducted experiments, analysed and interpreted results, and wrote paper 3. Yuri Surace and M. Reda provided support in conducting SEM and calorimetry measurements, respectively. Hans Flandorfer and Damian M. Cupid provided research guidance and edited the paper.

Abbreviation list

CEP - constant phase element	NCA - $\text{LiNi}_x\text{Co}_y\text{Al}_z\text{O}_2$
CV - cyclic voltammetry	NGC - non-graphitic carbon
EIS - electrochemical impedance spectroscopy	NMC - $\text{LiNi}_x\text{Co}_y\text{Mn}_z\text{O}_2$
EMF - electromotive force	NMP - N-methyl-2-pyrrolidone
EVs- electric vehicles	OCV – open circuit voltage
ETD - Everhart–Thornley	PVDF - polyvinylidene fluoride
GC – graphitic carbon	PVC - polyvinyl chloride
GCPL - galvanostatic cycling with potential limitation	PP/PE/PP - polypropylene/polyethylene/polypropylene
HT - high temperature	SEI – solid electrolyte interphase
ICE - internal combustion engine	SEM - scanning electron microscopy
LIB - Li-ion battery	TAA - thioacetamide
LCO - LiCoO_2	TEM - transmission electron microscopy
LMO - LiMnO_2	TLD - Through-Lens
LNO – LiNiO_2	TM - transition metal
LNMO - $\text{LiNi}_x\text{Mn}_y\text{O}_4$	W – Warburg impedance
LTO - lithium titanium oxide	XPS - X-ray photoelectron spectroscopy
LT – low temperature	XRD - X-ray diffraction

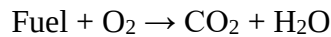
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1. Introduction

Since the 19th century, vehicles propelled by an internal combustion engine (ICE) have been the most common mean of transportation. Although the vehicles with ICE offer high power and energy densities and have low refuel time, they are not environmentally benign and highly contribute to climate change. In order to propel a vehicle, ICE combusts fuel with the help of an oxidiser (typically oxygen from the air). The combustion reaction can be represented with the following equation:



CO₂ is a greenhouse gas which is desirable in the atmosphere in small amounts as it absorbs infrared energy emitted by the Earth. The emitted energy is re-emitted in all directions, and part returns to Earth. If there were no greenhouse gasses, the Earth would be frozen. However, when present in larger quantities, greenhouse gasses cause a greenhouse effect, creating a coat that traps the heat in the atmosphere, thus warming the planet. The greenhouse effect significantly impacts Earth's temperature as the average global temperature has risen 0.8 °C since 1880. Governments and experts around the globe are expeditiously working on finding solutions for this threatening problem to our planet.

In order to meet European Union's objective to be climate neutral by 2050¹, alternatives to vehicles with ICE must be developed. An alternative should be environmentally friendly with low CO₂ emissions and deliver comparable or higher energy and power densities. Electrochemical energy storage and conversion devices, such as batteries, fuel cells, and supercapacitors, represent an array of device alternatives to the ICEs. However, Li-ion battery technology is currently a forerunner and a market leader for electric propulsion.

The principle behind rechargeable batteries has been known for over 100 years; however, their potential was only utilised in the late 80s. In 1859 the first rechargeable battery was introduced by French physicist Gaston Planté, and it consisted of a lead anode and lead(IV) oxide cathode immersed in sulfuric acid. The sulfuric acid, which acts as an electrolyte, dissociates to SO_4^{2-} and H^+ ions, free to move. During the discharge of a lead acid battery, the lead is oxidised to Pb^{2+} at the anode, whereas Pb^{4+} is reduced to Pb^{2+} at the cathode. Altogether, PbSO_4 is precipitated on both electrodes consuming sulfate ions. Even though this type of battery still finds its use today, several factors limit its application in electric vehicles. First, it exhibits relatively low specific energy (high weight, relatively low voltage), which is insufficient for battery energy requirements targeting specific energy $> 400 \text{ Wh kg}^{-1}$ and energy density $> 1000 \text{ Wh L}^{-1}$. Secondly, lead acid batteries require constant maintenance due to the production and the escape of hydrogen and oxygen gasses on charge. After lead acid batteries, several other types have been developed; however, the invention of the Li-ion battery (LIB) was a giant leap forward in electrochemical storage systems. Unlike lead acid batteries, whose primary electrode mechanism is oxidation/reduction of lead, Li-ion batteries work on the principle of intercalation-deintercalation of Li-ions.

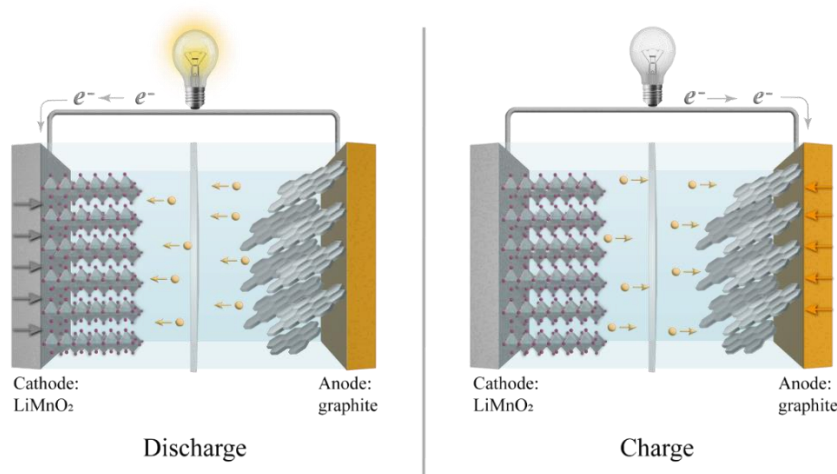


Figure 1. Scheme of working principle of Li-ion batteries

The prototype of lithium-ion batteries (LIBs) was based on earlier works of M. Stanley Whittingham, John Goodenough, Rachid Yazami, Koichi Mizushima and it was developed by Akira Yoshino in 1983. The prototype consisted of conductive polyacetylene as a negative electrode (anode) and lithium cobalt oxide as a positive electrode (cathode)². The polyacetylene electrode was chemically unstable with a low specific capacity, and it was later replaced by carbonaceous materials. Eight years after the first LIB prototype was developed, SONY Group Corporation commercialised a Li-ion battery with a carbon-based anode and CoO_2 as a cathode. The invention of this kind of Li-ion battery was a huge success; to this day, albeit with alternative cathode materials, it is still a primary electrochemical storage system used in most portable devices and electric vehicles (EVs). LIBs have four main components: positive and negative electrodes, separator, and electrolyte. The basic principle of LIBs operation is shown in Figure 1. In this theoretical battery cell, graphite is chosen as an anode material and LiMnO_2 as a cathode material. The cell is charged when an external current is applied, and the electrons flow through the external electric circuit and a current collector (copper) into the graphite. Simultaneously, an equal amount of Li^+ ions must pass from the cathode side through a Li-ion conducting electrolyte to the anode side to match the charge flux. On the discharge, the reverse happens, the electrons flow from the anode side through an external circuit to the cathode side, and Li^+ ions move towards the cathode through the electrolyte.

Through the last three decades in which LIB research has been in the spotlight, several types of anode and cathode materials have been thoroughly explored. Cathode materials which were in the spotlight in the past few decades included LiCoO_2 (LCO)³, LiNiO_2 (LNO)⁴, LiMnO_2 (LMO)⁵, $\text{LiNi}_x\text{Co}_y\text{Mn}_z\text{O}_2$ (NMC)⁶, $\text{LiNi}_x\text{Co}_y\text{Al}_z\text{O}_2$ (NCA)⁷ and $\text{LiNi}_x\text{Mn}_y\text{O}_4$ (LNMO)^{8,9}. Commonly researched anode materials include graphite modifications^{10,11,12,13}, Si ^{14,15,16,17}, Ge ^{18,19,20,21}, Sn ^{22, 23}, lithium titanium oxide (LTO)^{24,25}.

However, the introductory thermodynamics of battery cells and materials will be discussed in the next chapter before diving deeper into the properties of anode materials.

1.1. Introductory thermodynamics of battery cell and materials

When current does not flow across a cell, there is still a potential difference between the cathode and anode, defined as an open circuit voltage (OCV), equilibrium potential, or electromotive force (EMF). Due to the difference in the chemical potential of the active species (Li-ions in LIBs) at the anode and cathode, a chemical driving force is present, which balances the electric charge separation in the double layer at the electrode/electrolyte interface. This charge separation results in an electric potential which remains constant when the electrochemical equilibrium is established. Accordingly, in this state, the electric potential is related to the chemical potential. Generally, the electrostatic force can be expressed as $-zFE$, where E is the equilibrium potential, F is the Faraday constant (electric charge of one mole of electrons), and z is the number of electrons transferred per mole of active species. The chemical driving force can be expressed as the change of standard Gibbs free energy per mol, ΔG_r° (J/mol), and the balance between chemical and electric forces upon the ions under OCV can be expressed as:

$$E = - \Delta G_r^\circ / zF \quad (1.1.1.)$$

The expression above is valid only when the system is in electrochemical equilibrium, and no reaction occurs anymore on the anode or cathode side; therefore, the cell voltage will remain constant. The partial molar Gibbs Energy is equal to the chemical potential:

$$\mu_i = \left(\frac{\Delta G}{\partial n_i} \right)_{p,T,n \neq n_i} \quad (1.1.2)$$

where μ_i is the chemical potential (or partial molar Gibbs Energy) of species i . If this species is the only one which is electrochemically active, the measured potential of a galvanic cell in electrochemical equilibrium corresponds to the difference in the chemical potential of the species in the anode and cathode material

$$\Delta\mu_i = \Delta G_r = -z.F.E \quad (1.1.3)$$

1.2. Electrochemical potential and voltage profile of multicomponent systems

By imagining a simple mixture of two pure compounds, A and B, the molar Gibbs free energy of the mixture of the system will be:

$$G_M = x_A\mu_A + x_B\mu_B \quad (1.2.1)$$

According to the Gibbs phase rule, in a system where two phases coexist at fixed temperature and pressure, the system does not have any degree of freedom, leading to a constant chemical potential and, thus, a linear change of the Gibbs free energy of the mixture, G_M , with the concentration.

The Gibbs free energy comprises the enthalpy of mixing, ΔH_m , and the configurational entropy, ΔS_m :

$$G_M = \Delta H_m - T \Delta S_m \quad (1.2.2.)$$

Depending on the effect of mixing enthalpies and compound formation, there are several possible cases, shown in Figure 2.

1. The mixing enthalpy is negative – it further reduces the Gibbs energy of the mixture, and the system results in a complete solid solution (Figure 2a)

2. The mixing enthalpy is positive – the free energy has two minimal values at the composition α and β . The free energy of mixture $\alpha + \beta$ is lower than that of solid solution between α and β , and phase separation occurs (Figure 2c).
3. Pure solid phases A and B have different crystal lattices, limited mutual solubility, and possibly compound formation (Figure 2e)

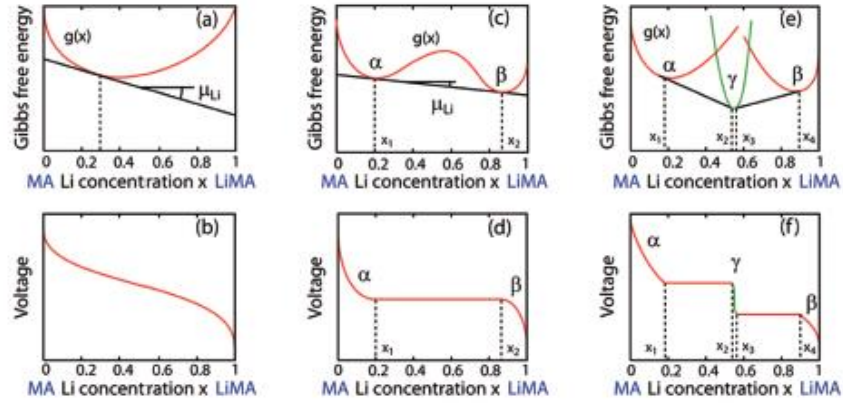


Figure 2. Voltage curves are directly related to the Gibbs energy curves²⁶

According to the Gibbs phase rule, if a solid solution reaction of the active species into the electrode material occurs, the number of degrees of freedom at constant temperature and pressure will be one as only one phase is present. Therefore, the voltage changes continuously, and its profile is a smooth curve, as shown in Figure 2b. When there is a phase decomposition into an α -phase and a β -phase, a voltage plateau appears along the miscibility gap since the chemical potential of the components needs to be the same in both phases for each component (Figure 2d). When mutual solid solutions and possibly compounds exist, the cell voltage remains constant along the two-phase regions but changes along the single-phase regions. The slope of the change depends on the homogeneity range and the phase stabilities (Figure 2f).

1.3. Anode materials in Li-ion batteries

An anode is one of the four essential elements of any battery, along with a cathode, anode, electrolyte, and separator. Several properties are essential when considering a material for an anode. An ideal anode material for Li-ion batteries is highly electrically and ionically conductive for Li-ions with a high charge capacity and fast Li-ion kinetics, and it shows mechanical durability at a low cost. Another critical parameter is the voltage match; see below.

Potentially one of the best materials for an anode for high-voltage and high-capacity Li-ion batteries is metallic Li as it is the lightest metal in the periodic table of elements exhibiting a high specific capacity (3860 mAh g^{-1}) and meagre normal standard potential (-3.04 V versus standard hydrogen electrode).¹ Therefore, metallic Li could provide high gravimetric specific energy. However, metallic Li has several safety issues which severely hinder its use in rechargeable Li-based batteries. One is the formation of lithium dendrites at low potentials due to an unstable interface between metallic lithium and the electrolyte during the charge of a battery. During the cycling, the dendrites can break down, resulting in irreversible capacity loss, poor cycling efficiency and further degradation of electrolytes²⁷. Moreover, the formation of sharp dendrites can be highly lethal as it can penetrate the separator and causes internal short circuit leading to fire and explosions.

The suitable alternative, still in use in major commercially available batteries, is a graphite anode based on the intercalation principle. Depending on the interaction with Li, anode

¹ A full Li-ion battery is, per definition, made of intercalation anodes and cathodes, and no Li/Li⁺ redox reaction takes place. For this reason, using Li-metal as an anode and an intercalation cathode results in a half Li-ion battery.

materials can be sorted into two categories: 1) insertion electrodes and 2) conversion/alloying reaction electrodes.

1.3.1. Insertion electrodes

The critical feature of insertion electrodes is the intercalation of mobile guest species into a host structure which distinguishes itself with lattice stability. The intercalation is reversible; thus, the mobile guest can be deintercalated from the host structure. During the intercalation/deintercalation process, the crystal structure of the host is preserved, and there is only minor cell volume or bond length changes. The host usually exhibits an open framework or a layered type of crystal structure offering enough space for the presence of guest ions.

Carbon-based materials

The most known anode material that intercalates Li ions is graphite, generally divided into graphitic carbon (GC) and non-graphitic carbon (NGC). In graphite, each sp^2 - hybridised carbon atom is directly planarly bonded with another three carbon atoms forming a single layer called graphene. The layers can be stacked and bonded due to the remaining p_z -orbitals, which form a delocalised π -electron system. During charge, Li-ions move across the battery cell from cathode to anode and are inserted between the graphene layers. In graphite, one Li-ion can be intercalated on every six C atoms, forming LiC_6 resulting in a theoretical specific capacity of 372 mAh g^{-1} .

Graphite can be gained from natural sources or by heating soft carbon to very high temperatures (3000°C). Soft carbons are generally produced by the pyrolysis of materials such as petroleum pitch or PVC, and the carbon atoms in their structure are initially arranged

in small graphene-type groups. However, there is generally a significant amount of imperfection in their two-dimensional honeycomb networks and randomness in how the layers are vertically stacked upon each other.

The pyrolysis of materials, such as chars or glassy carbon, at high temperatures typically produces hard carbons (non-graphitising carbon). The hard carbons exhibit a significant amount of initial cross-linking and substantial nano-porosity.

Carbon exhibits different electrochemical behaviour depending on the structure and texture. For example, the charge-discharge profile looks different for carbon heated to high temperatures, which is well-ordered and carbon that is not well-ordered.

Other insertion reaction materials

Besides carbonaceous anodes, several other materials are well-researched and recognised as insertion-type anode materials. Spinel (LTO) is one of them due to its excellent thermal stability, relatively high volumetric capacity and long lifetime²⁸. LTO is considered a "zero-strain" material, showing a minimal volume expansion of only 0.3 % on lithiation. Additionally, LTO is exceptionally safe because its high potential (1.55 V vs Li/Li⁺) prevents Li dendrite formation, even at high charge rates. On the other hand, the high potential vs Li/Li⁺ reduces the voltage and thus the energy density of the full cell. LTO can reversibly store only up to three Li ions per formula unit, yielding a relatively low theoretical specific capacity of 175 mAh g⁻¹. Moreover, at the surface of the LTO anode, several reactions between the organic electrolyte solvent and the LTO active material occur, which cause severe gassing²⁹.

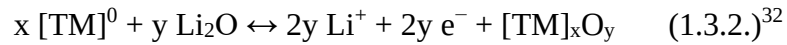
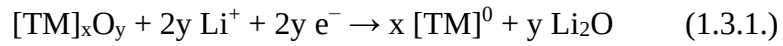
Li_3VO_4 ³⁰ has surfaced as another alternative to carbon-based anode materials. The theoretical capacity of Li_3VO_4 material of 323 mAh g^{-1} is slightly lower than the theoretical capacity of graphite; however, its higher Li intercalation potential (between 0.5 and 1.0 V vs Li/Li^+) prevents Li-plating and dendrite formation.

1.3.2. Conversion materials

Another group of materials explored as anode materials in Li-ion batteries are conversion materials. Those types of material undergo a chemical conversion reaction with lithium ions. In some cases, during the first lithiation reaction, the starting conversion materials are irreversibly converted into two compounds. Onwards lithiation includes only alloying reaction of only one compound yielded in the conversion reaction and Li-ion. Therefore, the conversion reaction is an initial step and does not contribute to the electrochemical performance beyond the first discharge cycle. One example of conversion material is SnO_2 . Due to the exceptionally high theoretical lithium storage capacity of SnO_2 (790 mAh g^{-1}), which surpasses graphite's capacity (370 mAh g^{-1}) by more than double, this material has garnered significant attention. Additionally, the lithium absorption and release of Sn occur at a potential of approximately 0.6 V vs Li/Li^+ , enabling the delivery of an overall cell potential exceeding 3 V when combined with other cathode materials such as LiCoO_2 and LiFePO_4 . Nevertheless, the practical application of SnO_2 as an anode for lithium-ion batteries has been impeded by its substantial initial capacity loss and pronounced capacity degradation during prolonged cycling.³¹

Hematite ($\alpha\text{-Fe}_2\text{O}_3$) and magnetite (Fe_3O_4) have attracted considerable interest among various iron oxides and oxyhydroxides and have been extensively studied due to their potential

applications in Li-ion batteries. Hematite is known for its high theoretical specific capacity, while magnetite is valued for its moderate electronic conductivity. In an initial structural investigation, the structural transformations that take place during the incorporation of lithium were emphasised, and it was revealed that further lithiation led to irreversible phase separation, leading to the creation of Fe and Li₂O. The conversion reactions of most transition metal oxides (TMOs, TM= Fe, Co, Ni, Cu...) have shown a surprising level of reversibility compared to other metal oxides (SnO, SnO₂, Sb₂O₃...), despite displaying a noticeable polarisation between their discharge and charge curves. A comprehensive reaction scheme was proposed to explain the conversion and de-conversion processes of TMOs, involving the absorption and release of lithium according to:



The reaction mechanism of these metal oxides with lithium differs from classical mechanisms that involve either reversible insertion/removal of lithium into host structures or lithium alloying reactions. This distinction arises because most of these materials, such as CoO, adopt a rock-salt structure that lacks empty sites for lithium ions. Additionally, none of the 3d metals considered in this context form alloys with lithium. Reaction (1.3.1.) is expected and thermodynamically feasible. On the other hand, it is surprising that the reaction (1.3.2.) can be driven electrochemically. Traditionally, Li₂O has been regarded as electrochemically inert, further supported by unsuccessful attempts to decompose Li₂O powders. However, it is essential to exercise caution when working with nano-sized materials, as their properties greatly influence chemical and physical phenomena.

1.3.3. Alloy-forming anodes

Since it was discovered that Li metal could form alloys with other metals in an organic electrolyte in an electrochemical cell³³, there has been continued consideration for using metals, intermetallic and metal–metalloid alloys as active materials in LIBs. So-called alloy materials show significant increases in specific capacity for Li-uptake but have rarely been used in commercial batteries. A competitive battery to SONY Group Corporation battery cell, which has a carbon-based anode, was invented in 1996 by Fuji Photo Film Co. The Stallion[®] lithium-ion cell was constructed using an amorphous Sn-based composite oxide anode³⁴. Due to Sn-oxide's poor electric conductivity, carbon and a polymer binder were added. Fuji claimed that the amorphous Sn-based composite oxide anodes delivered a specific capacity of $> 600 \text{ mAh g}^{-1}$, almost double what is expected from carbonaceous materials. This development caused further interest in Li-alloy-forming electrodes.

Although alloying materials offer much higher specific capacity when compared to carbon-based materials, they are known for their excessive volume expansion during the alloying reaction, which can extend to several hundred per cent. When an electrode is repeatedly charged and discharged, the active material particles experience continuous expansion and contraction, ensuing enormous mechanical stress. As a consequence of sizeable mechanical stress, particles start to fracture, and eventually, they disintegrate and pulverise, resulting in a loss of electric contact between them. Furthermore, constant expansion and contraction can destroy the protective SEI layer resulting in the continuous reduction of the electrolyte, loss of Li inventory and increase in cell impedance. The most commonly researched alloy anodes for Li-ion batteries are elements/ composites of the 14th and 15th groups in the periodic system. The overview of the specific capacities of several such elements is presented in Figure 3. The capacities are calculated based on the corresponding fully lithiated phases.

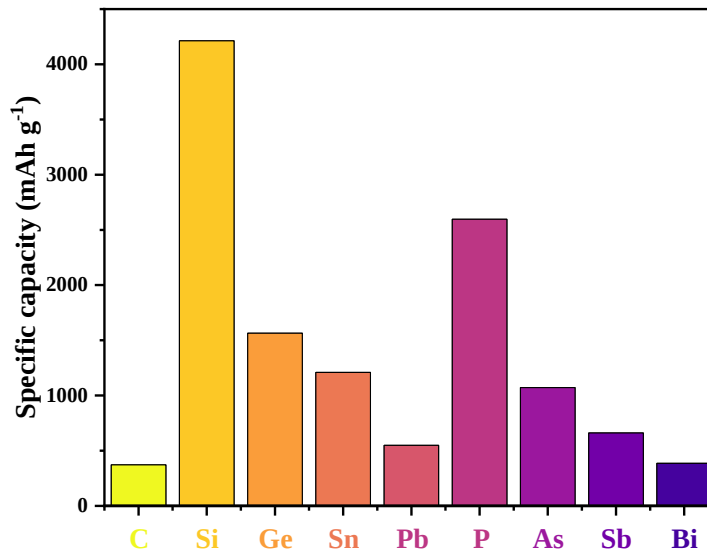


Figure 3. Specific capacity of group 14 and 15 elements for the formation of fully lithiated phases: C (LiC₆), Si (Li_{4.4}Si), Ge (Li_{4.25}Ge), Sn (Li_{4.25}Sn), Pb (Li_{4.25}Pb) P (Li₃P), As (Li₃As), Sb (Li₃Sb) and Bi (Li₃Bi)

1.4. Tin (Sn) as an anode material

After commercialising the Stallion[®] cell, tin and tin-based intermetallics and composites have received significant attention. The theoretical specific charge capacity of 994 mAh g⁻¹ for Sn in a Li-ion battery is almost three times larger than that of graphite. During the lithiation, Sn can form several stable phases with lithium. The equilibrium phase diagram for the *lithium-tin system* is shown in Figure 4 and presents all known stable phases: Li₂Sn₅, LiSn, Li₇Sn₃, Li₅Sn₂, Li₁₃Sn₅, Li₇Sn₂, and lastly, Li₁₇Sn₄.

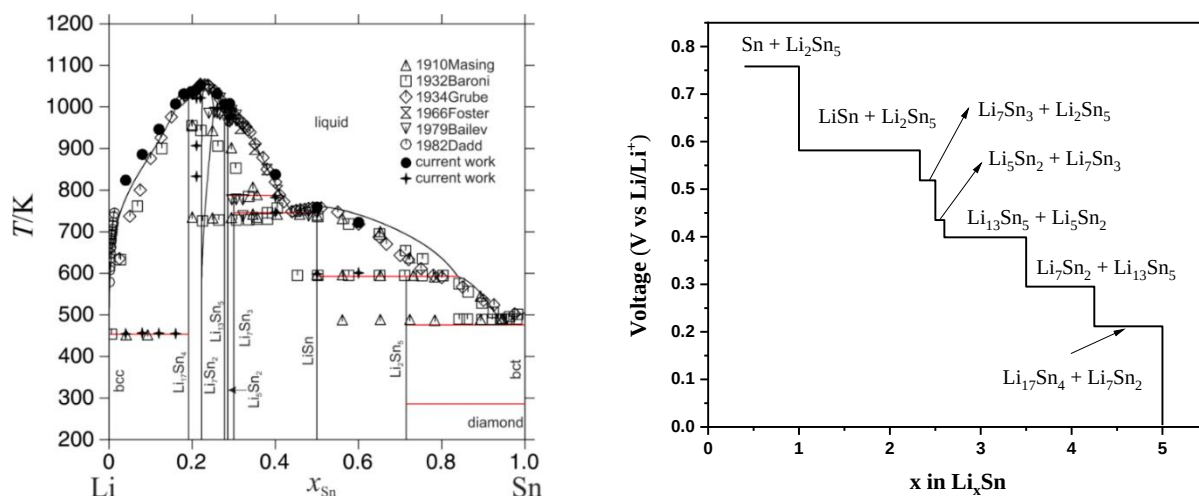


Figure 4. Equilibrium phase diagram of the *lithium-tin system*³⁵ on the left. The equilibrium lithiation pathway of Sn and calculated EMF values vs Li/Li⁺ on the right.

Under equilibrium conditions, the formation of Li-Sn intermetallic compounds in an electrochemical titration curve is represented by several potential plateaus, see Figure 4 on the right. Those are listed in Table 1.

Table 1. Li-Sn phases formed under equilibrium conditions during the lithiation reaction

Li_xSn_y	x in Li_xSn	Specific capacity/ mAh g ⁻¹ at the starting point	Plateau potential for the formation (V vs. Li/Li ⁺)
Li_2Sn_5	0.75	175.0	0.4
LiSn	1	213.3	0.660
Li_7Sn_3	2.33	463.5	0.530
Li_5Sn_2	2.5	492.5	0.485
$\text{Li}_{13}\text{Sn}_5$	2.6	509.6	0.485
Li_7Sn_2	3.5	656.0	0.420
$\text{Li}_{17}\text{Sn}_4$	4.25	790.2	0.380

As mentioned, alloying materials are prone to significant volume changes during lithiation and delithiation, and Sn is no exception. The density of Sn (7.265 g cm^{-3}) is much higher than that of Li (0.534 g cm^{-3}), and the formation of intermetallic Li_xSn_y compounds on lithiation of Sn is accompanied by tremendous volume expansion of theoretically more than 280 %. Chao et al. investigated the internal microstructure of Sn particles by *in-situ* transmission microscopy³⁶. The study concluded that the extent and speed of Sn particle expansion strongly correlate with particle size. Furthermore, larger Sn particles were found to expand up to 380 % (far from the theoretical expansion of $\text{Li}_{4.25}\text{Sn}$ at 283 %), whereas small Sn particles expand up to 180 % upon the lithiation. Smaller Sn particles are lithiated faster, and re-crystallisation is hindered; therefore, particles incline to retain their original dimensions due to more disordered lattice features. The larger particles expand more due to slower lithiation rates and better crystallisation.

Apart from lowering the particle size, several other strategies were employed to combat the mechanical degradation of Sn particles during lithiation. Many of them included the formation of active-inactive composites in which a matrix (inactive component) allows rapid transport of the electroactive species (Li-ions) and limits the mechanical stress on volume expansion of the active component. For example, Mao et al. synthesised SnFe and Sn_2Fe particles³⁷. During the lithiation, Sn acts as a reactant forming different Li_xSn_y phases, whereas Fe does not alloy with Li and is precipitated on lithiation; however, it contributes to the electric conductivity and restrains stress on volume expansion. Active-active composites^{38, 39} were also explored to increase the longevity of Sn electrodes, e.g., Sb-Sn and Sn-Bi intermetallic anodes⁴⁰.

1.5. Tin sulfides

Since Sn active anode material suffers from excessive volume expansion, tin sulfides were proposed as a potential replacement for Sn. There are three stable tin sulfides, SnS, Sn₂S₃, and SnS₂; among them, SnS and SnS₂ are the most frequently researched for use as an anode material in lithium-ion batteries. The appeal lies in the high theoretical specific capacity, 1111 mAh g⁻¹ for SnS and 1209 mAh g⁻¹ for SnS₂. However, more importantly, the reversible specific capacity of 755 mAh g⁻¹ for SnS and 645 mAh g⁻¹ for SnS₂ (see also below) is still double that of the conventionally used graphite (372 mAh g⁻¹)⁴¹.

SnS forms two stable orthorhombic structures and three metastable cubic structures. The orthorhombic modifications of SnS are low temperature (LT) α -SnS with the GeS-type structure (space group *Pnma*), shown in Figure 5a, and the high temperature (HT) β -SnS with the TII-type structure (space group *Cmcm*), which is shown in Figure 5b. In the crystal structure of α -SnS, the Sn²⁺-ion is coordinated to three sulphur ions within the plane, with the Sn 5s² lone pair of electrons “occupying” the last position in hypothetical tetragonal geometry occurring in the ZnS-type structure⁴². The 5s lone pair distorts the hypothetical ZnS-type structure, resulting in an orthorhombic crystal system. At 878 K, the transformation from α -SnS to β -SnS occurs. Sn atoms are displaced along [1 0 0] direction during the process. Moreover, a decrease in the axial ratio a/c from $a/c > 1$ for α -SnS to $a/c < 1$ for β -SnS⁴³ occurs.

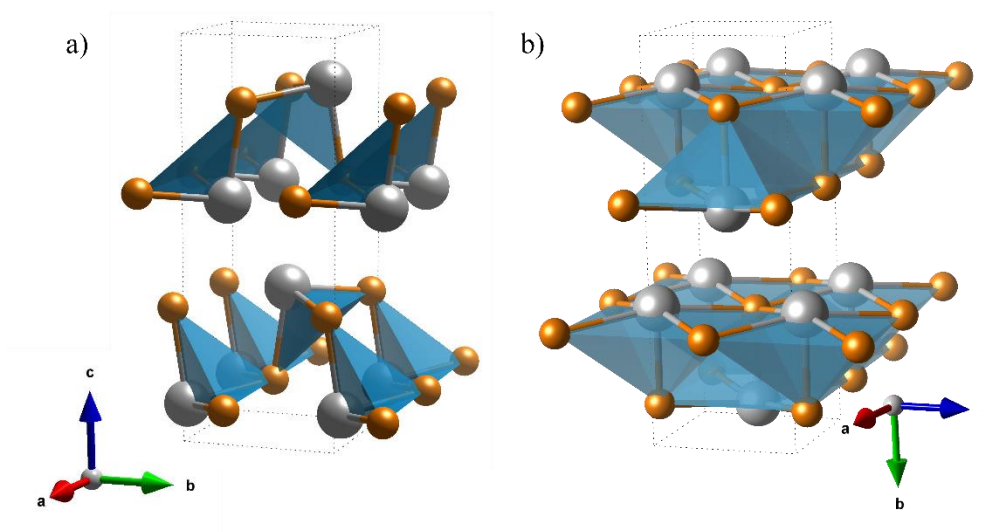


Figure 5. Crystal structure of a) low-temperature α -SnS (space group: $Pnma$), b) high-temperature SnS (space group: $Cmcm$). Sn atoms are represented as grey spheres, and S atoms as orange spheres.

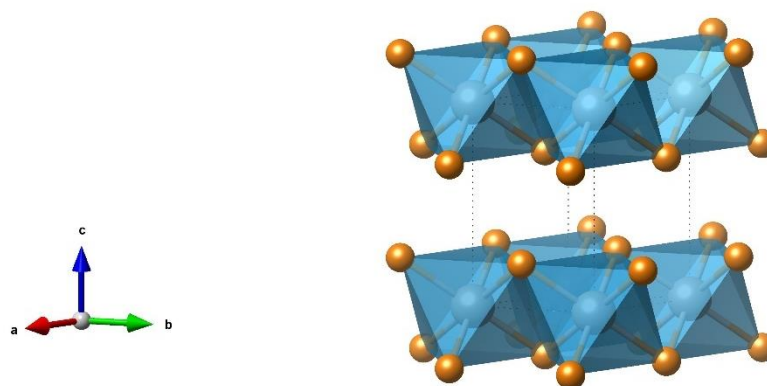


Figure 6. Crystal structure of SnS_2 (space group: $P-3m1$). Sn atoms are represented as grey spheres, and S atoms as orange spheres.

SnS_2 adopts the CdI_2 -type structure with a trigonal unit cell and $P-3m1$ space group. In that structure, Sn^{4+} ions are coordinated to six S^{2-} ions in octahedral geometry (Figure 6), whereas S^{2-} ions are coordinated by 3 Sn^{4+} ions showing a symmetry like this in SnS. In SnS_2 , the Sn

and S atoms are bonded by strong covalent bonds within the layers, whereas Van der Waals bonds loosely hold the layers of SnS₆ octahedra. Accordingly, SnS₂ is a layered structure with mechanical properties similar to graphite.

Lithiation mechanism of SnS₂

The calculated ternary Li-Sn-S phase diagram at 298.15 K, along with the equilibrium lithiation pathway of SnS₂ presented as the solid grey line, as well as calculated EMF values vs Li/Li⁺ and the phase constitution on lithiation are shown in Figure 7.

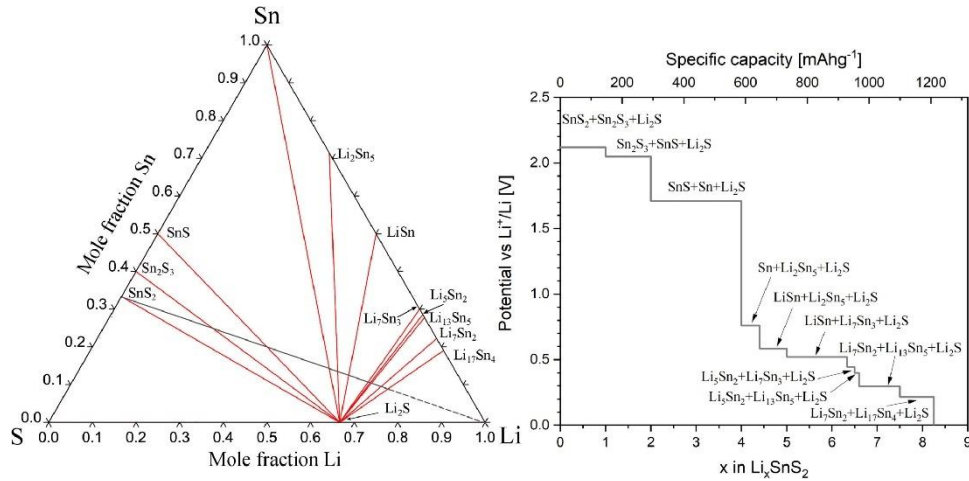
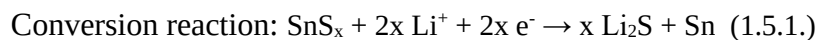


Figure 7. The calculated ternary Li-Sn-S phase diagram at 298.15 K, along with the equilibrium lithiation pathway of SnS₂ and calculated EMF values vs Li/Li⁺ ⁴⁴

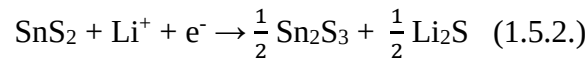
This phase diagram calculation is based only on data extrapolated from the constituent binary systems. No experimental data from the ternary system have been regarded. According to this phase diagram, the lithiation mechanism of tin sulfides unfolds in two steps. The first step in the lithiation process is the irreversible conversion reaction in which SnS/SnS₂ are finally converted into Li₂S and Sn according to:



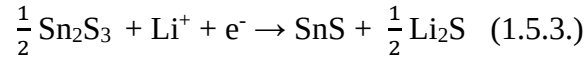
In the next step, the newly formed Sn is further lithiated, forming several Li_xSn phases, with the $\text{Li}_{4.25}\text{Sn}$ phase being the highest lithiated phase according to:



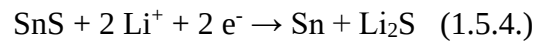
Considering in more detail the lithiation of SnS_2 , the initial conversion reaction results in the formation of Sn_2S_3 and Li_2S , giving a potential plateau at 2.12 V vs Li/Li^+ . During this reaction, half of the Sn^{4+} cations are reduced to Sn^{2+} according to:



Further reaction and complete reduction of Sn^{4+} cations to Sn^{2+} converts all SnS_2 to SnS and additional Li_2S at a potential plateau of 2.05 V vs Li/Li^+ according to the reaction:



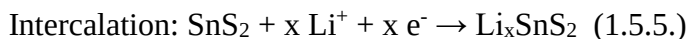
Upon the completion of the second reaction, Sn^{2+} ions from SnS are further reduced, resulting in the formation of elemental Sn at a potential plateau of 1.71 V vs Li/Li^+ according to the reaction:



With the reaction represented by equation (1.5.4.) conversion reaction is completed, and further lithiation involves the Li-Sn alloys formation, see equ. 1.5.1.

Contrary to the calculated lithiation path, experimental investigations of the electrochemical lithiation of SnS_2 show an additional step prior to the conversion reaction, see Fig.???. The intercalation of Li ions between the SnS_6 - octahedra layers is possible due to the relatively weak Van der Waals bonding between the sulphur layers and tin's ability to reduce its

oxidation state from 4+ to 2+. Therefore, the Li_xSnS_2 compound can be formed according to the following reaction:



To fully understand the lithiation mechanism in more detail, the crystal structure of SnS_2 must be considered. Different vacant sites in the SnS_2 crystal structure are available to Li ions. These sites include a) the interlayer sites, which are octahedrally coordinated to sulphur atoms; b) the interlayer sites, which are tetrahedrally coordinated to sulphur atoms; and c) the intralayer sites, which are tetrahedrally coordinated to sulphur atoms and are close to three tin atoms. In the first instance (Li_xSnS_2 , $x \leq 0.6$), Li ions are inserted into the octahedral sites, and thereby, part of the Sn^{4+} atoms are reduced to Sn^{2+} . Further increase of lithium content leads to Li-ions being inserted into the tetrahedral sites, decreasing the interlayer interactions. Finally, at $\text{Li}_{1.66}\text{SnS}_2$, the Li_xSnS_2 structure becomes unstable, and the conversion reaction is triggered⁴⁵.

The formation of Li_2S has negative and positive attributions to the electrochemical performance of Sn-S-based electrodes. On the one hand, to form Li_2S , additional lithium must be consumed, decreasing the Li inventory drastically already in the first lithiation cycle. On the other hand, Li_2S is a rigid matrix compound that can restrict active Sn-particles' mechanical degradation on volume expansion during alloying.

Several additional strategies have been implemented to curb the volume expansion, including designing various SnS_x nanostructures with different morphologies, such as hierarchical structures^{46,47}, nanoplates^{48,49,50}, nanobelts⁵¹, nanowalls⁵², nanoflakes⁵³, nanoflowers^{54,55}, nanorods⁵⁶ and nanospheres⁵⁷. Further strategies included the fabrication of various composites with SnS_x materials^{58,59,60,61}, doping^{62,63,64}, coating^{65,66}.

Objective and the outline the thesis

Currently, the most commonly used active anode materials in LIBs are carbon-base. Carbon-based electrodes have many advantages: mechanical strength over many cycles, high electronic and ionic conductivity, an affinity for Li ions and low cost. However, their low specific capacity is insufficient to provide batteries with a more extended working range. Several candidates for replacing carbon-based anodes are being intensively researched, including tin sulfides. The publication statistics presented in Figure 8 indicated that in the last 10 years there have been significantly fewer research done on Sn-S-based materials compared to carbon-based materials (The data was generated using Dimensions)².

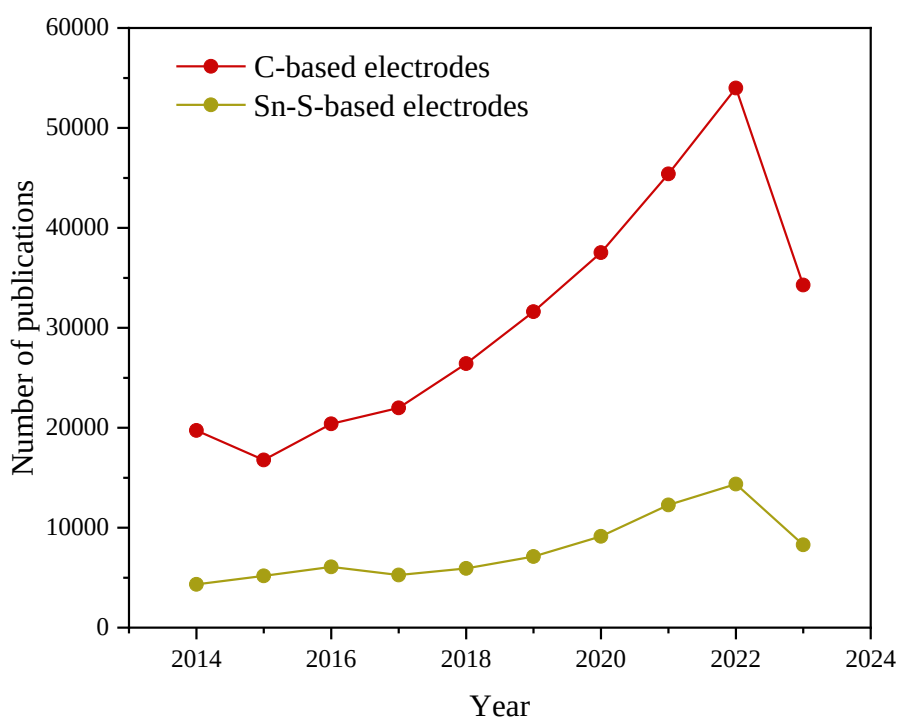


Figure 8. Number of research publications dedicated to carbon-based and Sn-S-based electrodes in Li-ion batteries

² <https://www.dimensions.ai/>

For the possible application of the material in LIBs, detailed and extensive investigations are necessary to understand the material's fundamental properties and electrochemical capacities. Therefore, the main objective of this thesis is to enhance the existing knowledge base on tin sulfides by comprehensively investigating and elucidating the fundamental properties of pure tin sulfide materials and their correlation with cycling performance. Particular emphasis is placed on understanding the relationships between the structure, processing methods, and resulting properties. The aim is to provide valuable insights into the structure-processing-property relations of tin sulfides. In addition to the introductory chapter, the thesis comprises three additional sections. Firstly, Chapter 2 provides a comprehensive overview of the characterisation techniques employed to determine synthesised materials' fundamental physiochemical and electrochemical properties. Subsequently, Chapter 3 includes the published articles that are interconnected and closely related to the main thesis alongside a submitted article. Finally, Chapter 4 concludes the findings and insights obtained throughout the thesis, providing a comprehensive summary. Additionally, an outlook is presented, highlighting potential future research directions and areas that warrant further investigation.

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2. Experimental

This chapter will define and describe different synthesis approaches utilised to synthesise SnS and SnS₂ materials. The final products were subjected to several physiochemical and electrochemical characterisation techniques, which will also be defined and described in detail in this chapter.

2.1. Synthesis of SnS

In order to synthesise SnS, two synthesis methods were performed: precipitation and hydrothermal methods. SnCl₂ and thioacetamide (TAA) were used as Sn and S sources and weighed in a stoichiometric 1:1 molar ratio in both methods.

2.1.1. Hydrothermal reaction

In separate beakers, 5.271 g of SnCl₂ and 2.089 g of TAA were dissolved in 25 ml of deionised water. 15 mL of conc. HCl was added to the aqueous solution of SnCl₂ before adding the TAA solution. The resulting solution was transferred into a 100 ml Teflon vessel of a steel autoclave. Subsequently, the autoclave was heated at 180 °C for 2 h. After 2 h, the autoclave was removed from the furnace and cooled to room temperature (Figure 9).

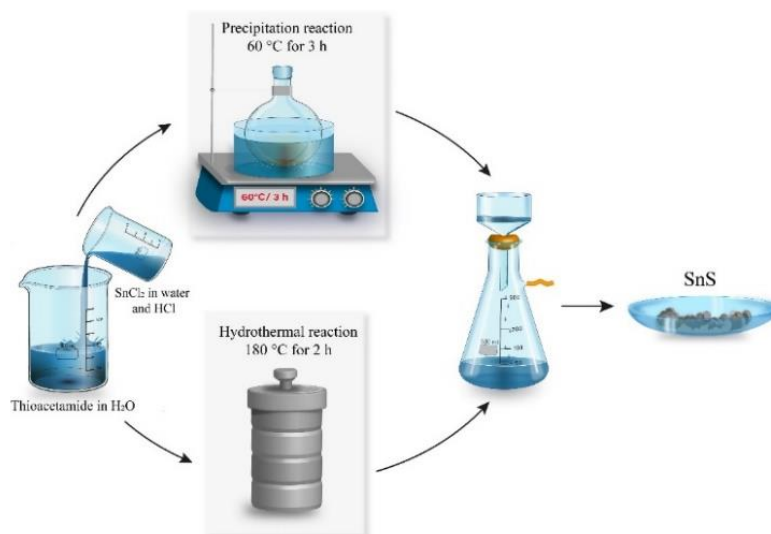


Figure 9. Schematic presentation of the synthesis of SnS via the precipitation and hydrothermal reaction methods.

2.1.2. Precipitation reaction

In separate beakers, 0.9 g of SnCl₂ and 0.3 g of TAA were dissolved in 20 mL of deionised water. 15 mL of concentrated HCl was added to the aqueous SnCl₂ solution, which was subsequently poured into the aqueous TAA solution. The final solution was transferred into a round bottom Schlenk flask with a volumetric capacity of 150 mL. The ground glass joint of the flask was capped with a stopcock, and the sidearm was connected to a rubber tube immersed in a 1M NaOH solution. This prevents a build-up of pressure in the flask and the release of H₂S gas into the atmosphere. Such a setup is required since Sn²⁺ ions can be easily oxidised to Sn⁴⁺ in aqueous solutions in the presence of air. The reaction was heated to 60 °C through an oil bath. The reaction was kept at 60 °C for 3 h with a light stirring. Subsequently, the flask was taken out of the bath and let to cool down to room temperature.

2.2. Synthesis of SnS_2

Two synthesis methods were used to synthesise SnS_2 : precipitation and hydrothermal methods. In both methods, $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ and thioacetamide (TAA) were used as Sn and S sources and weighed in a stoichiometric 1:2 molar ratio.

2.2.1. Hydrothermal reaction

In the first step, 3.26 g of $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ and 1.0 g TAA for a molar ratio 1:2 were weighed. Because of the insolubility of $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ in water, concentrated hydrochloric acid was used as a solvent. $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ was dissolved in concentrated hydrochloric acid (8 mL), whereas TAA was dissolved in deionised water (52 mL). The $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ and HCl mixture was poured into the TAA solution and stirred for approx. 1 min. Afterwards, the solution was transferred into a 100 mL Teflon-lining of a steel autoclave. The autoclave was placed in a furnace at 120 °C for 24 h. After the reaction, the yellow precipitate was filtrated via vacuum filtration and washed three times with deionised water and ethanol before it was dried in a vacuum at 60 °C for 4 h.

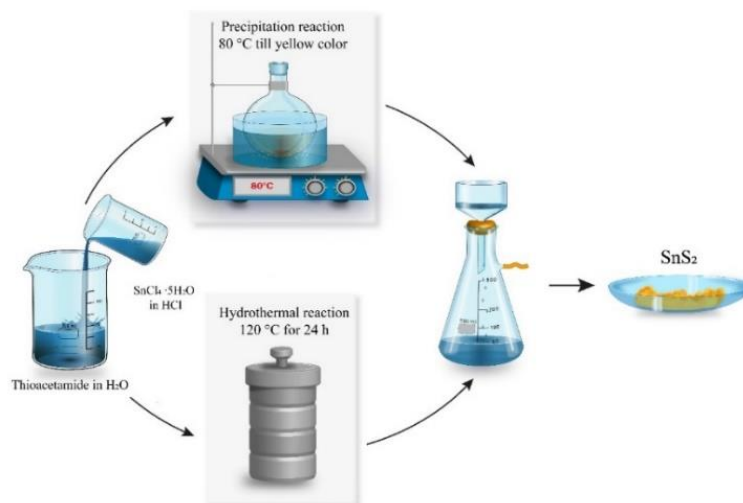


Figure 10. Schematic presentation of the synthesis of SnS_2 via the precipitation and hydrothermal reaction methods.

2.2.2. Precipitation reaction

According to the procedure 0.701 g of $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ was dissolved in 8 mL of concentrated hydrochloric acid. It was subsequently added to 32 mL of a 0.125 M TAA solution (0.301 g dissolved in 32 mL of deionised water). 40 mL of the transparent, colourless liquid was transferred into a round-bottomed flask heated to 80 °C. The solution adopted an opaque yellow colour during heating at temperatures > 70 °C. After reaching 80 °C, a yellow SnS_2 precipitated, and the reaction was left for an additional 5 min at that temperature. Afterwards, the flask was removed from the oil bath and cooled down to room temperature. The precipitate was collected by vacuum filtration using a Büchner flask and borosilicate glass funnel with a built-in porous filter plate (1–1.6 μm pore diameter), washed three times with water and ethanol and subsequently dried under vacuum at 60 °C for 4 h.

2.3. Physiochemical characterisation

X-ray diffraction (XRD)

XRD is one of the essential techniques in solid-state chemistry used to identify crystalline materials (phase analysis) and determine their structural features. When a focused X-ray beam interacts with a periodic arrangement of atoms, the diffraction phenomenon occurs, among others. Diffraction is a combination of scattering and interference of the scattered electromagnetic waves. Although the electrons interact with X-rays, the atoms can roughly be considered the scattering centres. Due to the strictly periodic arrangement of atoms in crystalline materials, the scattered waves show regular interference like a grid in the case of optical light. The diffraction angles and intensities depend on which atoms make up the crystal lattice and how these atoms are arranged spatially. When X-rays hit a crystalline sample and

are diffracted, the distances between the crystallographic planes of the atoms can be measured by applying Bragg's Law:

$$n \lambda = 2d \sin \theta$$

where the integer n is the order of the diffracted beam, λ is the wavelength of the incident X-rays, d is the distance between adjacent planes of atoms, and θ is the angle between the beam and the respective plane. Since λ is known and θ is determined from the diffraction peak position, d -spacings for the respective (h k l) -planes can be calculated. In addition, with the intensities of the respective peaks, X-ray diffraction provides a so-called XRD pattern which is significant for the phases present in the exposed powder sample. This pattern is further determined by many other parameters like, for instance, instrument and measurement settings or powder texture.

H. Rietveld has developed a computational method to refine crystallographic parameters based on a least-square fit of experimental powder-XRD patterns⁶⁷. Since the whole powder pattern and not only the peak/intensity profile is reproduced, the accuracy of the phase analysis is much higher, overlapping peaks can be deconvoluted, and additional information about the texture and crystallinity of the phases can be obtained.

A Bruker D8 diffractometer ($\theta/2\theta$ -geometry) with a copper radiation source (40 kV / 40 mA) and a Ni-filter was used for all XRD measurements. The powder samples were fixed onto silicon mono-crystal sample holders using petroleum jelly. Signals were detected by a Lynxeye strip detector covering $\pm 1.5^\circ$ in 2θ simultaneously. The obtained patterns (in a 2θ range of 10 - 120°) were evaluated based on full-profile Rietveld-refinements using Topas4[®] software.

Scanning and transmission electron microscopy (SEM and TEM)

Electron microscopes use electron beams for imaging, using reflected (SEM) or transmitted (TEM) electrons similar to optical light microscopes, which use visible light. SEM creates an image by backscattered or secondary electrons from near-surface regions of a sample. Electrons have a shorter wavelength than light, so their resolution is superior to light microscopes. The electron beam is created by producing electrons at the top of the column, accelerating them down, and passing them through several lenses and apertures to produce a focused beam that strikes the sample. Various vacuum pumps, in combination, evacuate the column and the electron microscope chamber, where the sample is mounted on a stage. Using a focused, high-energy electron beam (1-2 μm diameter) which scans the sample surface point by point, similar to a screen tube, the scanning electron microscope (SEM) produces images. Interactions between electrons and the sample result in secondary electrons, backscattered electrons, and characteristic X-rays. Detection of secondary and backscattered electrons is used to produce an image which is displayed on a computer screen. Depending on the accelerating voltage and the sample density, the electron beam penetrates a few microns into a sample when it strikes its surface. The spectral analysis of the characteristic X-rays emitted by the respective elements can be used to determine the chemical composition of the surface area exposed to the electron beam. Calibration and mathematical correction are necessary for accurate quantification. Fixing the electron beam at a certain point on the surface allows phase-selective composition analysis.

Sample morphologies were investigated by scanning electron microscopy (SEM) using a Carl Zeiss Supra 40 scanning electron microscope with Everhart–Thornley (ETD) and Through-Lens (TLD) detectors with primary electron-beam energy of 5 keV.

The TEM creates images using a high-voltage electron beam emitted from an electron gun at the top of a TEM and travels through the vacuum tube. In contrast to a light microscope, which uses a glass lens to focus light, the TEM uses electromagnetic lenses to focus electrons into a beam. After passing through the specimen, which is very thin, the electrons scatter or hit on a fluorescent screen at the bottom of the microscope. The screen displays an image of a specimen with its assorted parts shaded according to their density. Transmission electron microscopy (TEM) images were collected on the SnS and SnS₂ powders at 200 keV on a CM200 transmission electron microscope (TEM, Philips, Amsterdam, the Netherlands) with a LaB6 electron source. A 512 × 1024-pixel JUNGFRU detector with a 320 μm thick silicon sensor and a pixel size of (75 μm) was used.

X-ray photoelectron spectroscopy (XPS)

In X-ray photoelectron spectroscopy, X-ray photons at energies lower than 6 keV hit the surface of a material, releasing electrons and measuring their kinetic energy. The emitted photoelectron results from the complete transfer of the X-ray energy to a core-level electron. XPS determines the characteristic binding energy of electrons of atoms in a compound using the equation:

$$E_{\text{binding}} = E_{\text{photon}} - (E_{\text{kinetic}} + \Phi)$$

Where E_{binding} is referred to as the energy of an electron attracted to a nucleus, E_{photon} is the energy of x-ray photons, and E_{kinetic} is the energy of electrons ejected from the sample. The work function, Φ , is a correction factor correlated to the energy required for an electron to leave an atom. As the work function and E_{photon} are known, and the kinetic energy of the expelled electrons is measured, the characteristic binding energy can be calculated. In addition to its elements sensitivity, this technique can reveal valence state and chemical

bonding information from the elements within the sample, making it a robust surface analytical method. Since the emitted electrons can only penetrate up to 10 nm of matter, XPS is a technique for surface analysis. It does not allow any statement about the bulk properties of the material.

In the XPS study, Al K α radiation at 72 W and a pass energy of 200 eV, a spot size of 400 μm , “Standard Lens Mode”, CAE Analyser Mode, an energy step size of 1 eV for the survey spectrum (50 passes), and integrated flood gun were used. Samples were analysed before and after the surface was treated with Ar-clusters (1000 Ar atoms, 6000 eV, 60 s). The single elements' high-resolution spectra (step size 0.1 eV and 0.05 eV, respectively, for Sn and S) were acquired with 50 passes at pass energies of 50 eV. Peak deconvolution was performed with Thermo Advantage v5.9925 Build 06702 using Simplex algorithm with Gauss-Lorentz Product.

Drop solution calorimetry

Calorimetry refers to the measurement of heat quantities. At constant pressure, the heat exchanged corresponds to the enthalpy change, ΔH . The standard enthalpy of the formation of a compound,

$\Delta_f H_{298}^\circ$ is the enthalpy change during the formation of 1 mole of the substance from its constituent elements in their reference state, with all substances in their standard states (298.15 K, 100 kPa). It can be directly determined by running the formation reaction in a calorimeter. If this is not possible indirect methods have to be applied. One of those is the drop solution calorimetry performed to determine the enthalpy of formation of Sn-S compounds. Therefore, both constituents, S and Sn, as well as the compound S_xSn_y , respectively, have been dropped into a liquid tin bath at 600 °C from ambient temperature in

separate runs. The molar heat effects versus molar fractions of the dropped material were recorded for several drops and extrapolated towards pure tin. The resulting limited molar enthalpies of solution, $\Delta_{sol}\bar{H}^\infty$, can then be used to calculate the enthalpy of formation of the compound:

$$3. \quad \Delta_f H_{298}^\circ (A_x B_y) = x \cdot \Delta_{sol} \bar{H}_A^\infty + y \cdot \Delta_{sol} \bar{H}_B^\infty - \Delta_{sol} \bar{H}_{AxBy}^\infty$$

The drop calorimeter used and the experimental procedure and conditions are detailed in the manuscript 3.

2.4. Electrochemical characterisation

Electrode preparation and coin cell assembly

The first step in electrode preparation was slurry production, which consisted of 80 wt.% of active material (SnS or SnS₂), 10 wt.% of carbon black C45 and 10 wt.% of polyvinylidene fluoride (PVDF) in N-Methyl-2-pyrrolidone (NMP). Carbon black was added to increase the conductivity of the electrodes, and PVDF, dissolved in NMP, was added to act as a binder. After combining all the components, the slurry was stirred in a THINKY mixer before casting onto Cu foil. Initial drying took place at 60°C in air. After drying, several electrodes were punched in the form of discs with a diameter of 15 mm and heated under vacuum at 120 °C for 12 h using a Büchi® glass oven. After drying, the electrodes were introduced directly into an Ar-filled glove box without any contact to ambient air.

For coin cell construction, Li metal (thickness 0.6 mm) was used as the counter electrode, a single PP/PE/PP Celgard 2325 membrane (polypropylene film, thickness 0.25 µm) was used

as the separator, and 75 μL of the 1 M LiPF_6 in EC/EMC (3:7 wt.%) with 2 wt.% VC electrolyte solution was added. A detailed sequence of cell assembly is shown in Figure 11.

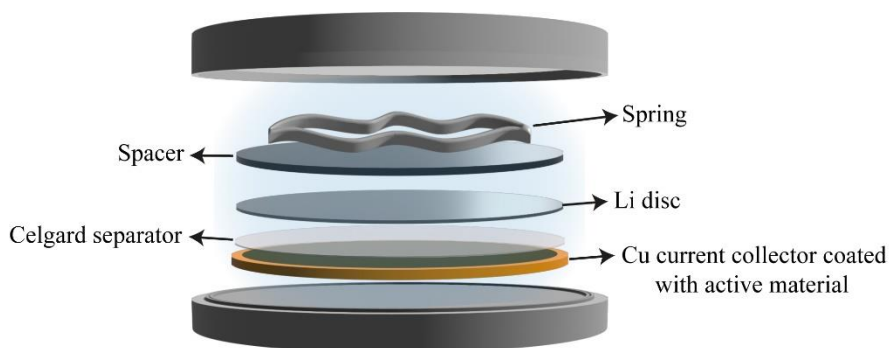


Figure 11. Schematic illustration of a typical coin cell in a half cell (vs Li/Li^+) configuration.

Galvanostatic cycling with potential limitation (GCPL)

GCPL is one of the standard techniques for studying the cycling behaviour and electrochemical performance of batteries and their active materials. Using this method, the capacity of the battery can be determined as a function of cycle number. Under various experimental conditions over increasing cycle numbers, the amount of charge transferred between the anode and cathode is measured. During a typical GCPL measurement, a constant current is applied to the working electrode and its resulting potential is measured against a reference electrode as a function of time. Li acts as a counter and reference electrode in two-electrode Li-ion cells. A typical discharge and charge process of a half-cell configuration constructed using an anode active material (in full cell configuration) as the working electrode in the half cell is described in Figure 12.

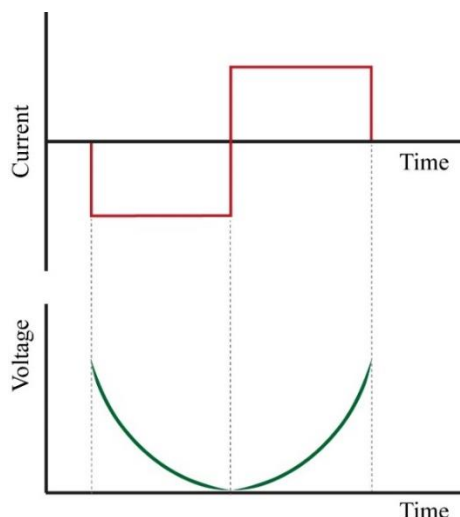


Figure 12. a) A typical GCPL current signal which is applied and b) the measured output voltage signal

Information about a battery cell and electrode materials, such as specific capacity, voltage profile, rate capability, stability, and life expectancy can be extracted using the GCPL technique. In this thesis, the specific capacity of SnS and SnS₂ materials, their electrochemical stability over 100 cycles, and their rate capability have been determined. A Maccor battery tester (Maccor Series 4000) was used for the GCPL and rate capability tests. The raw data were further evaluated using the Origin2021G software. During the GCPL measurements, the cells were cycled for 100 cycles in the voltage window of 0.01- 1 V vs Li/Li⁺ with an applied specific current of 100 mA g⁻¹. For the rate capability tests, the cells were discharged at a sequential specific current of 100, 200, 400, 800, and 1000 mA g⁻¹ and back to 100 mA g⁻¹ for 10 cycles at each rate. A specific charge current of 100 mA g⁻¹ was used in all cases.

Cyclic voltammetry (CV)

The cyclic voltammetry technique is often employed to investigate reaction mechanisms which include electron transfer. A linear change in electrode potential between two limits is performed at a specific rate and the resulting current is measured in an electrochemical cell. When the voltage is applied during a CV experiment, the concentration of species in the solution adjacent to the electrode changes over time according to the Nernst equation:

$$E = E^{\circ} - \frac{RT}{zF} \ln Q$$

Where E° is the standard potential, R is the universal gas constant, T is the temperature, z is ion charge, F is the Faraday constant, and Q is the reaction quotient.

The typical CV experiment for battery assessment purposes is performed in a two-electrode configuration, with the working electrode being the tin sulfides and the counter/ reference electrode being Li. The technique measures the current response to a sweeping voltage potential applied at a linear scan rate usually defined in mV s^{-1} to the working electrode. The current response is measured and plotted against applied voltage potential in a voltammogram. The input and output of CV measurements are presented in Figure 13.

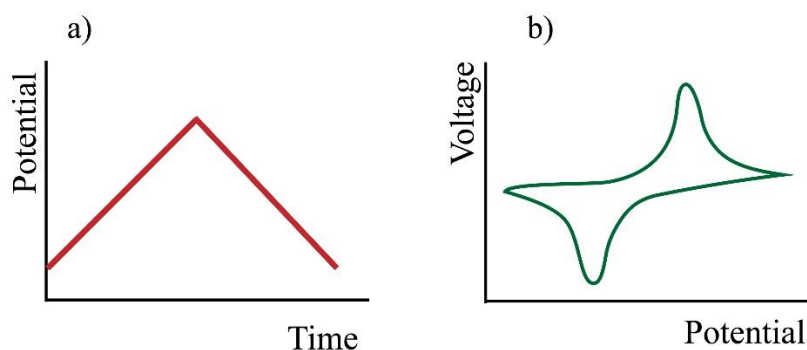


Figure 13. The change in voltage of a typical CV measurement as a function of time and b) the resulting voltammogram of a redox reaction

Electrochemical impedance spectroscopy (EIS)

EIS is a valuable technique to investigate internal processes within a battery. Using EIS, it is possible to divide and quantify different resistance contributions such as the resistances of the bulk (R_s), interface layer (R_{SEI}), charge transfer (R_{ct}) and diffusion process (W).

By measuring the current response while an AC voltage is applied to an electrochemical cell, the resistance (R), capacitance (C) and inductance (L) can be measured. The impedance $Z(\omega)$ ($\omega = 2\pi f$ - angular frequency) under AC voltage is applied to an electrochemical cell and can be expressed as $V(\omega)/I(\omega)$ (Figure 14). The impedance is the resistance that interrupts the current flow under AC voltage.

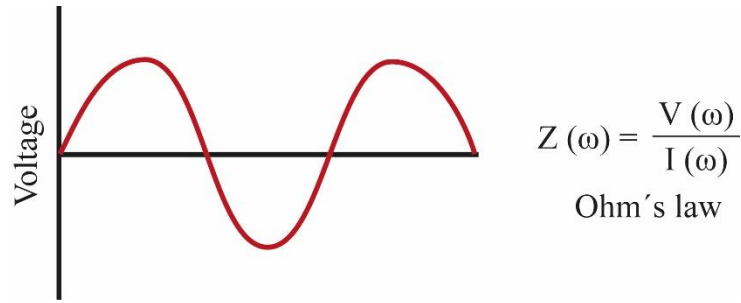


Figure 14. Schematic diagram for AC voltage

A careful equivalent circuit must be designed for the whole electrochemical cell system in order to properly evaluate the resistance contributions. Although an electrical double layer between an electrode and electrolyte exists and has capacitive characteristics, its characteristics are far from those of ideal capacitors. Therefore, additional elements, such as the constant phase element (CEP) and Warburg impedance (W), must be introduced into the equivalent circuit. A typical equivalent circuit model for the Li-ion battery half system which was used in this thesis is shown in Figure 15.

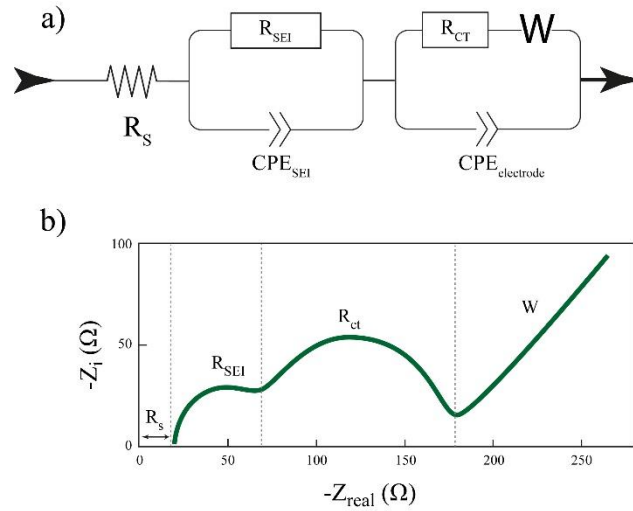


Figure 15. a) Equivalent circuit and b) corresponding Nyquist plot

Accordingly, there are three contributors to impedance:

- 1) Bulk impedance, R_s , which represents the internal resistance of the bulk materials of a battery (current corrector, separator and electrolyte)
- 2) Interface layer impedance, R_{SEI} , which originates from the layer formed between the electrode and electrolyte as a result of electrolyte decomposition at that interface
- 3) Charge transfer impedance, R_{CT} , which is linked to the kinetics of the electrochemical reaction
- 4) Warburg impedance, W , which is related to the Li-ion diffusion process within the electrode material

Electrochemical *in-situ* dilatometry

Electrochemical *in-situ* dilatometry measures the changes in thickness of the tin sulfide electrodes along the surface normal direction of the electrodes during cycling. The technique can therefore be used to quantify the expansion and shrinkage of the electrodes. A schematic illustration of a typical *in-situ* electrochemical dilatometry cell used in this study is shown in Fig. 16. The vertical movement of the working electrode (orange) during the dilatometry measurements was carried through the thin metal membrane to the sensor. By fixing a porous glass fibre T-frit between the working and counter electrodes, only the dimensional changes of the working electrode were detected. Normalised height changes express the relative dimensional change of the working electrode according to the formula:

$$\text{Height change} = \frac{l - l_0}{l_0} \cdot 100 (\%)$$

where l is the displacement during the measurement and l_0 is the initial thickness of the electrode active layer.

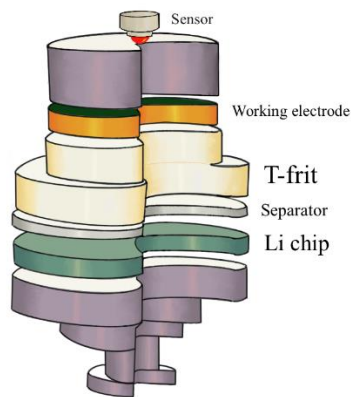


Figure 16. Schematic illustration of a typical electrochemical dilatometry cell.

3. Conclusions

Tin sulfide materials are promising anode active materials for lithium-ion batteries. However, a fundamental understanding of these materials in the context of anode applications is not yet complete. Therefore, the primary objective of this thesis is to deepen the understanding of the electrochemistry and thermochemistry of tin sulfide materials. To achieve this, the materials were synthesised using two wet chemical routes: precipitation and hydrothermal reaction, allowing us to obtain materials with varying morphologies and crystallinities. Subsequently, the as-synthesised materials underwent a series of physicochemical and electrochemical analyses to characterise their properties. The structure-processing-property relations were established by comparing the results obtained from different materials.

The first study compared the electrochemical properties of partially amorphous SnS_2 , synthesised via the precipitation reaction, and fully nano-crystalline SnS_2 , which was synthesized via the hydrothermal reaction method. The electrochemical cycling results showed that partially amorphous SnS_2 performed better than nano-crystalline SnS_2 . After 100 discharge and charge cycles, partially amorphous SnS_2 has a reversible specific capacity of 364 mAh g^{-1} , whereas that of nano-crystalline SnS_2 is only 271 mAh g^{-1} . The main reason for this result is the differing thickness of the electrochemically inactive Li_2S layer around the tin particles, which form after the conversion reaction. The Li_2S layer can reduce the mechanical stress associated with the volume changes of the active material particles. Initially, partially amorphous SnS_2 has only about 12 % lower surface area than nano-crystalline SnS_2 . However, the amorphous SnS_2 particles tend to agglomerate during electrode processing, thereby achieving a more stable state. The decreased total surface area of the agglomerated particles leads to the formation of thicker Li_2S layers on the Sn particles, offering a stronger constraint to the mechanical stress from volume expansion. Since the Li_2S layer is thinner on the Sn particles which form after lithiation of hydrothermally

synthesised SnS_2 , the Sn particles experience a higher volume expansion, confirmed by *in-situ* dilatometry experiments. As the particles expanded and contracted continuously during cycling, they lose contact with each other, causing some active material to be isolated and ultimately become dead weight. Therefore, Li_2S indeed has a role in improving the electrochemical performance of the electrodes by restricting the volume expansion of the Sn particles; however, the thickness of the formed Li_2S layer is also an essential factor.

Over the years, significant effort has been placed into synthesising nano-crystalline materials and designing unique morphologies of anode active materials. However, it is shown that in this specific case, fully crystalline SnS_2 has a significant disadvantage over the partially amorphous material. However, this is due to the difference in particles sizes of the pristine material after synthesis, which can lead to agglomeration during electrode fabrication. Therefore, special attention should be devoted to better understand the influence of electrode processing on particle morphology, which can then impact the electrochemical performance of the material during cell operation.

The electrochemical properties of SnS_2 synthesised via the precipitation reaction method were further compared to SnS synthesised with the same synthesis method. The use of similar synthesis methods allows the formation of SnS and SnS_2 materials with comparable morphologies, crystallinity and particle size. SnS_2 exhibited superior electrochemical performance during cycling with a specific capacity at 364 mAh g^{-1} after 100 discharge and charge cycles, whereas SnS exhibited a mere 133 mAh g^{-1} . Previously it was determined that the thickness of the Li_2S layer plays a vital role in the stability of SnS_2 materials. Since, from the stoichiometric point of view, the atomic ratio between S and Sn in SnS_2 is higher than that in SnS, the comparison of the two materials can shed even more light on the effects and influences of Li_2S on the electrochemical performance of Sn-S materials. Naturally, the higher amount of the Li_2S formed, the more stable

is the Sn-S-based anode. Even though that is true, there are also other factors which influence the stability of the SnS₂ electrodes. The crystal structure of SnS₂ and the oxidation state of Sn in SnS₂ play an important role in the eventual distribution of Li₂S within the electrode. Initially, during the lithiation of SnS₂, Li ions intercalate into interstitial positions between the edge-sharing Sn-S octahedra layers. Concurrently, some of the Sn⁴⁺ ions are reduced to Sn²⁺ ions, and a Li_xSnS₂ solid solution is formed. As the lithiation reaction progresses, Li starts to react with S to form Li₂S. Since the Li ions are already distributed inside the SnS₂ host crystal lattice, a fine distribution of Li₂S and Sn upon the conversion reaction is produced on an atomic level. This results in an in-situ encapsulation of the Sn particles.

Lastly, the as-prepared materials were subjected to drop solution calorimetry measurements to accurately determine the enthalpy of the formation of SnS and SnS₂. Using this method, the limiting molar enthalpies of solution of sulfur, the as-prepared materials, and a commercially available macro-crystalline SnS₂ in tin were established. The formation enthalpies were derived based on the results of the limiting molar enthalpies of solution. The enthalpies of formation obtained for SnS ranged from -48.8 to -52.8.2 kJ mol⁻¹ of atoms, while for SnS₂, they ranged from -50.2 to 51.0 kJ mol⁻¹ of atoms, aligning well with existing literature. For SnS, a trend was observed towards less exothermic enthalpy of formation with decreasing crystallite size. However, no noteworthy deviation was observed for the SnS₂ samples synthesised in this study.

Furthermore, the enthalpy of formation of as-synthesised SnS₂ was compared to commercially purchased macro-SnS₂. Interestingly, the macro-SnS₂ exhibited a less negative enthalpy of formation. This finding is surprising because the nano-crystalline state is generally considered to be less stable than the macro-crystalline state. Further investigation showed that after the macro-sized SnS₂ was ball-milled, it transformed into a nano-crystalline material. The enthalpy of formation of this product was also determined using drop solution calorimetry. The results showed

that the ball-milled material had a significantly more negative enthalpy of formation than the pristine material. This could be due to the high energy state of the large flat particles, which is released during ball-milling. Therefore, the amount of energy released by creating more spherical particles during the ball milling process is higher than the amount of energy introduced into the material due to higher surface energy of the ball-milled particles.

Furthermore, both the as-synthesised and commercially available Sn-S anode active materials were subjected to electrochemical discharge at slow current rates. The Gibbs free energies of the lithiation reactions were derived from the resulting voltage curves as a function of the mole fraction of lithium in Li_xSnS and Li_xSnS_2 . A correlation was found between the stability of the starting materials and the electric work released during electrochemical lithiation at low current rates (C/200 i.e., discharge to 0.01 V vs Li/Li^+ in 200 hours). The starting materials with more negative enthalpies of formation release less electric work during lithiation reactions. This observation aligns well with the concept that more energy is required to decompose the more stable reactants.

4. Outlook

Lithium-ion battery research has made great strides in recent decades, and prices per kWh for lithium-ion batteries have dropped dramatically. One of the main contributors to the cost reduction is the investment in the research, which only further emphasises the critical role of fundamental research into understanding the mechanisms within a battery cell. Cathode and anode improvement is highly necessary to pursue the ultimate goal of increasing the cell energy density and reducing battery pack cost. On the anode side, a move from graphite and its replacement with a material offering a high specific capacity over many cycles will be needed. Using SnS_2 instead

of pure Sn, on the one hand, enhances the battery's cyclability by forming a Li_2S layer around the Sn particles; on the other hand, this irreversible formation of Li_2S lowers the reversible capacity. Eventually, the remaining theoretical reversible capacity is still higher than graphite's. However, experimental cycling shows that the remaining capacity after 100 cycles is similar to that of graphite.

Tin sulfides alone may never replace graphite as the anode material in LIBs, particularly due to low first cycle coulombic efficiency. In addition, the cycling stability has to be improved by, e.g., via optimisation of the active materials texture or slurry processing. In another approach, composite active anode materials based on SnS_2 , for example, $\text{SnS}_2/\text{Si}/\text{graphite}$ or $\text{SnS}_2/\text{Sn}/\text{graphite}$, should be investigated. Since the alloying reaction of Si or Sn with Li occurs at a lower voltage than the reaction between SnS/SnS_2 with Li, the Li_2S layer would be formed first, and can surround the Si or Sn particles before the alloying reaction, therefore reducing the volume expansion during repeated lithiation and delithiation. This would potentially prolong the cycling life of the anode. Another route could be *in-situ* coating of Sn particles with Li_2S via the reaction of Li_2SO_4 and carbon. By introducing the Li_2S prior to the lithiation step, the initial irreversible capacity loss can be avoided without compromising the volume-restricting properties of Li_2S .

5. Appendix 1

5.1. Synthesis and comparative performance study of crystalline and partially amorphous nano-sized SnS₂ as anode materials for lithium-ion batteries

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Contents lists available at ScienceDirect

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Synthesis and comparative performance study of crystalline and partially amorphous nano-sized SnS₂ as anode materials for lithium-ion batteries



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Anode

ABSTRACT

A facile, time effective, and energy efficient precipitation reaction method was developed to synthesize amorphous/nano crystalline SnS₂ using SnCl₄·5H₂O and thioacetamide (C₂H₅NS) as Sn and S sources, respectively. As a comparison, nano-crystalline SnS₂ was also synthesized via the already established hydrothermal method using the same Sn- and S precursors. The crystal structure, chemical composition, and morphology of both obtained products were characterized by X-ray diffraction, scanning electron microscopy, transmission electron microscopy and X-ray photoelectron spectroscopy. The electrochemical performance properties of the as-synthesized SnS₂ samples were investigated using galvanostatic cycling with potential limitation, cyclic voltammetry, electrochemical impedance spectroscopy and electrochemical *in-situ* dilatometry. The results show that SnS₂ prepared via the precipitation reaction method electrochemically outperforms that from the hydrothermal method. This is due to the formation of thicker Li₂S layers on the particle surfaces, which drastically limits the volume expansion of the Sn particles during the alloying reaction with lithium.

1. Introduction

In order to meet climate goals stipulating a maximum two degree increase in global temperatures compared to pre-industrial levels (see the Paris Agreement [1]), the usage of renewable and carbon-neutral energies needs to be increased and greenhouse gas emissions must be cut. As the transportation industry currently contributes to more than 26% of global CO₂ emissions [2], the development and more widespread use of re-chargeable batteries for automotive applications is seen as a viable strategy to reduce emissions and achieve the targeted climate goals.

Lithium-ion batteries (LIBs) currently use graphite as the anode active material due to its combined properties of low cost, abundant availability, low de-lithiation potential vs Li/Li⁺, high Li diffusivity, high electrical conductivity, relatively low volume change during lithiation/de-lithiation and the ability to use sustainable anode processing with aqueous solvents instead of toxic N-Methyl-2-Pyrrolidone (NMP) [3]. However, graphite's theoretical specific capacity of 372 mAh g⁻¹ for the intercalation of Li ions into its crystal lattice is not sufficient

for future applications, where specific energies and energy densities exceeding 400 Wh kg⁻¹ and 750 Wh L⁻¹, respectively, are targeted. Several alternative materials have generated interest as anode active materials, such as silicon [4,5], graphite-silicon composites [5], SiO₂ [6], Sn [7], Sn-oxides [8,9] and -sulfides [10].

Tin (IV) sulfide is a promising anode active material for LIBs as it exhibits a high theoretical reversible capacity of 644 mAh g⁻¹, which is almost double that of graphite. The application of SnS₂ is not only restricted to the field of rechargeable batteries but also extends to those of photovoltaics [11,12] and photocatalytic hydrogen generation [13–15]. In fact, due to its band gap in the range between 2.18–2.44 eV, SnS₂ is a good photocatalyst for hydrogen generation and can act as an absorber material in solar cells.

SnS₂ is an n-type semiconductor adopting a layered CdI₂-type structure with a trigonal unit cell and P3m1 space group. In the crystal lattice of SnS₂, the Sn⁴⁺ ion is coordinated to six S²⁻ ions in octahedral geometry, where the S–Sn octahedra share edges along the layer. The layers are stacked along the *c*-axis and loosely held by weak Van der Waals bonds [16]. Depending on the stacking, several SnS₂ polytypes

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Table 1

Summary of available literature on the synthesis of pure SnS_2 via the solvothermal method for use as anode active materials for lithium-ion batteries. In order to compare the first cycle charge capacities with each other, the capacities up to a potential of 1.0 V vs Li/Li^+ were estimated from the graphs provided by extracting the data using OriginLab.

Synthesis method and details (reactants, temperature, time)	Sample morphology	Lattice Parameters [Å]	Voltage window/ [V]	Current rate [mA g^{-1}]	First cycle discharge capacity	First cycle charge capacity [mAh g^{-1}]
Hydrothermal method with cetyltrimethylammoniumbromide (CTAB) as a surfactant [27]	SnS_2 hollow microspheres	N/A	0.001–1.2	64.5	2080	552
	SnS_2 3D nanoflake-based hollow microspheres	N/A	0.001–1.2	64.5		
Hydrothermal method, $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ and TAA, 160–240 °C for 24 h [28]	nanoplates with a lateral size ranging of	$a = 3.162 \pm 0.003$	0.005–1.2		1439	506
	100–150 nm.				1506	531
$\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ and S powder [18]						
Solvothermal method, $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ and TAA, 180 °C for 24 h [26]				100		
Solvothermal method, $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ and solid S, 160–200 °C for 24 h [29]	3D flowerlike structures	$a = 3.649$ $c =$	0.0–3.0	200	1423	458
One-pot biomolecule (L-cys)-assisted hydrothermal method with $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ as an Sn source	SnS_2 nanosheets	5.899	0.05–2.0	80	1524	665
		N/A	0.0–1.15	323	1500	427
Microwave-assisted solvothermal approach with thiourea and $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ as sources of S and Sn, respectively	3D hierarchical SnS_2 microspheres	$a = 3.638$ $c =$	0.001–1.3	N/A	2286	503
	flower-like	5.880	0.05–1.1	100	1847	485

Table 2 Summary of all chemicals used in the study.

Material	Vendor	Purity	State	Role
$\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$	Alfa Aesar	98%	Powder	Reactant, source of Sn
Thioacetamide (TAA)	Alfa Aesar	99%	Powder	Reactant, source of S
Conc. HCl	Honeywell	/	liquid	Solvent
Carbon black C45	Imerys	/	Powder	Conductive additive
Polyvinylidene fluoride (PVDF)	Solvay	99%	Powder	Binder
N-methyl-2-pyrrolidone (NMP)	Sigma Aldrich	99.9%	liquid	Solvent
Li metal	PI-KEM	/	bulk	counter/ reference electrode
1 M solution of LiPF_6 in 3:7 wt mixture of ethylene carbonate and ethyl methyl carbonate with 2 wt% of vinylene carbonate	Soulbrain		liquid	electrolyte
Dimethyl-carbonate (DC)	Sigma Aldrich	$\geq 99\%$	liquid	solvent

can be formed, and to date, more than 70 polytypes of SnS_2 have been reported [17].

In literature, several approaches toward synthesizing SnS_2 have been explored and reported. Some of the more elaborate routes include the wet chemical [18], sonochemical [19], and ionothermal [20] methods as well as the liquid-solid phase reaction [21] and polyol routes [22]. Even though these methods do indeed yield phase pure SnS_2 , they often include complex reaction set-ups and reagents which are expensive and/or not readily accessible. Therefore, the solvothermal route is prevalent in literature as a method to synthesize bulk SnS_2 [23–26], particularly in works which explore the potential of SnS_2 as an anode material for LIBs. A summary of the electrochemical performance properties of SnS_2 prepared via the solvothermal route is given in Table 1.

In this work, we present a facile and effective method to synthesize SnS_2 via a precipitation reaction using $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ and thioacetamide (TAA) as reagents. Not only is the precipitation reaction an effective

method to synthesize SnS_2 , but it is also highly energy and time efficient and can be easily upscaled to industrial needs. We also synthesized SnS_2 via the hydrothermal method using a known route from the literature (Gou et al. [24]) to elucidate the structure–property–electrochemical performance characteristics of both materials using the same slurry processing, cell preparation, and electrochemical measurement test conditions. In this way, the electrochemical performance of SnS_2 synthesized via the precipitation and hydrothermal routes were compared to each other for the first time.

2. Experimental

2.1. Materials

The chemicals used for the synthesis of the active materials as well as for the preparation of electrodes and construction of coin cells are summarised in Table 2. All chemicals were used without any additional purification.

2.2. Synthesis

2.2.1. Precipitation reaction

$\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ and TAA were used as the tin and sulphur sources, respectively. Since $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ is insoluble in water, concentrated hydrochloric acid was used as a solvent. In the procedure, 0.701 g of $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ was dissolved in 8 mL of concentrated hydrochloric acid before it was added to 32 mL of a 0.125 M TAA solution (0.301 g dissolved in 32 mL of de-ionized water). 40 mL of the transparent, colourless liquid was transferred into a round bottomed flask which was heated to 80 °C (Fig. 1). During heating, the solution adopted an opaque yellow colour at temperatures > 70 °C. After reaching 80 °C, a yellow precipitate was formed, and the reaction was left for an additional 5 min at that temperature. Afterward, the flask was removed from the oil bath and allowed to cool down to room temperature. The precipitate was collected by vacuum filtration using a Büchner flask and borosilicate glass funnel with a built-in porous filter plate (1–1.6 μm pore diameter), washed three times with water and ethanol and subsequently dried in vacuum at 60 °C for 4 h. Samples prepared via the precipitation reaction method were designated as PR- SnS_2 .

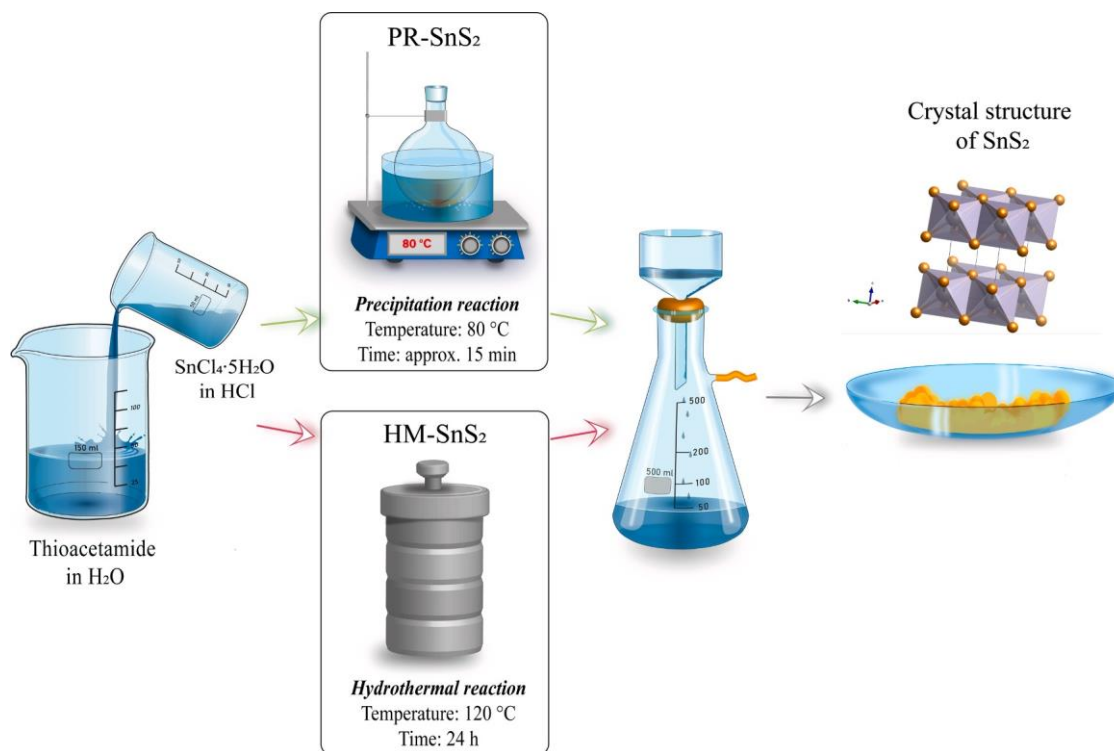


Fig. 1. Schematic presentation of the synthesis of SnS_2 via the precipitation and solvothermal reaction methods. In the depicted crystal structure of SnS_2 , the S atoms are shown as yellow spheres, whereas the Sn atoms at the centre of the octahedra are shown as metallic grey spheres. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.).

2.2.2. Hydrothermal reaction

The hydrothermal method used for synthesizing SnS_2 was adopted from the work of Gou et al. [24] Similar to the precipitation reaction, $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ and thioacetamide (TAA) were used as sources of tin and sulphur, respectively. In the first step, appropriate amounts of $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ (3.26 g) and TAA (1.0 g) for a molar ratio of 1:2 were weighed. $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ was dissolved in concentrated hydrochloric acid (8 mL) whereas TAA was dissolved in deionized water (52 mL). The $\text{SnCl}_4 \cdot 5\text{H}_2\text{O} + \text{HCl}$ solution was poured into the TAA solution and stirred for approx. 1 min before the final solution was transferred into a 100 mL Teflon-lining of a steel autoclave (Fig. 1). The autoclave was placed in a furnace for 24 h at 120 °C. After the reaction, the yellow precipitate was filtrated via vacuum filtration and washed three times with deionized water and ethanol before it was dried in vacuum at 60 °C for 4 h. Samples prepared via the hydrothermal reaction method were designated as HM- SnS_2 .

2.3. Characterization methods

2.3.1. Powder X-ray diffraction (PXRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and BET surface area analysis

The chemical composition and purity of the yellow powder products were investigated by PXRD using a Bruker D8 diffractometer ($\theta/2\theta$ -geometry) with a copper radiation source (40 kV / 40 mA) and a Ni-filter. The powder samples were fixed onto silicon mono-crystal sample holders using petroleum jelly. Signals were detected by a Lynxeye strip detector covering $\pm 1.5^\circ$ in 2θ at the same time. The obtained patterns (in a 2θ range of 10–120°) were evaluated based on Rietveld-refinements using Topas4® software. Sample morphologies were investigated by scanning electron microscopy (SEM) using a Carl Zeiss Supra 40 scanning electron microscope with Everhart-Thornley (ETD) and Through-Lens (TLD) detectors with a primary electron-beam energy of 5 keV. High-resolution transmission electron microscopy [30] (TEM)

images were collected at 200 keV on a CM200 transmission electron microscope (TEM, Philips, Amsterdam, the Netherlands) with a LaB6 electron source. A 512×1024 pixel JUNGFRUA detector with a 320 μm thick silicon sensor and a pixel size of (75 μm) was used.

The Brunauer-Emmett-Teller (BET) specific surface areas of the as-synthesized materials were measured using a Quantachrome Autosorb iQ Station via the adsorption of N_2 at -196°C . Prior to the measurement, the samples were degassed at 60 °C for 12 h under vacuum.

2.3.2. X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS, Nexsa, Thermofisher) was employed to study the surface composition of synthesized SnS_2 . Al K α radiation at 72 W and a pass energy of 200 eV, a spot size of 400 μm , "Standard Lens Mode", CAE Analyser Mode, an energy step size of 1 eV for the survey spectrum (50 passes), and integrated flood gun were used. Samples were analysed prior to and after the surface was treated with Ar-clusters (1000 Ar atoms, 6000 eV, 60 s). The high-resolution spectra (step size 0.1 eV and 0.05 eV, respectively for Sn and S) of the single elements were acquired with 50 passes at pass energies of 50 eV. Peak deconvolution was performed with Thermo Avantage v5.9925 Build 06702 using Simplex algorithm with Gauss-Lorentz Product.

2.3.3. Electrochemical investigation

The same procedures were used for the slurry formulations, electrode preparation and cell construction of the SnS_2 samples synthesized via both methods. The slurries were prepared using 80 wt.% of SnS_2 as the active material, 10 wt.% of carbon black C45 as the conductive additive, and 10 wt.% of PVDF as binder. NMP was used as the solvent for slurry preparation by dissolving the PVDF binder in NMP to create a 6 wt.% PVDF in NMP solution. The SnS_2 active material and C45 conductive additive were homogenized in a mortar before being placed into a beaker and adding the required amounts of the PVDF in NMP solution to maintain the 80:10:10 ratios of SnS_2 : C45: PVDF. The slurry was stirred over night before casting onto Cu foil. Initial drying took place at 60 °C

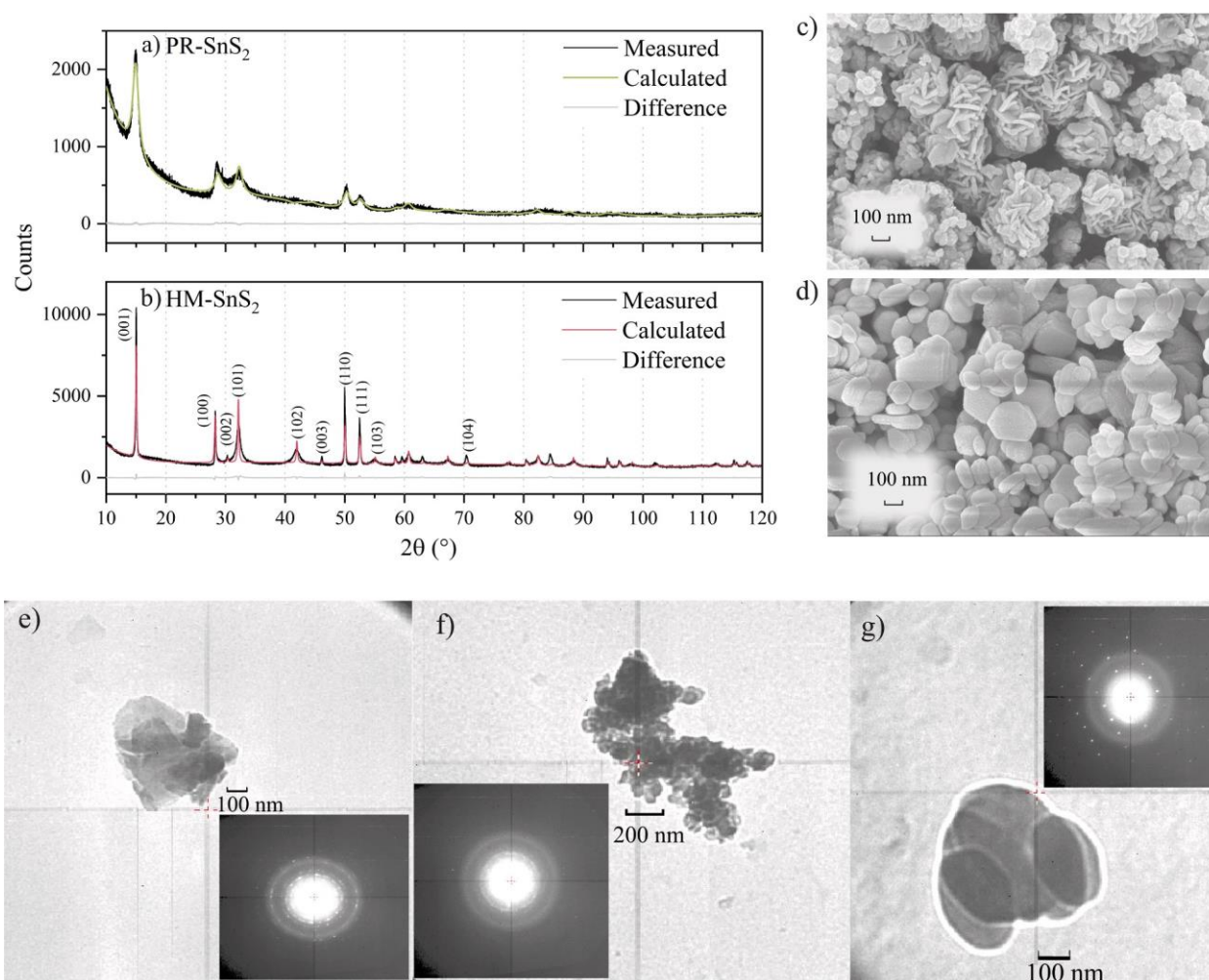


Fig. 2. PXRD pattern for (a) PR-SnS₂ and (b) HM-SnS₂ along with corresponding Rietveld refinements. SEM images of (c) PR-SnS₂ and (d) HM-SnS₂. The TEM images of (e and f) PR-SnS₂ and (g) HM-SnS₂ material clusters with corresponding selected area electron diffraction (SAED) patterns.

in air. After drying, several electrodes were punched in the form of discs with a diameter of 15 mm and heated under vacuum at 120 °C for 12 h using a Büchi® glass oven before being introduced into an Ar filled glove box. All electrochemical investigations of the electrodes prepared from the synthesized materials were performed in coin cells (type 2016) using Li/Li⁺ as the counter electrode. For coin cell construction, Li metal (thickness 0.6 mm) was used as the counter electrode, a single PP/PE/PP Celgard 2325 membrane (polypropylene film, thickness 25 μm) was used as the separator and 75 μL of the 1 M electrolyte solution (LiPF₆ in 3:7 wt mixture of ethylene carbonate and ethyl methyl carbonate with 2 wt% of vinylene carbonate) was used as the electrolyte.

Galvanostatic cycling was performed on a Maccor Series 4000 battery tester, and the raw data were evaluated using the Origin2015G software. After cycling, the cells were disassembled in an Ar-filled glove box and the electrodes were washed three times with dimethyl carbonate and left to dry. Subsequently, a representative sample of the electrode was fixed with the help of petroleum jelly onto an XRD sample holder and then sealed with an air-tight, polycarbonate dome inside the Ar-filled glovebox to prevent exposure of the electrodes to ambient air

during the XRD measurement. Another representative sample of the electrodes was fixed onto a SEM sample holder in the glovebox and transferred to the SEM in air-tight vessels. The maximum contact time of the electrodes with air during transfer to the SEM chamber is 10 s on average.

Electrochemical impedance spectroscopy (EIS), cyclic voltammetry and *in-situ* electrochemical dilatometry techniques were all conducted at ambient temperature using a BioLogic MPG-2 potentiostat. EIS measurements were performed in a two-electrode configuration in the frequency range from 20 kHz to 100 mHz with a sinus amplitude of 10 mV. The impedance data were analysed and fitted using AfterMath Electrochemical Studio. For the cyclic voltammetry measurements, the electrodes were cycled in the voltage window between 0.01–3.0 V vs Li/Li⁺ with a scanning rate of 0.2 mV s⁻¹. Electrochemical *in-situ* dilatometry was performed using an ECD-3-nano dilatometry cell (EL-Cell) to evaluate the relative thickness changes of the electrodes during the galvanostatic discharge and charge cycles. After the cell was assembled and connected to the potentiostat, it was allowed to relax for 30 h recording the voltage every 30 s before it was discharged and charged using

Table 3 Details of the Rietveld refinement of PR-SnS₂ and HM-SnS₂ products synthesized in this study.

Sample	Conditions	Phases	Lattice Parameters [Å]	Cell Volume [Å ³]	Crystallite size [nm]	R _{wp}
PR-SnS ₂	Sample after synthesis via the precipitation reaction	P-3m1 SnS ₂	$a = 3.622 \pm 0.002$ $c = 5.9109 \pm 0.0003$	67.149 ± 0.004	10	9.61
HM-SnS ₂	Sample after synthesis via the hydrothermal method	P-3m1 SnS ₂				

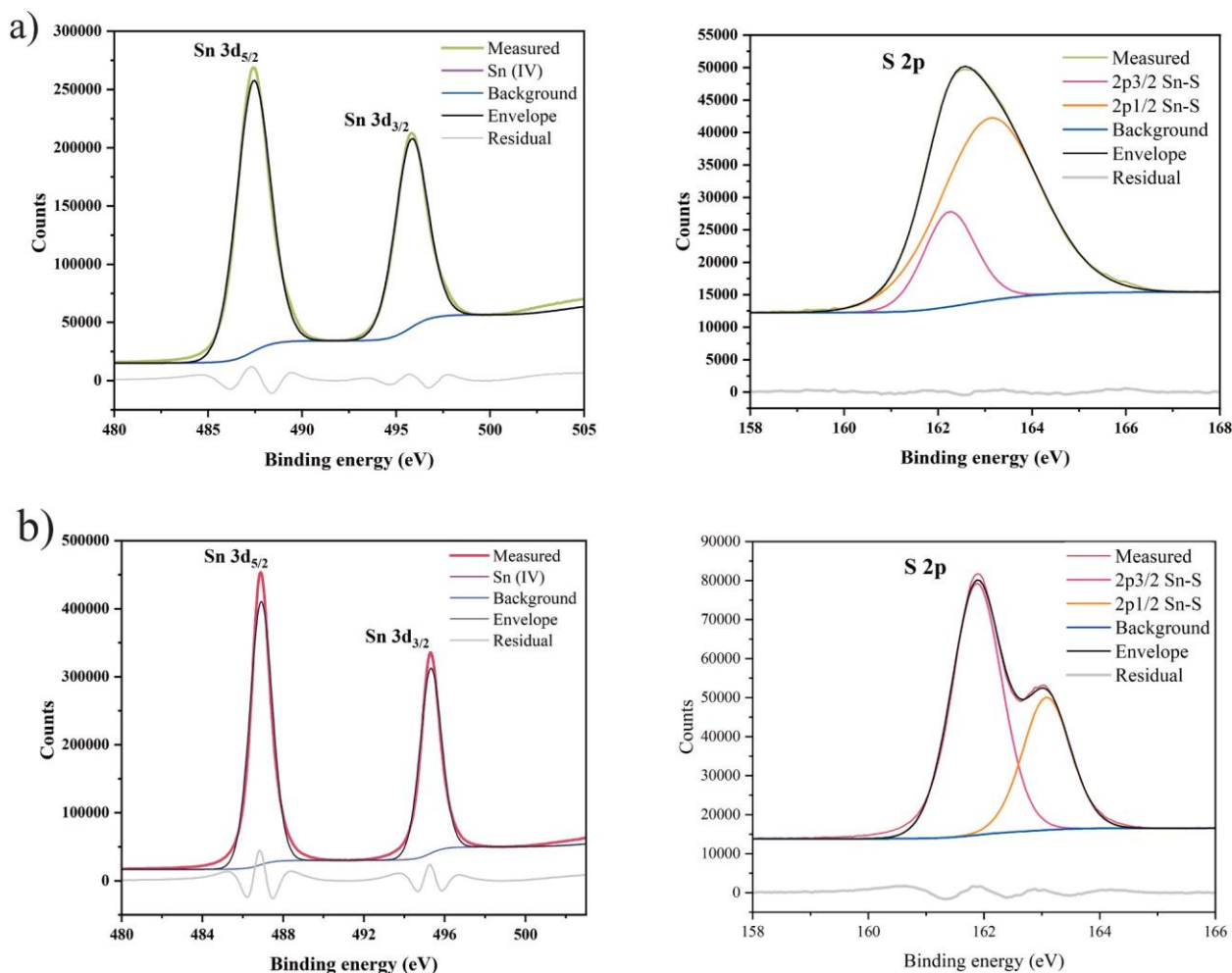


Fig. 3. XPS Sn 3d and S 2p spectra of (a) PR-SnS₂ and (b) HM-SnS₂.

constant current of 100 mA g⁻¹ in the voltage range from 0.01 to 1.0 V vs Li/Li⁺.

3. Results and discussion

Phase identification of the reaction products was performed by Rietveld refinement of the measured PXRD patterns. The measured, calculated and difference patterns of the bulk samples are shown in Fig. 2a and b for the precipitation and hydrothermal reaction products, which are designated as PR-SnS₂ and HM-SnS₂, respectively. According to the Rietveld refinement, PR-SnS₂ and HM-SnS₂ were phase pure SnS₂ with the basic trigonal cell, space group $\bar{P}3m1$. The crystallographic parameters obtained by Rietveld analysis are given in Table 3. The lattice parameters of the two products varied slightly from each other, resulting in minor deviations of the unit cell volumes. However, the lattice parameters of HM-SnS₂ were in good agreement with those reported by Gou et al. [24] ($a = 3.6486$ Å, $c = 5.8992$ Å), whose synthesis method was adopted in this study. Both the PR-SnS₂ and HM-SnS₂ samples exhibited preferred orientations in the [0 0 1] and [0 1 1] directions, which is in accordance with the hexagonal layered symmetry along the *c*-axis of SnS₂.

According to the measured PXRD patterns of PR-SnS₂, in addition to the crystalline phase, an amorphous phase was also present, as evidenced by the high background. The results of the Rietveld refinement show an average crystallite size of ~10 nm for PR-SnS₂. On the other hand, HM-SnS₂ was nano-crystalline with an average crystallite size of ~60 nm. Accordingly, the reflections in the PXRD pattern of HM-SnS₂

were more defined than those for PR-SnS₂. However, the (1 0 *l*) reflexes, i.e., the (1 0 1), (1 0 2), (1 0 3), and (1 0 4) peaks for HM-SnS₂ were still very broad (Fig. 2b), indicating the presence of stacking faults along these distinct crystallographic directions.

The SEM images of the as-prepared PR-SnS₂ and HM-SnS₂ samples are shown in Fig. 2c and d, respectively. The PR-SnS₂ sample exhibited a heterogeneous morphology characterized by the co-existence of nanoplates arranged in flower-like structures and close-to-spherical nano-sized secondary particles (Fig. 2c). On the other hand, the HM-SnS₂ sample had a well-defined, homogeneous morphology, which consisted of significantly larger but still nano-sized platelets (Fig. 2d).

The crystallinity of the samples was further investigated by transmission electron microscopy (TEM). The TEM images and the corresponding selected area electron diffraction (SAED) patterns are shown in Fig. 2e-g. Both TEM and SAED confirmed the heterogeneous nature of PR-SnS₂ in terms of crystallinity, as exemplified by the two clusters which were selected for investigation. In Fig. 2e, the spots in the SAED pattern show that this PR-SnS₂ cluster was nano-crystalline, whereas the diffuse bands in Fig. 2f indicate that the second PR-SnS₂ cluster selected for investigation was amorphous. On the other hand, the SAED image of the HM-SnS₂ sample in Fig. 2g confirms that it was crystalline due to the bright spots observed. Therefore, the SAED images for the PR-SnS₂ and HM-SnS₂ were in accordance with the measured XRD data and Rietveld refinements, which show that the PR-SnS₂ samples contained both amorphous and crystalline components, whereas the HM-SnS₂ sample was predominantly crystalline.

To check the oxidation states of Sn in the PR-SnS₂ and HM-SnS₂

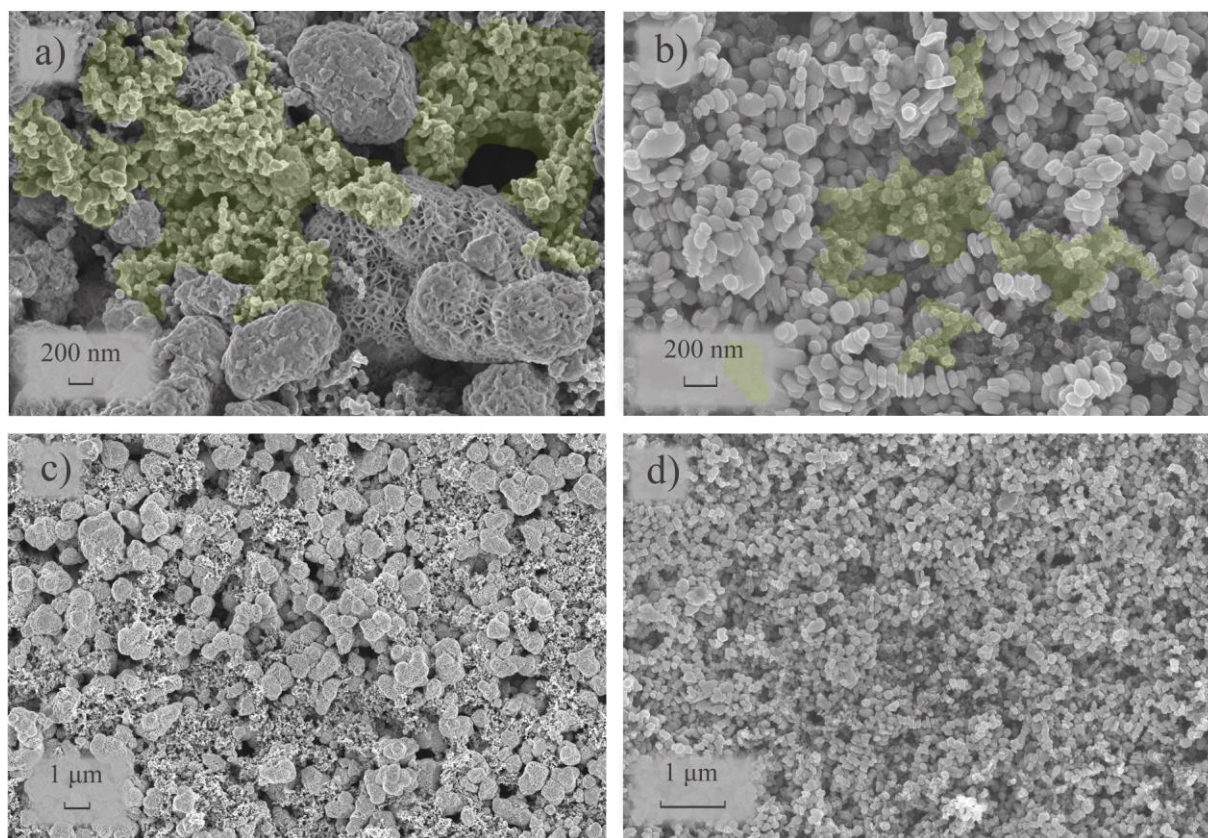


Fig. 4. SEM images of as-prepared (a and c) PR-SnS₂ and (b and d) HM-SnS₂ electrodes with different magnifications. A fraction of carbon C45 is highlighted in green at higher magnification. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.).

samples as further confirmation of their phase purities, as well as to check for the presence of any other surface impurities which may form during material synthesis, X-ray photoemission spectroscopy measurements were performed. The XPS results confirmed the presence of Sn and S elements in both samples. However, small amounts of oxygen and carbon were detected, as confirmed by the C 1s and O 1s peaks at around 285 eV and 534 eV, respectively. The amount of both elements was reduced in the XPS survey spectra after etching with Ar-clusters, indicating that they were only present at the sample surfaces. Information on the XPS survey spectra can be found in supplementary information (Table S1).

Fig. 3 shows the XPS-scans around the binding energies (eV) of the Sn-3d and S-2p electrons for PR-SnS₂ and HM-SnS₂. The Sn-3d spectra of PR-SnS₂ in Fig. 3a shows two separate peaks corresponding to the 5/2 and 3/2 splitting of the orbitals based on the electron spin-orbit interaction. The energy gap was approx. 8.4 eV, which corresponds well to literature data for tin sulfides [31]. There were no significant differences between the Sn-3d spectra of PR-SnS₂ and HM-SnS₂ (Fig. 3b) except that the Sn-3d peaks were wider for PR-SnS₂ than for HM-SnS₂, an effect which is attributed to the poorer crystallinity of PR-SnS₂. The splitting of Sn(II) and Sn(IV) based on the different oxidation states and coordination environments is very small, less than 0.5 eV [31] and could not be resolved here. The XPS valence spectra recorded up to 100 eV (see Fig. S1 in the supplementary information where the close-up of peaks is shown) show a strong peak at ~26.9 for PR-SnS₂ and at ~26.4 eV for HM-SnS₂. According to the NIST-XPS database [31] these peaks can be allocated to the Sn-4d_{5/2} photoelectrons of SnS₂. Therefore, neither in the PXRD data nor in the valence spectra was there any indication of the presence of SnS in the as-synthesized samples. As a result, the Sn-peaks were fitted based on Sn(IV) only.

The S-2p spectra for PR-SnS₂ and HM-SnS₂ are also shown in Fig. 3a and b, respectively. Two overlapping peaks corresponding to the 3/2

and 1/2 splitting of the 2p orbitals based on the electron spin-orbit interaction could be observed. According to the peak deconvolution, the energy gap for HM-SnS₂ was approx. 1.2 eV which corresponds well to literature data for metal sulfides [32]. In the case of PR-SnS₂, although the two peaks could not be well resolved, peak deconvolution still yielded a similar gap of 1.4 eV. It is assumed that the lower crystallinity of PR-SnS₂ affected peak broadening, as was also observed for the Sn-3d spectra. A summary of the fitted binding energies of the main core-level features of Sn and S is given in Table S2 in supplementary info. According to the element quantification, a Sn:S ratio of 1:2 was achieved for both preparation techniques, confirming their stoichiometric purities.

Lastly, the BET data showed that there are only slight differences in the specific surface areas of PR-SnS₂ and HM-SnS₂. Specifically, the PR-SnS₂ sample exhibited a specific surface area of 13.4 m² g⁻¹ whereas the HM-SnS₂ powder had a higher specific surface area of 15.1 m² g⁻¹. The details of BET surface analysis are presented in supplementary information.

3.1. Electrochemical investigation

SnS₂ exhibits a multi-step lithiation process which takes place via the intercalation, conversion and alloying mechanisms [33]. In the first step of the discharge reaction, lithium is intercalated into the vacant octahedral positions of the SnS₂ crystal structure to form Li_xSnS₂. Afterward, Sn and Li₂S are formed from Li_xSnS₂ via the conversion reaction, which is followed by the lithiation of Sn to yield various Li_xSn_y intermetallic compounds. Alloying materials, such as Sn and Si, suffer from excessive volume expansions during lithiation due to their structural reorganization accompanied by the formation of new phases. This volume expansion has a significant impact on the capacity loss of the electrode, as the particles lose contact with each other, resulting in reduced electric and

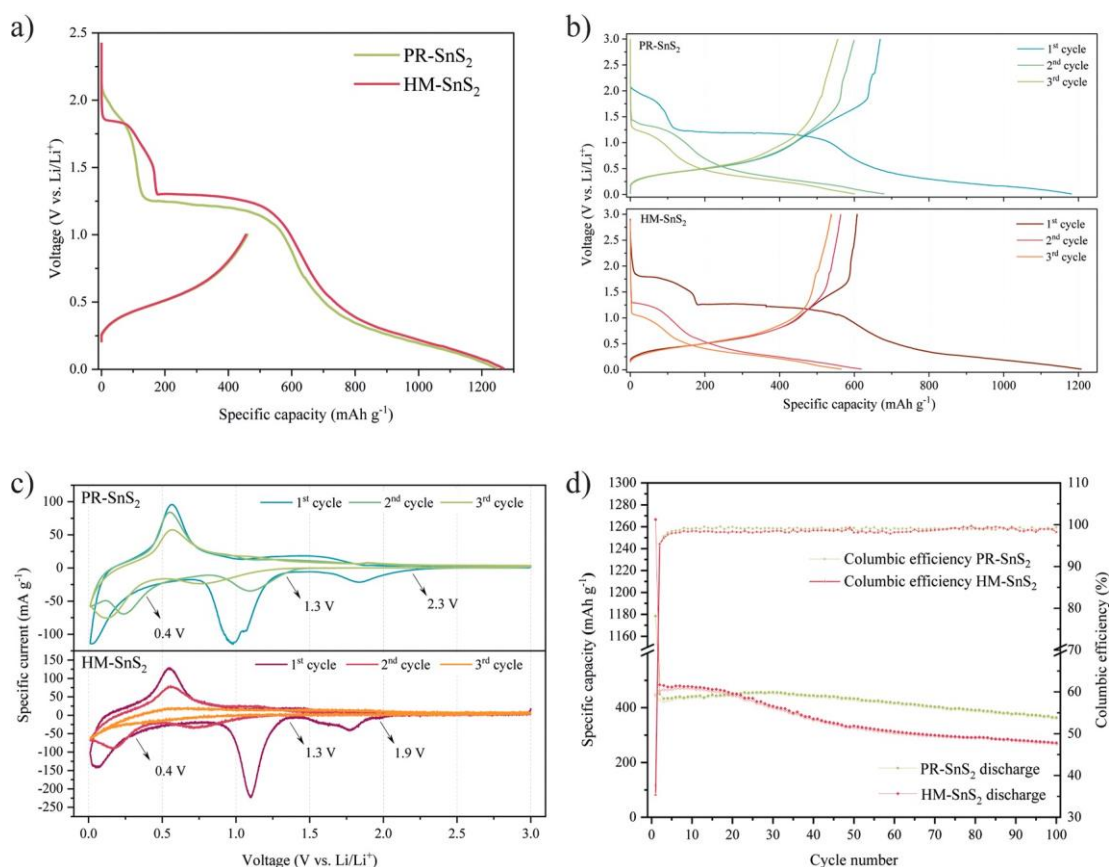


Fig. 5. (a) Galvanostatic charge–discharge profiles for the first cycles of the PR-SnS₂ and HM-SnS₂ electrodes. The cells were cycled in the voltage window from 0.01 to 1.0 V vs. Li/Li⁺ at a current rate of 100 mA g⁻¹. (b) Galvanostatic charge–discharge profiles for the first three cycles for the PR-SnS₂ and HM-SnS₂ electrodes, which were cycled in the voltage window from 0.01 to 3.0 V vs. Li/Li⁺. (c) Cyclic voltammograms of PR-SnS₂ (upper graph) and HM-SnS₂ (lower graph) with peak onsets indicated in the cathodic sweep. The measurements were conducted in the voltage window from 0.1 to 3.0 V vs. Li/Li⁺ and with a scanning rate of 0.2 mV s⁻¹. (d) Galvanostatic cycling for 100 cycles of PR-SnS₂ (green) and HM-SnS₂ (red) cycled with a current rate of 100 mA g⁻¹ in the voltage window between 0.01 to 1 V vs. Li/Li⁺. On the right y-axis, the calculated Columbic efficiency is presented. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.).

ionic conductivities and finally electrode degradation.

In this work several electrochemical tests were carried out on half-cells vs. Li/Li⁺ to assess the electrochemical performance properties of the synthesized SnS₂ materials. In order to characterize the microstructure of the electrodes before cycling, SEM was performed on the dried electrodes after coating (Fig. 4). The micrographs show that due to electrode processing, the PR-SnS₂ active material particles became spherical, whereas the HM-SnS₂ particles retained their platelet-like structure with contact points at the platelet edges. The PR-SnS₂ secondary particles were significantly larger than the HM-SnS₂ platelets, and the C45 conductive carbon surrounded and encompassed the PR-SnS₂ particles more effectively than the HM-SnS₂ platelets. XRD was also performed on the as-prepared electrodes to check if any changes to the phase composition of the active materials took place during electrode processing. The XRD patterns of the pristine electrodes and the results of the Rietveld refinements are presented in supplementary information (Fig. S2). The measurements show that the SnS₂ phase is retained, and the active materials did not suffer from any mechanochemical modifications during the slurry and electrode preparations.

The initial thickness (*l*₀) of the PR-SnS₂ electrode was 39 μm, whereas that of the HM-SnS₂ electrode was 29 μm. Using these data as well as the measured areal mass loadings, the porosity of the electrodes could be calculated. According to the calculations, the details of which are presented in the supplementary information, the porosity of the PR-SnS₂ electrodes was ~ 80%, whereas that of the HM-SnS₂ electrodes was ~ 48%. The areal capacity of the PR-SnS₂ electrode was 2.1 mAh cm⁻²

and that of the HM-SnS₂ electrode was 3.3 mAh cm⁻², assuming a theoretical initial first cycle discharge capacity of 1209 mAhg⁻¹ for SnS₂. The different thicknesses and porosities of the dried, non-calendered electrodes could be attributed to the packing densities of the PR-SnS₂ and HM-SnS₂ particles, i.e., the PR-SnS₂ electrodes adopt a more open arrangement of the active material particles, as shown in the SEM images in Fig. 4a and c, whereas the HM-SnS₂ electrodes achieve higher packing densities and lower porosities due to the re-arrangements of the smaller platelets during the drying step, as shown in Fig. 4b and d.

Fig. 5a shows the voltage profile of the first galvanostatic discharge and charge cycles for the PR-SnS₂ and HM-SnS₂ cells, which were discharged to 0.01 V vs. Li/Li⁺ and charged to 1.0 V vs. Li/Li⁺ at a specific current of 100 mA g⁻¹. While there were some differences in the discharge curves for the two samples, there were no significant differences in the charge curves for both materials and they could not be distinguished from each other in Fig. 5a. Therefore, a close-up of the first charge curves for both PR-SnS₂ and HM-SnS₂ electrodes is provided in the supplementary info (Fig. S3). The voltage profiles of the first three discharge and charge cycles of the PR-SnS₂ and HM-SnS₂ electrodes, which were cycled in the voltage range from 0.01 to 3.0 V vs. Li/Li⁺ with a current rate of 100 mA g⁻¹, are shown in Fig. 5b.

In a recent work, we reported a detailed thermodynamic and electrochemical investigation of the lithiation mechanism of SnS₂, supported by CALPHAD-based calculations, electrochemical experiments, and structural characterization of the electrodes [34]. Accordingly, the three regions in the discharge curve correspond to the three mechanisms

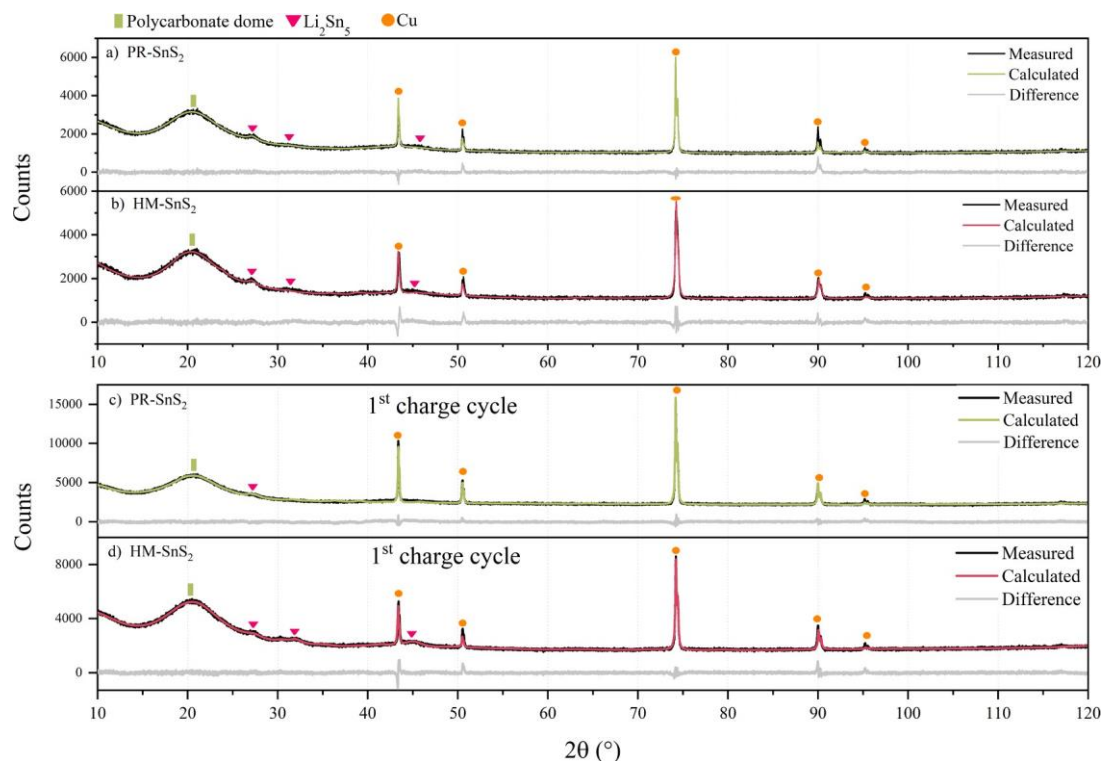


Fig. 6. Ex-situ XRD patterns and Rietveld refinement of (a) PR-SnS₂ and (b) HM-SnS₂ electrodes after 50 discharge and charge cycles, and for (c) PR-SnS₂ and (d) HM-SnS₂ after a single discharge and charge cycle. The reflections of Li₂Sn₃ phase are indicated by pink inverted triangle. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.).

which occur during discharge. In the first step, Li ions are intercalated into the SnS₂ crystal structure. During this step, specific capacities of approximately 117 and 150 mAh g⁻¹ were recorded for the PR-SnS₂ and HM-SnS₂ electrodes, respectively. Further lithiation triggers the atomic rearrangement of the lithiated SnS₂ structure and the onset of the conversion reaction, during which Sn and electrochemically inert Li₂S were formed. The plateau potentials measured during galvanostatic cycling of the electrodes (~1.25 V for PR-SnS₂ and ~1.28 V for HM-SnS₂) are indicative of the occurrence of the conversion reaction. For the PR-SnS₂ electrode, a capacity of 396 mAh g⁻¹ was attained for the conversion reaction, whereas for the HM-SnS₂ electrodes, the capacity associated with the conversion reaction was 369 mAh g⁻¹. After the conversion reaction, alloying of Sn and Li takes place, and various intermetallic Li_xSn_y phases are formed. At the lower cut-off potential of 0.01 V vs Li/Li⁺, the total capacity in the first discharge cycle was 1244 and 1266 mAh g⁻¹ for PR-SnS₂ and HM-SnS₂, respectively, both of which are slightly larger than the theoretical capacity of 1209 mAh g⁻¹. The higher capacity is most likely due to side reactions between the electrode material and electrolyte associated with the formation of solid electrolyte interphase (SEI). In the first charge step up to 1.0 V vs Li⁺/Li, an average reversible capacity of 458 mAh g⁻¹ was recorded for both electrodes.

The cyclic voltammetry (CV) scans for the as-prepared SnS₂ materials are shown in Fig. 5c. During the first cycle, three reduction peaks were observed to start at ~2.3, 1.3 and 0.4 V vs Li/Li⁺ for PR-SnS₂ and at 1.9, 1.3, and 0.4 V vs Li⁺/Li for HM-SnS₂ in the cathodic sweep. The peaks with onsets at ~2.3 and ~1.9 V vs Li/Li⁺ for PR-SnS₂ and HM-SnS₂, respectively, are attributed to the intercalation of Li ions into the SnS₂ host lattices. In both electrodes, the dominant peak with an onset at 1.3 V vs Li/Li⁺ corresponds to the conversion reaction, in which lithiated SnS₂ reacted with Li to form Sn and inert Li₂S. The cathodic peaks in the CV scan at lower voltages are indicative of the alloying reaction between Sn and Li, whereas during charge, a single anodic peak was measured for the de-alloying reactions. Although the alloying and de-alloying reactions should be reversible, the CV scans show a

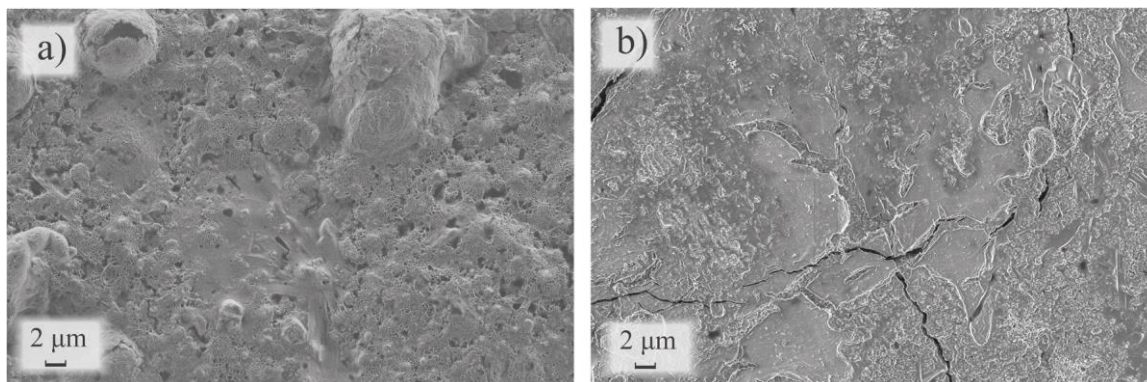
weakening of the reduction and oxidation peaks with increasing cycle number in the lower voltage region < 0.75 V vs Li/Li⁺. This phenomenon was more pronounced for the HM-SnS₂ electrodes than for PR-SnS₂. The absence of any significant oxidation peaks at potentials higher than 1.0 V vs Li/Li⁺ in the CV measurements of both samples (Fig. 5c) is in accordance with the 1st cycle charge profiles for both PR-SnS₂ and HM-SnS₂ up to 3.0 V vs Li/Li⁺ (Fig. 5b), as these curves show that neither the conversion nor the intercalation reaction is irreversible due to the absence of any voltage plateaus on charge. However, the short plateaus in the second and third discharge curves of PR-SnS₂ and HM-SnS₂, which seem to be slightly more significant for PR-SnS₂ than for HM-SnS₂ (see Fig. 5b), may be due to the conversion reaction of unreacted, residual SnS₂. This effect is also reflected in the 2nd CV scan of PR-SnS₂ (Fig. 5c), where a smaller but still significant reduction peak at ~1.25 V vs Li/Li⁺ is measured in the cathodic sweep.

The specific capacity and coulombic efficiency of the PR-SnS₂ and HM-SnS₂ electrodes in the first 100 discharge/charge cycles are presented in Fig. 5d. After 100 cycles, the PR-SnS₂ sample exhibited a capacity of 364 mAh g⁻¹, whereas the capacity of the HM-SnS₂ electrode was 271 mAh g⁻¹. Therefore, even though the HM-SnS₂ sample had a slightly higher first cycle discharge capacity compared to PR-SnS₂, its performance decayed faster than that of PR-SnS₂ over 100 cycles. Fig. 5d strongly suggests that the fundamental mechanisms leading to degradation of the electrochemical performance of the PR-SnS₂ and HM-SnS₂ electrodes were already established in the first 50 cycles. Therefore, ex-situ XRD and SEM measurements were performed at the end of the 50th cycle to investigate the changes in the crystal structures and morphologies of the PR-SnS₂ and HM-SnS₂ electrodes.

The measured XRD patterns of the PR-SnS₂ and HM-SnS₂ electrodes after 50 cycles, along with the calculated pattern from the Rietveld refinements, are presented in Fig. 6a and b, respectively. The broad peak at 2θ ~ 20° corresponds to the polycarbonate dome, whereas the peaks at 2θ = 43.4, 50.6, 74.2, 90.0 and 95.3° are attributed to the Cu-foil electrode substrate. Apart from the reflections associated with copper

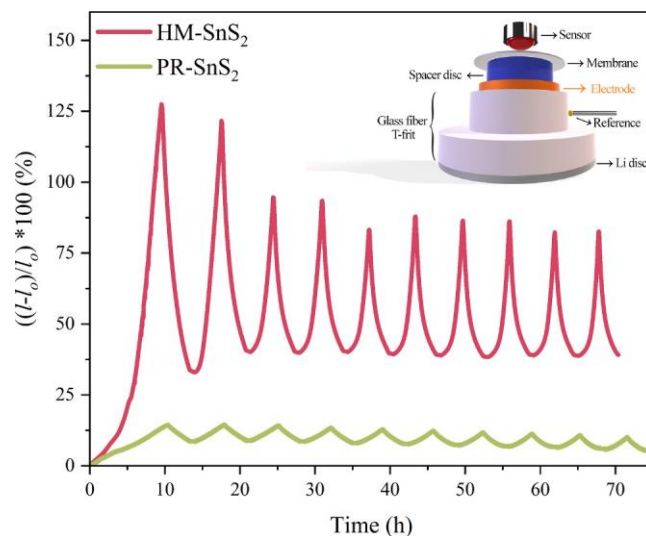
Table 4 Summary and crystallographic data of the phases found in the PR-SnS₂ and HM-SnS₂ electrodes after 50 galvanostatic discharge and charge cycles.

Sample	Conditions	Phases	Lattice Parameters [Å]	Cell Volume [Å ³]	R _W
PR-SnS ₂	Electrode from half-cell discharged and charged via constant current at 100 mA g ⁻¹ in voltage window 0.01–1.0 V vs Li/Li ⁺ for 50 cycles	$\overline{\text{Cu}}\text{Fm}3m$	$a = 3.6153 \pm 0.0005$	47.2528	3.2
		$\text{Li}_2\text{Sn}_5\text{P4}/\text{mbm}$	$a = 9.341 \pm 0.004$ $c = 3.302$	± 0.0002	
HM-SnS ₂	Electrode from half-cell discharged and charged via constant current at 100 mA g ⁻¹ in voltage window 0.01–1.0 V vs Li/Li ⁺ for 50 cycles	$\text{Li}_2\text{Sn}_5\text{P4}/\text{mbm}$	$a = 10.365 \pm 0.001$ $c = 3.327 \pm 0.007$	47.2347	3.4
				± 0.0003	

**Fig. 7.** Ex-situ SEM images of (a) PR-SnS₂ and (b) HM-SnS₂ after 50 charge and discharge cycles.

and the polycarbonate dome, additional weak reflections at $2\theta \approx 27^\circ$, 31° and 45° were observed, which are associated with the (3 1 0), (3 2 1) and (0 4 1) reflections of the Li_2Sn_5 phase according to the full-profile Rietveld refinement. This is an interesting result, as the cycling measurements were stopped in the charged state at 1.0 V vs Li/Li⁺, and only the presence of pure Sn and Li_2S was expected. However, neither of these phases could be detected in the XRD patterns of the cycled electrodes. In order to check if the Li_2S and Sn phases could not be detected due to an increasing amorphization of the crystalline phases in the electrode during cycling, the PR-SnS₂ and HM-SnS₂ electrodes were discharged to 0.01 V vs Li/Li⁺ and charged to 1.0 V vs Li/Li⁺ only once and then subjected to the ex-situ XRD measurements (Fig. 6c and d for PR-SnS₂ and HM-SnS₂, respectively). However, the results show that even after only one discharge/charge cycle, the existence of Li_2S and Sn could not be confirmed. This is most likely due to the fine microstructure of the PR-SnS₂ and HM-SnS₂ active materials, which leads to the absence of long-range ordering of the atoms after the conversion reaction and the consequent formation of amorphous Li_2S and Sn, especially at room temperature. However, both the plateau potential at 1.35 V vs Li/Li⁺ in the GCPL measurements (Fig. 5a and b) and the reduction peak with an onset at approx. 1.3 V vs Li/Li⁺ in the CV measurements (Fig. 5c) of the PR-SnS₂ and HM-SnS₂ electrodes are the electrochemical “footprints” associated with the formation of Li_2S and Sn. Therefore, from a thermodynamic and phase-diagrams perspective as reported in our previous work on the in-situ lithiation of SnS₂ [34], although Li_2S cannot be detected via XRD, we are convinced that Li_2S forms during the conversion reaction of SnS₂. As a result, the presence of reflections for the Li_2Sn_5 phase in the charged PR-SnS₂ and HM-SnS₂ electrodes (1.0 V vs Li/Li⁺) after 50 cycles indicates the occurrence of lithium trapping in the electrodes as the cycle number increases. This effect was observed in other anode materials such as Si [35] and Al [36]. The details of found phases in the electrodes after 50 discharge/charge cycles is shown in Table 4.

The SEM images of the surfaces of the PR-SnS₂ and HM-SnS₂

**Fig. 8.** Dimensional changes of the PR-SnS₂ (green) and HM-SnS₂ (red) electrodes during the cycling with schematic illustration of a typical electro-chemical dilatometry cell. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

electrodes after 50 cycles are shown in Fig. 7a and b, respectively. In both electrodes, the morphological changes of the electrode surface due to the formation of an SEI layer could be confirmed. In the case of PR-SnS₂, the SEI layer was both crack-free and more compact with better adhesion to the active material particles. However, the SEI layer of the HM-SnS₂ electrode was clearly damaged as evidenced by the presence of well-developed cracks.

The full lithiation of Sn via formation of $\text{Li}_{17}\text{Sn}_4$ is associated with a theoretical volume change of up to 258% [37]. However, to the best of

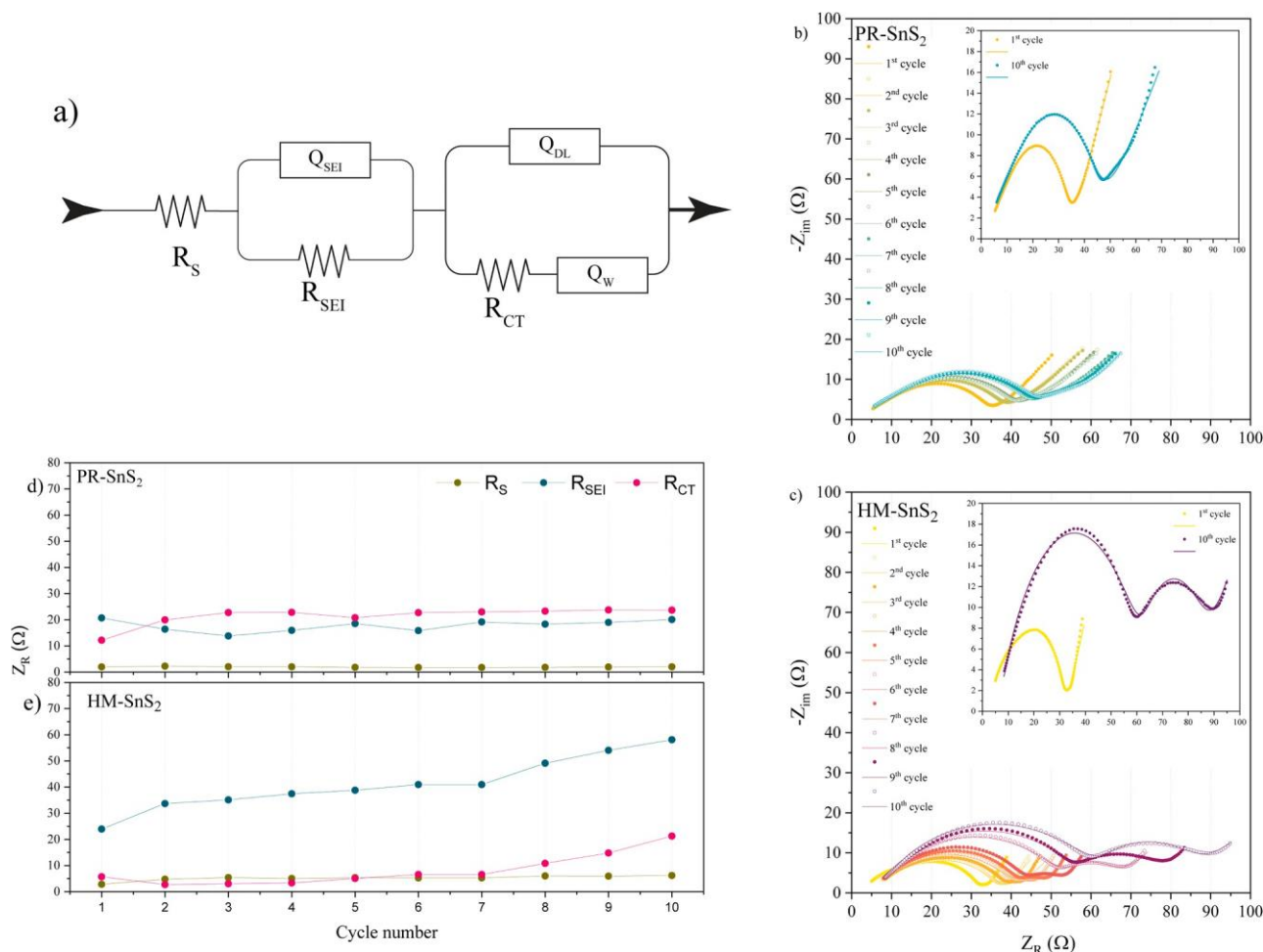


Fig. 9. (a) Equivalent circuit proposed for analysis of impedance spectra of as-prepared SnS₂ anodes. Electrochemical impedance spectra of (b) PR-SnS₂ and (c) HM-SnS₂ electrodes measured after each charge cycle for the first 10 cycles. The contribution of certain phenomena to the overall impedance of the (d) PR-SnS₂ and (e) HM-SnS₂ electrodes as a function of cycle number. The ohmic resistivity is presented in dark yellow, the SEI contribution in dark cyan, and the charge-transfer resistance is shown in pink. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.).

our knowledge, there are no measured data on the volume expansion of SnS₂-based electrodes in literature. To quantify the deformation of the electrodes during cycling, *in-situ* dilatometry was performed on the PR-SnS₂ and HM-SnS₂ electrodes to measure their change in length along the surface normal direction. A schematic illustration of a typical *in-situ* electrochemical dilatometry cell used in this study is shown in Fig. 8. During the dilatometry measurements, the vertical movement of the working electrode (orange) was carried through the thin metal membrane to the sensor. A porous glass fibre T-frit was fixed between the working and counter electrodes, ensuring that only dimensional changes of the working electrode were detected.

The dimensional changes of the PR-SnS₂ and HM-SnS₂ electrodes during lithiation/ de-lithiation as a function of time are shown in Fig. 8. The displacement data from the dilatometry measurements were translated to normalized height changes according to the formula: $Height\ change = \frac{l-l_0}{l_0} \cdot 100\%$ (%), where l is the displacement during the

measurement and l_0 is the initial thickness of the electrode active layer. The initial thickness (l_0) of the PR-SnS₂ electrode was 39 μm , whereas that of the HM-SnS₂ electrode was 29 μm . The dimensional change of the PR-SnS₂ electrode was $\sim 14\%$ after full lithiation in the first discharge cycle whereas that of the HM-SnS₂ electrode was $\sim 125\%$. During the de-lithiation charge step up to 1.0 V vs Li/Li⁺, a partial contraction of the electrodes was observed. The PR-SnS₂ electrode contracted $\sim 4\%$, resulting in $\sim 8\%$ of irreversible expansion. However, the irreversible volume expansion of the HM-SnS₂ electrode was $\sim 33\%$. The voltage

profiles obtained during cycling as a function of time are presented in supplementary information (Fig. S4).

Electrochemical impedance spectroscopy (EIS) measurements were performed to further investigate the effect of morphology and structure of the SnS₂ samples on performance. Data were recorded after each charge and discharge step for the first ten cycles. Cells were cycled at a current rate of 100 mA g⁻¹ in the voltage window from 0.01 to 1 V vs Li/Li⁺. The equivalent circuit used to fit the measured impedance data is shown in Fig. 9a. A constant phase element (CPE) was used in the circuit instead of ideal capacitance due to the porous nature of the electrodes. The Ohmic resistance, which is denoted as R_s , represents the internal resistance value of the bulk materials in the cell, such as the electrolyte, separator, and current collector. The contribution to impedance from the SEI layer is denoted as R_{SEI} , and it originates from the formation of both the SEI layer as well as the electrochemically inert Li₂S, whereas Q_{SEI} represents the corresponding constant phase element. R_{CT} is associated with the charge-transfer resistance arising from the charge transfer between the electrolyte and the solid surfaces (electrode surface) and Q_{DL} is the constant phase element related to electric double-layer capacitance on active materials.

The Nyquist plots for PR-SnS₂ and HM-SnS₂ can be seen in Fig. 9b and c, respectively. The impedance spectra included a high frequency semicircle for the combined contribution of the SEI and Li₂S, a semicircle at the medium frequency region for the effect of current passing through both double layer capacitance and the charge transfer

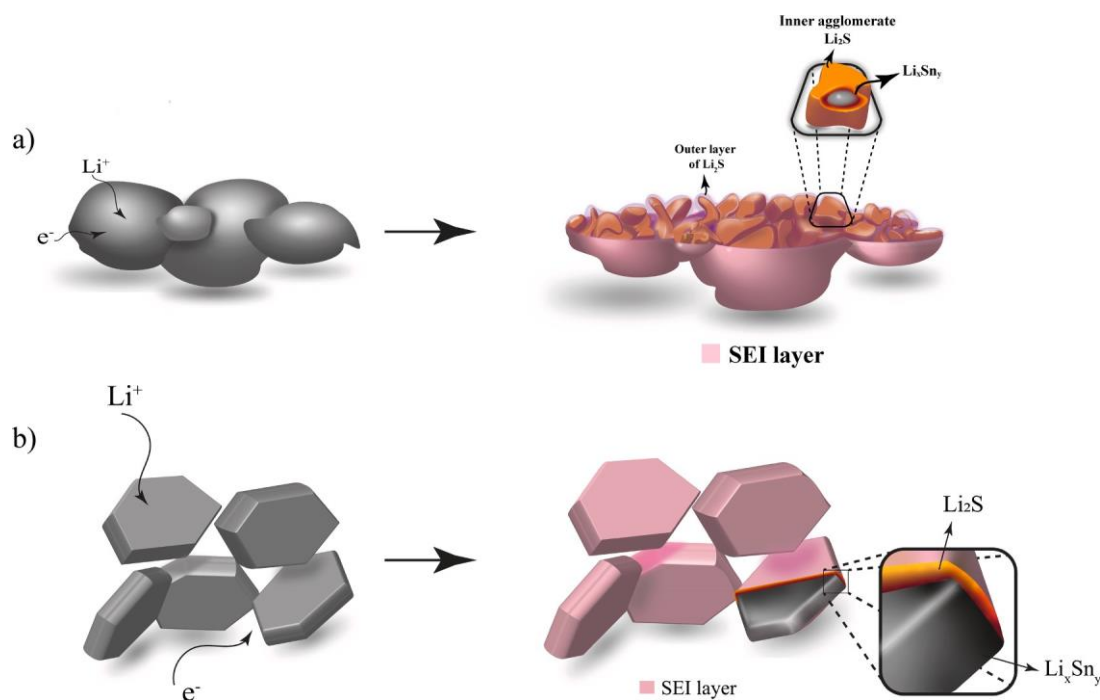


Fig. 10. Proposed mechanism of the lithiation and the formation of Li_2S and SEI layers of (a) PR- SnS_2 and (b) HM- SnS_2 .

resistance, and an inclined line in the low frequency region for the diffusion of ions and mass transport processes that show the Warburg contribution. The impedance parameters derived using the equivalent circuit model for HM- SnS_2 and PR- SnS_2 are shown in Fig. 9d and e, respectively. According to the data, the ohmic impedance across all ten cycles for the HM- SnS_2 and PR- SnS_2 cells did not change significantly, which confirms the stability of the electrolyte in the cell. For HM- SnS_2 , the SEI layer resistance increased with increasing cycle number (Fig. 9e), with a dramatic increase after seven discharge and charge cycles. On the other hand, the SEI and charge transfer impedances for PR- SnS_2 (Fig. 9d) were stable throughout the measurement, illustrating the stability of the SEI and Li_2S formed in the electrode. However, it should be noted that the charge transfer impedance of PR- SnS_2 was always higher than that of HM- SnS_2 in the first 10 cycles. The exact values of the impedances yielded from fitting the experimental data are summarized in supplementary information (Table S3).

The galvanostatic cycling data in Fig. 5 indicate that the partially amorphous PR- SnS_2 sample displayed superior cycling performance compared to well-crystallized, nano-sized HM- SnS_2 . According to the EIS data in Fig. 9, the resistance of the SEI layer on the HM- SnS_2 electrodes increased with increasing cycle number, whereas that for the PR- SnS_2 electrodes remained comparatively constant. The increase in SEI impedance is usually a result of the growth and thickening of the resistive SEI layer. The charge transfer impedance also increases, as the transfer of Li^+ ions between the electrolyte and the active material particles is hindered by the thick SEI layer. In the ideal case, a stable SEI layer should be formed in the first few cycles to protect the active material particles from direct contact with the electrolyte, while still being permeable for Li^+ ion diffusion. This appears to be the case for the PR- SnS_2 electrodes. However, if the particles of the electrode active material expand and contract significantly during lithiation and de-lithiation, as was observed in the dilatometry data for the HM- SnS_2 electrodes (Fig. 8), cracking of the active particles can take place, which constantly exposes fresh surfaces to the electrolyte. This leads to the growth of an unstable SEI, which will influence cell performance via: 1) over-consumption and loss of Li inventory, 2) increase in resistance of the electrode due to SEI's electrically insulating nature, and 3) increasing the total Li^+ ion diffusion pathway due to the thicker SEI [38]. The SEM

micrographs of the HM- SnS_2 electrodes show that the growth of the SEI is so unstable that cracks develop in the layer during cycling (Fig. 7b). In contrast, the SEI layer formed during cycling of the PR- SnS_2 electrodes is more stable, as evidenced by the constant SEI and charge transfer impedances in the EIS data for the PR- SnS_2 electrodes (Fig. 9d) and the absence of cracks in the SEM images of the electrode surfaces after 50 cycles (Fig. 7a).

The results of the *in-situ* dilatometry experiments in Fig. 8 confirmed that the dimension change of the HM- SnS_2 electrodes was significantly larger than that for PR- SnS_2 . This may be attributed to the microstructure of the active material particles in the electrode and the resulting distribution of Li_2S after the conversion reaction. Li_2S should form as a layer which should act to restrict the volume changes of the Sn particles during the successive alloying and de-alloying reactions. The BET surface area measurements showed the difference in specific surface areas of the bulk PR- SnS_2 and HM- SnS_2 materials was only $\sim 2\text{ m}^2\text{ g}^{-1}$. However, electrode processing led to the agglomeration of the PR- SnS_2 primary particles to form larger secondary particles in the electrodes (see the SEM images in Fig. 4). The larger agglomerates may have been advantageous, as they lowered the surface area of the PR- SnS_2 active material. Since the thermodynamics of the lithiation reactions of SnS_2 dictate that the amount of Li_2S formed for both PR- SnS_2 and HM- SnS_2 must be the same, the lower surface area of the PR- SnS_2 electrode active material after electrode processing means that the Li_2S layer was thicker for PR- SnS_2 than for the HM- SnS_2 electrodes. The evaluated EIS data in Fig. 9 support this theory, as the charge transfer resistance of PR- SnS_2 , despite its stability, was always higher than that of HM- SnS_2 , and was a result of the overall lower electronic conductivity of Li_2S . However, due to the thicker Li_2S layers in the PR- SnS_2 electrodes, the amorphous Sn which forms after the conversion reaction was more confined, resulting in lower volume expansions during cycling and an improved stability of the SEI layer. Therefore, it appears that the mechanical stresses and degradation mechanisms associated with the volume expansion of the SnS_2 anodes has a larger impact on their electrochemical performance than the increased charge transfer resistance resulting from the presence of Li_2S . A schematic illustrating the growth mechanism and the distribution of the Li_2S and SEI layers for the PR- SnS_2 and HM- SnS_2 electrodes is shown in Fig. 10.

4. Conclusion

This work reports a novel synthesis for SnS via a facile precipitation reaction method, which is both time and energy efficient. The product of the precipitation reaction exhibits a heterogeneous morphology characterized by the co-existence of amorphous and nano-sized particles. The electrochemical performance properties of the as-synthesized SnS_2 were compared to those of nano-crystalline SnS_2 synthesized via the hydrothermal method, which is an ubiquitous method in the literature for the synthesis of SnS_2 . We show that the partially amorphous SnS_2 prepared via the precipitation reaction electrochemically outperforms nano-crystalline SnS_2 . Quantitatively, partially amorphous SnS_2 has a reversible specific capacity of 364 mAh g^{-1} after 100 discharge and charge cycles, whereas that for nano-crystalline SnS_2 is only 271 mAh g^{-1} . The better cycling performance of SnS_2 prepared via the precipitation reaction is a result of electrode processing, during which larger agglomerates are formed to decrease the total surface area of the electrode active material. As a result of the lower surface area, thicker Li_2S layers are developed during the conversion reaction of SnS_2 to Sn and Li_2S , which are more effective in restricting the volume expansion of amorphous Sn. Furthermore, as the electrodes prepared from nano-crystalline SnS_2 exhibit higher degrees of volume expansion due to the comparatively thinner Li_2S layers, an unstable SEI layer is formed in those samples, which can even lead to SEI cracking. The results presented in this study thereby underscore the importance of assessing and understanding the structure-processing-property relations for SnS_2 -based electrodes using a variety of complimentary techniques, as this can lead to quantitative improvements in the electrochemical performance of this class of materials.

CRedit authorship contribution statement

Albina Glibo: Conceptualization, Methodology, Data curation, Writing – original draft, Writing – review & editing, Formal analysis. **Nicolas Eshraghi:** Data curation, Writing – review & editing, Formal analysis. **Andreas Mautner:** Data curation, Writing – review & editing, Formal analysis. **Marcus Jahn:** Supervision. **Hans Flandorfer:** Conceptualization, Methodology, Writing – review & editing, Formal analysis. **Damian M. Cupid:** Conceptualization, Methodology, Writing – review & editing, Formal analysis.

Declaration of Competing Interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.electacta.2022.140869.

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5.2. Comparative study of electrochemical properties of SnS and SnS₂ as anode materials in lithium-ion batteries

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Comparative study of electrochemical properties of SnS and SnS₂ as anode materials in lithium-ion batteries



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ABSTRACT

Phase pure SnS and SnS₂ were synthesized via the precipitation reaction and investigated as active anode materials for lithium-ion batteries. The crystal structure, morphology and chemical composition of the as-synthesized materials were determined by various physico-chemical techniques such as powder X-ray diffraction, scanning electron microscopy, transmission electron microscopy and X-ray photoelectron spectroscopy. The electrochemical properties of the SnS and SnS₂ active anode materials were investigated by galvanostatic cycling with potential limitation, cyclic voltammetry, electrochemical impedance spectroscopy and electrochemical *in-situ* dilatometry. It was shown that the SnS₂ electrodes exhibit superior cycling performance properties compared to the SnS electrodes. This is due to the higher amount of Li₂S which is produced during the conversion reaction of SnS₂ as well as to the intercalation of Li into the SnS₂ crystal structure prior to conversion, which allows for a finer distribution of Li₂S within the electroactive material.

1. Introduction

Climate change is currently one of the largest challenges facing humanity, with CO₂ emissions driving drastic changes in the Earth's temperatures. As the transportation industry currently contributes to 26 % of overall CO₂ emissions [1], environmentally friendly and sustainable solutions must be developed for this sector. Lithium-ion batteries (LIBs) are currently seen as the most promising drivetrain technologies for electric vehicles. Commercially available LIBs use carbon-based anodes in their cell chemistries, as graphitic anodes exhibit several desirable properties such as low cost, abundance, low de-lithiation potential vs Li/Li⁺, high Li diffusivity, relatively low volume change during lithiation/de-lithiation and high electronic conductivity. Despite these excellent characteristics, graphite only stores 1 Li atom per 6 C atoms, thereby yielding a relatively low theoretical specific capacity of only 372 mAh g⁻¹ [2]. To fulfil the battery requirements of the future, safe anodes with high specific capacities and good fast charging properties up to 3 C are required.

Several metals and semiconductors such as Al [3], Si [4], Sn [5] and Ge [6] have attracted the interest of researchers for application as active anode materials for LIBs. These elements conventionally react with lithium via a conversion mechanism to produce various lithium-based intermetallic alloy compounds with high specific capacity. For example, the full lithiation of Sn results in the formation of the Sn₄Li₁₇ alloy at a theoretical specific capacity of 994 mAh g⁻¹. However, even though the metals and semiconductors exhibit high specific capacities, they suffer from excessive volume expansion during lithiation, which destroys the contact between active material particles over prolonged cycling and consequently causes capacity decay. To circumvent this degradation mechanism, several compounds such as metal oxides [7,8], phosphorous-based materials [9], nitrides [10] and chalcogenides have been investigated as potential anode materials for LIBs.

The SnS and SnS₂ chalcogenides are attractive as they exhibit high theoretical reversible capacities of 755 and 645 mAh g⁻¹, respectively, which are at least double that of graphite (372 mAh g⁻¹). However, their first cycle coulombic efficiencies may be low, as a significant part of the

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first cycle capacity is attributed to the irreversible conversion reaction to Li_2S and Sn (356 mAh g^{-1} for SnS and 564 mAh g^{-1} for SnS_2). Various techniques have been used to synthesize the tin-based chalcogenides with different morphologies, including 2D SnS_2 nanoplates [11], SnS_2 3D nanoflake-based hollow microspheres [12] and SnS nanobelts [13]. To improve the long-term cycle lifetime of tin sulfide electrodes, scientific approaches have focused on chemical and morphological modification via composite formation [14–17] and the application of surface coatings [18,19]. For example, Huang et al. prepared SnS_2 nano-powders on carbon-paper via the hydrothermal method to enable their use as binder-free anodes [20]. In another work, Syum et al. [16] grew SnS_2 on 3D hierarchical carbon nanotube-carbon cloth composites to improve the electronic conductivity of the SnS_2 -based anode. On the other hand, Li et al. [21] prepared $\text{SnS}_2\text{-SnO}_2$ heterostructures with carbon coatings as a cathode catalyst for aprotic Li-O_2 batteries. In an interesting application, Yang et al. [22] applied SnS_2 as a cathode material for thermal batteries operating at 500°C with a LiCl-KCl electrolyte. Wang et al. [23] investigated the shrinkage of SnS during calcination with glucose at different temperatures and evaluated the functionality of the cathode active material in solid-state batteries employing a sulfide-based electrolyte ($75\text{Li}_2\text{S-25P}_2\text{S}_5$). Finally, Huang et al. [24] used a simple freeze-drying and annealing synthesis approach to couple SnS with nitrogen-doped porous carbon nanosheets.

The diverse nature of tin sulfides has not only been recognized by the battery research community but also by various research groups in the field of photovoltaics [25,26], electrocatalysis [27] and photocatalytic hydrogen generation [28–30]. Due to its bandgap energy in the range between 2.18 – 2.44 eV, SnS_2 is a viable photocatalyst for hydrogen generation and can also work as an absorber material in solar cells. Similar to SnS_2 , SnS has been investigated for applications as photocatalysts [31], absorption materials in solar cells [32] and for hydrogen storage devices [33]. The low price, chemical stability and non-toxicity of the tin sulfides further contribute to their appeal. Finally, since tin and sulphur are abundant in the Earth's crust, SnS and SnS_2 are considered environmentally friendly and sustainable materials.

Both SnS and SnS_2 adopt layered crystal structures. SnS exists in the form of two stable structures with orthorhombic symmetry as well as three metastable structures with cubic symmetry. The orthorhombic modifications of SnS are low temperature (LT) $\alpha\text{-SnS}$ with the GeS-type structure (space group $Pnma$), shown in Fig. 1a, and the high

temperature (HT) $\beta\text{-SnS}$ with the TII-type structure (space group $Cmcm$). In the $\alpha\text{-SnS}$ crystal structure, the Sn^{2+} -ion is coordinated to three sulphur ions within the plane, with the Sn $5s^2$ lone pair of electrons “occupying” the last position in hypothetical tetragonal geometry stemming from the ZnS-type structure [34]. The $5s$ lone pair distorts the cubic ZnS-type structure, resulting in an orthorhombic unit cell. The transformation from $\alpha\text{-SnS}$ to $\beta\text{-SnS}$ occurs at 878 K via displacement of the Sn atoms along the $[1\ 0\ 0]$ direction and a decrease in the a/c axial ratio from $a/c > 1$ for $\alpha\text{-SnS}$ to $a/c < 1$ for $\beta\text{-SnS}$ [35].

SnS_2 adopts the CdI_2 -type structure with a trigonal unit cell and $P\text{-}3m1$ space group. In that structure, the Sn^{4+} ions are coordinated to six S^{2-} ions in octahedral geometry (Fig. 1b). In both SnS and SnS_2 , the Sn and S atoms are bonded by strong covalent bonds within the layers. Furthermore, the bonding between the layers of the tetrahedrally coordinated Sn atoms in SnS is slightly covalent, whereas the SnS_6 -octahedra layers in SnS_2 are loosely held together by Van der Waals bonds. Several approaches towards synthesizing SnS and SnS_2 have been reported. The hydrothermal and solvothermal methods are ubiquitous, representing the most commonly used methods to produce both SnS_2 [12,36–38], and SnS [17,39,40] bulk materials on the laboratory scale. Other more elaborate routes which are used to synthesize SnS_2 include the wet chemistry method [41], liquid-solid phase reaction [42], the ionothermal method [43], the sonochemical method [44] and the polyol route [45]. Apart from the solvothermal methods, the synthesis of bulk and single crystals of SnS is carried out mainly by the mechanochemical method [46], melt mixing [47] or crystal growing [48].

This work aims for the first time to understand and clarify the complex relations between crystal-chemistry, crystal-structure, particle morphology and electrochemistry for SnS and SnS_2 active anode materials and electrodes, which are synthesized via the same method. The precipitation reaction method was selected as the procedure to synthesize both compounds since it is simple, cost- and time effective and environmentally friendly as it does not require the use of harsh reactants. Although the synthesis of SnS via the precipitation reaction method has already been reported by Gou et al. [49], the procedures presented there had to be modified in this work in order to achieve phase pure SnS. On the other hand, phase pure SnS_2 could be prepared via the method already developed in our group [50]. The electrochemical properties of the SnS and SnS_2 active anode materials were compared to each other using the same electrode preparation and cycling procedures.

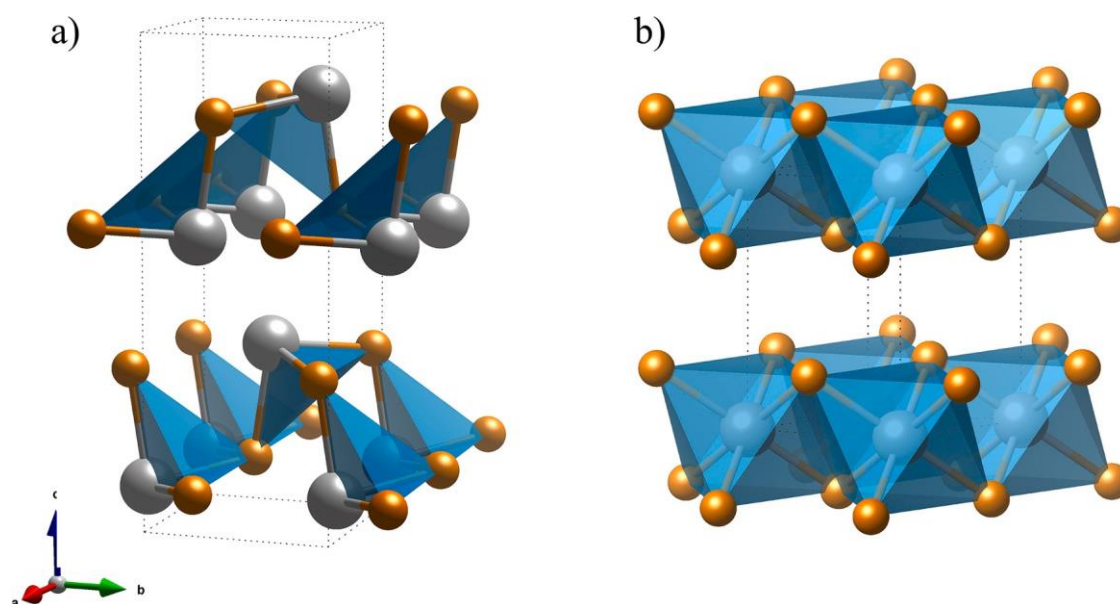


Fig. 1. Crystal structure of a) low temperature $\alpha\text{-SnS}$ (space group: $Pnma$), b) SnS_2 (space group: $P\text{-}3m1$). Sn atoms are represented as grey spheres and S atoms as orange spheres.

The results of galvanostatic cycling with potential limitation (GCPL), cyclic voltammetry (CV), rate capability, electrochemical impedance spectroscopy (EIS), and *in-situ* dilatometry combined with *ex-situ* X-ray diffraction (XRD) and *ex-situ* scanning electron microscopy (SEM) were used to comprehensively relate their electrochemical performance to their crystal structures and chemistries. To our knowledge, a similar, comparative study of the processing-structure-properties-performance relations for SnS and SnS₂ active anode materials does not yet exist in the literature.

2. Experimental

2.1. Synthesis of SnS and SnS₂

All chemicals used were of analytical grade without further purification (Table 1). For the synthesis of SnS via the precipitation reaction, the procedure by Gou et al. [49] had to be modified. Firstly, the sources of Sn and S, which are SnCl₂·2H₂O and thioacetamide (TAA), respectively, were weighed in a molar ratio 1:1. Accordingly, 0.9 g of SnCl₂·2H₂O and 0.3 g of TAA were each dissolved separately in 20 mL of deionized water. 15 mL of concentrated HCl was added to the aqueous solution of SnCl₂ in order to re-dissolve Sn(OH)Cl, which forms at higher pH values. The SnCl₂, water and HCl mixture was subsequently poured into the TAA water solution. The final solution was transferred into a round bottom Schlenk flask with volumetric capacity of 150 mL. The ground glass joint of the flask was capped with a glass stopper and the side arm of the flask was connected to a washing bottle filled with 1M NaOH solution to prevent the release of H₂S into the environment. Therefore, the reaction takes place under an H₂S-rich atmosphere, which prevents the oxidation of Sn²⁺ ions to Sn⁴⁺. The flask was heated to a temperature of 60°C in a bath containing paraffin oil placed onto a heating plate. The reaction was kept at 60°C for 3 h before the flask was taken out of the bath and allowed to cool down to room temperature. The black precipitate was separated from the liquid via vacuum filtration using a Büchner flask and borosilicate glass funnel with a built-in porous filter plate (with pore diameter of 1–1.6 µm). The product was washed three times with water and ethanol before being dried for 4 h at 60°C in a vacuum furnace.

For the synthesis of SnS₂, a similar procedure was performed using SnCl₄·5H₂O and TAA as sources of Sn and S, respectively. 0.701 g of

SnCl₄·5H₂O was dissolved in 8 mL of concentrated HCl and 0.301 g of TAA was dissolved in 20 mL of deionized water. Subsequently, The SnCl₄ + HCl solution was poured into the TAA solution and transferred to the round-bottom flask as described above for the SnS synthesis. The flask was again placed in a paraffin oil bath, which was this time heated to 80°C. As the temperature of the oil bath reached 70°C, the previously transparent solution of SnCl₄+HCl+TAA changed its colour to opaque yellow and at 80°C, a thick bright yellow precipitate was observed to form. The flask was taken out of the oil bath and the precipitate was separated from the liquid by vacuum filtration using the same set-up as applied for SnS synthesis. The yellow product was washed three times with deionized water and ethanol before it was placed to dry in a furnace for 4 h at 60°C.

2.2. Characterization methods

2.2.1. X-ray diffraction (XRD), Scanning electron microscopy (SEM) and transmission electron microscopy (TEM)

The purity of the products was investigated by X-ray diffraction using a Bruker D8 diffractometer (θ/2θ-geometry) with a copper radiation source (40 kV / 40 mA) and a Ni-filter. Using petroleum jelly, the powder samples were fixed onto a silicon mono-crystal sample holder. Signals were detected by a Lynxeye strip detector covering ±1.5° in 2θ at the same time. Once the XRD patterns were obtained, they were evaluated based on Rietveld-refinements using Topas4® software. The average crystallite size was determined from the full profile refinement using fundamental parameter (FP) peak type and volume weight mean column height based on integral peak breadth (LVol-IB). For the scanning electron microscopy, a small amount of the powders was placed on a piece of double-sided conductive carbon tape, which was fixed on a sample holder. A Carl Zeiss Supra 40 scanning electron microscope with Everhart-Thornley (ETD) and Through-Lens (TLD) detectors with a primary electron-beam energy of 5 keV was used to obtain the SEM images. For the *ex-situ* XRD and SEM measurements, the cycled SnS and SnS₂ electrodes were extracted from the cells in an argon filled glove box. The electrodes were washed three times with dimethyl carbonate solvent and dried before they were cut in half. One half was fixed onto the center of an XRD silicon mono-crystal sample holder with petroleum jelly and tightly sealed with the polycarbonate dome to ensure an oxygen- and moisture-free atmosphere during the XRD measurements. The second half of the electrode was placed on double-sided conductive carbon tape, which was fixed on a SEM sample holder and transferred to the SEM room in an air-tight vessel. The exposure to atmospheric air during SEM measurements was miniscule with air exposure not exceeding 10 sec.

Transmission electron microscopy (TEM) images were collected on the SnS and SnS₂ powders at 200 keV on a CM200 transmission electron microscope (TEM, Philips, Amsterdam, the Netherlands) with a LaB6 electron source. A 512 × 1024-pixel JUNGFRU detector with a 320 µm thick silicon sensor and a pixel size of (75 µm) was used.

2.2.2. X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS, Nexsa, Thermofisher) was employed to study the surface compositions of SnS and SnS₂. Al Kα radiation at 72 W and a pass energy of 200 eV, a spot size of 400 µm, "Standard Lens Mode", CAE Analyser Mode, an energy step size of 1 eV for the survey spectrum (50 passes), and integrated flood gun were used. Samples were analyzed prior to and after the surface was treated with Ar-clusters (1000 Ar atoms, 6000 eV, 60 s). The high-resolution spectra (step size 0.1 eV, 0.05 eV for Sn and S) of the single elements were acquired with 50 passes at pass energies of 50 eV. Peak deconvolution was performed with Thermo Advantage v5.9925 Build 06702 using Simplex algorithm with Gauss-Lorentz Product.

2.2.3. Electrochemical investigation

The electrochemical investigation of the SnS and SnS₂ active anode

Table 1

The summary of all the material used both for the syntheses of the materials, preparation of the electrodes and construction of the coin cells.

Material	Vendor	Purity	State	Role
SnCl ₂ ·2H ₂ O	Sigma	≥	Powder	Reactant, source of Sn
SnCl ₄ ·5H ₂ O	Aldrich Alfa Aesar	99.99%	Powder	Reactant, source of Sn
Thioacetamide (TAA)	Alfa Aesar	99 %	Powder	Reactant, source of S
Conc. HCl	Carbon	/	Liquid	Solvent
black C45	Honeywell Imerys	/	Powder	Conductive additive
Polyvinylidene fluoride (PVDF)	Solvay	/	Powder	Binder
N-methyl-2-pyrrolidone (NMP)	Sigma Aldrich PI-KEM	99% 99.9 %	Liquid Bulk	Solvent Counter/reference electrode
1M solution of LiPF ₆ in 3:7 weight mixture of ethylene carbonate (EC) and ethyl methyl carbonate (EMC) with 2 wt% of vinylene carbonate (VC)	Soulbrain	/	Liquid	Electrolyte
Dimethyl-carbonate (DC)	Sigma Aldrich	≥ 99%	Liquid	Solvent

materials was conducted in 2016 coin cells in which the tin-sulfide electrode acted as the working electrode and Li metal was used as the counter-electrode. The working electrode consisted of 80 wt.% of active material (SnS or SnS₂), 10 wt.% conductive additive C45, and 10 wt.% of binder (PVDF (polyvinylidene difluoride)). To prepare the electrode slurry, a 6 wt.% PVDF in NMP (N-Methyl-2-Pyrrolidone) solution was used as the source of PVDF binder and liquid solvent. Appropriate amounts of the active material (SnS or SnS₂) and the conductive additive were mixed using a mortar and pestle and added to the 6 wt.% PVDF in NMP solution in order to maintain the 80:10:10 ratio. The slurry was stirred overnight using a magnetic stirrer, after which it was casted onto a copper current collector using a doctor-blade with a gap thickness of 60 μm . The coated electrodes were allowed to dry in air at 60°C on the heated substrate of the coating machine. Once the electrode sheets were completely dried, several discs with a diameter of 15 mm were punched, placed into a Büchi® glass oven and heated at 120°C under vacuum for 12 h. Finally, the electrodes were introduced into an Ar filled glove box without any contact with air.

Coin cells were constructed using the as-prepared working electrodes and Li metal. A single trilayer polypropylene/polyethylene/polypropylene (PP/PE/PP) membrane Celgard 2325 was used as the separator with 75 μL of the 1M LiPF₆ in EC/DMC with 2 wt.% VC as electrolyte. A Maccor battery tester (Maccor Series 4000) was used for the galvanostatic cycling with potential limitation (GCPL) and rate capability tests, whereas the raw data were further evaluated using the Origin2021G software. During the GCPL measurements, the cells were cycled for 100 cycles in the voltage window of 1-0.01 V vs Li/Li⁺ with an applied specific current of 100 mA g⁻¹. For the rate capability tests, the cells were discharged at a sequential specific current of 100, 200, 400, 800, and 1000 mA g⁻¹ and back to 100 mA g⁻¹ for 10 cycles at each rate. In all cases, a specific charge current of 100 mA g⁻¹ was used. Cyclic voltammetry measurements were carried out on an Arbin potentiostat (LBT 96-channel battery tester). The scanning rate was set to 0.2 mV s⁻¹ in the voltage window from 0 to 3 V vs Li/Li⁺. A BioLogic MPG-2 potentiostat was used for the electrochemical impedance measurements, which were conducted in the frequency range from 20 kHz to 100 mHz with a sinus amplitude of 10 mV. The impedance data were fitted

and analysed using AfterMath Electrochemical Studio. Electrochemical *in-situ* dilatometry measurements were conducted using a three-electrode ECD-3-nano dilatometry cell (EL-Cell). Once the cell was assembled and connected to the potentiostat, it was allowed to relax for 30 h and the voltage was recorded every 30 s before it was discharged and charged using a constant current of 100 mA g⁻¹ in a voltage window from 0.01 to 1.0 V vs Li/Li⁺.

3. Results and discussion

3.1. Physico-chemical investigations

By following the original procedure as reported by Gou et al. for the synthesis of SnS [49], a light grey powder was obtained as the precipitate, which was determined to be pure SnO₂ via powder x-ray diffraction (PXRD) (See supplementary information, Fig. S1). Generally, Sn-hydroxide complexes such as Sn(OH)Cl, which can be formed when SnCl₂ reacts with water [51] at higher pH values, are considered as precursors for SnO₂. The addition of concentrated HCl to the SnCl₂ aqueous solution lowered the pH values of the solution (~ 2) and may have dissolved the hydroxy-chloride complex. Therefore, after the addition of HCl, no SnO₂ was formed in the precipitation reaction.

The measured PXRD patterns of the as-prepared SnS sample with corresponding Rietveld refinements are shown in Fig. 2a. In order to fit the measured pattern via Rietveld refinement, two α -SnS phases with orthorhombic cell structure in the *Pnma* space group had to be included, with each exhibiting slightly different lattice parameters. This was also required to account for the anisotropic crystallization of SnS, as the results of the Rietveld refinement showed that strict periodicity was better developed in some crystallographic directions rather than in others.

The Rietveld refinement of the measured PXRD pattern in Fig. 2b showed that the product of the reaction using tin (IV) chloride was SnS₂ with the basic trigonal cell and *P-3m1* space group. Both SnS and SnS₂ exhibited preferred orientations; SnS in the [1 0 0] direction and SnS₂ in the [0 0 1] direction. The detailed crystallographic parameters obtained by Rietveld analysis are given in Table 2. The broad peaks along with the

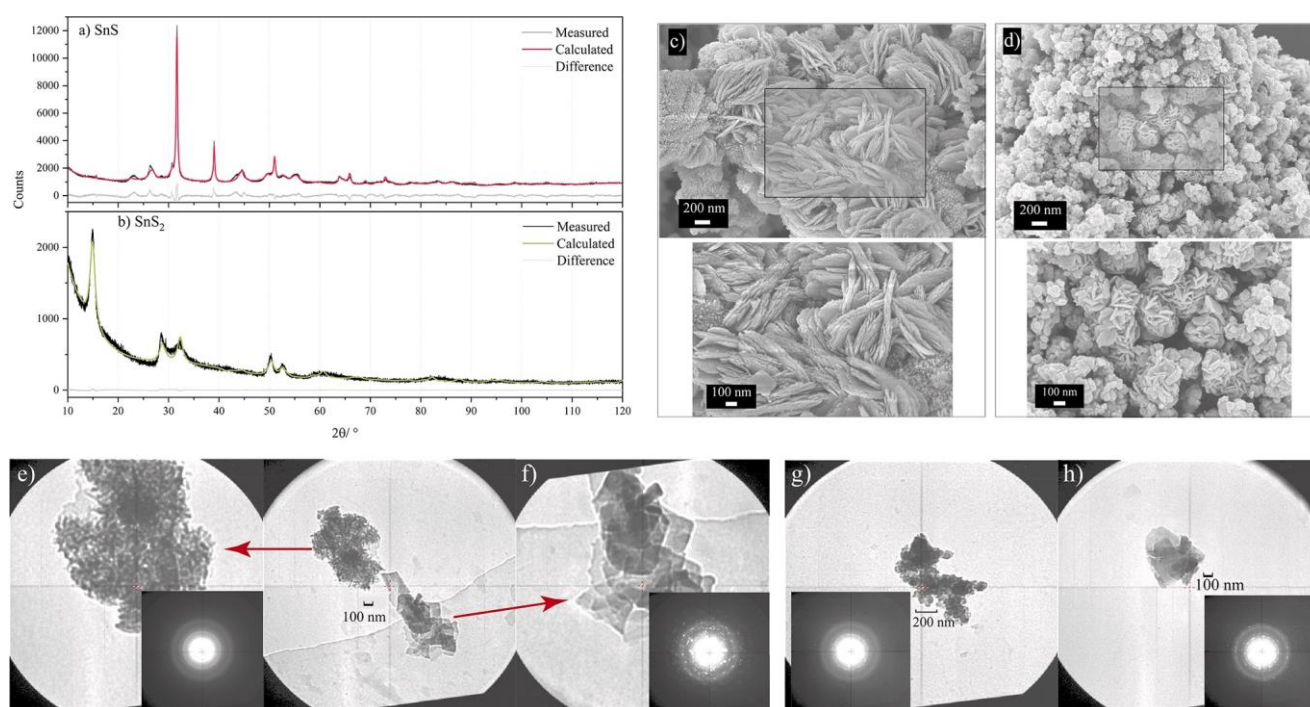


Fig. 2. PXRD patterns of as-prepared a) SnS and b) SnS₂ with corresponding Rietveld refinement. SEM images of c) SnS and d) SnS₂ powders along with images with higher magnification and e) TEM images with the respective SAED patterns of e), f) SnS and g), h) SnS₂.

Table 2 The details of the Rietveld refinement of SnS and SnS₂ products both synthesized via precipitation reaction.

Material	Conditions of precipitation reaction	Phases/Space group	Lattice Parameters [Å]	Cell Volume [Å ³]	Crystallite size [nm]	R _{wp}
SnS	Sample after synthesis at 60 °C with SnCl ₂ and TAA as sources of Sn and S, respectively	SnS/ <i>Pnma</i>	$a = 11.34 \pm 0.09$	193.06 ± 0.07	45	6.46
			$b = 4.08 \pm 0.01$			
		SnS/ <i>Pnma</i>	$c = 4.17 \pm 0.01$	195.49 ± 0.09	10	
SnS ₂	Sample after synthesis at 80 °C with SnCl ₄ ·5H ₂ O and TAA as sources of Sn and S, respectively	SnS ₂ / <i>P-3m1</i>	$a = 11.41 \pm 0.04$	$67.149 \pm$	8	9.61
			$b = 4.08 \pm 0.09$			

higher background in both patterns indicate that the as-synthesized materials were nano-crystalline and/or exhibited some amorphous contents, with SnS having slightly larger crystallites compared to as-prepared SnS₂; see Table 2. In addition, the relative amount of amorphous material seemed to be higher in the case of SnS₂.

The SEM images of the as-prepared SnS and SnS₂ products are shown in Fig. 2c and d, respectively. Both samples exhibited a heterogeneous morphology. SnS consisted of 1) nano-plates arranged in flower-like structures of 500–600 nm and 2) round-shaped secondary particles with primary particle sizes of 5–10 nm. On the other hand, SnS₂ was composed of nano-plates arranged in flower-like structures, which were much smaller in size, 100–250 nm and 2) irregularly shaped nanoparticles with a size of 50–100 nm.

The crystallinity of the samples was further investigated using transmission electron microscopy (TEM). The TEM images, along with corresponding selected area electron diffraction (SAED) patterns, are shown in Fig. 2e–h. Four clusters were selected for the TEM studies, which was in accordance with the heterogeneous nature of the SnS and SnS₂ samples as determined by PXRD and SEM. Fig. 2e and g show two amorphous clusters which were part of the SnS and SnS₂ samples, respectively. The measured SAED patterns resemble that expected from an amorphous material with characteristic halo rings and the absence of distinct diffraction spots. On the other hand, Fig. 2f and h show the crystal clusters of SnS and SnS₂ with their corresponding SAED patterns. Both SAED patterns are characterized by bright, periodically arranged spots superimposed on diffuse rings, which is characteristic of a polycrystalline, nanocrystalline material. The TEM investigations, therefore, confirm the conclusions deduced from the Rietveld refinements of the measured PXRD results, showing that both SnS and SnS₂ exhibited a heterogeneous morphology consisting of co-existing nanocrystalline and amorphous clusters.

The presence of any surface impurities formed during the precipitation reactions, as well as the oxidation states of Sn in both samples, were investigated with X-ray photoemission spectroscopy (XPS). In both samples, a small amount of impurities was found, mostly oxygen and carbon, which were confirmed by the O 1s and C 1s peaks. The samples

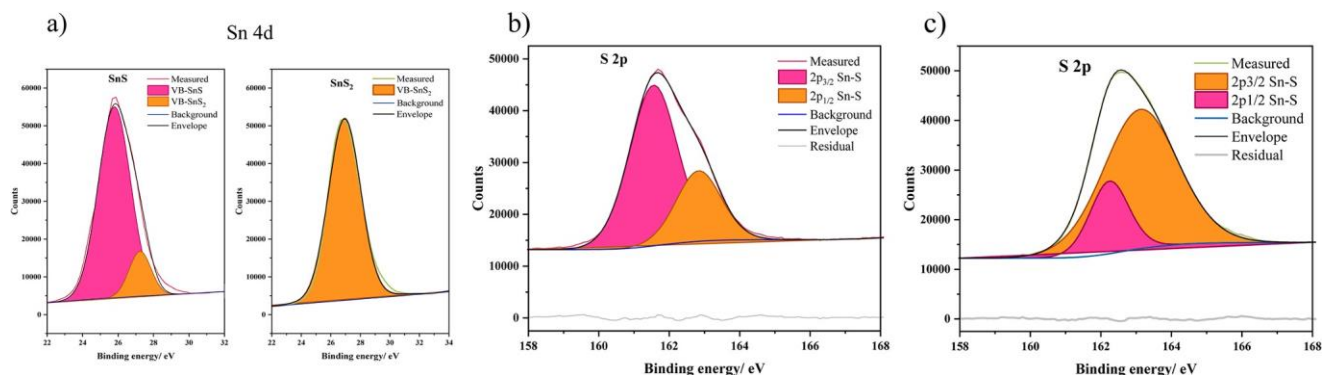
were etched several times with Ar-clusters, after which the impurity concentration was significantly reduced, indicating that the impurities were localized at the sample surfaces. The XPS survey spectra, along with Sn 3d spectra of the products, can be found in the supplementary information (Fig. S2). Sn 4d and S 2p spectra of the as-prepared SnS (red line) and SnS₂ (green line) are presented in Fig. 3a, b, and c, respectively. The Sn 4d valence band XPS spectra of both samples show strong peaks in the binding energy region from 20 to 30 eV. The SnS₂ sample exhibited a single maximum at 26.9 eV, whereas the SnS sample could be fitted with two peaks, one with a maximum at 26.6 eV and the other with a maximum at 24.7 eV. According to the NIST-XPS database [52], the Sn 4d spectrum for SnS has a peak at 24.9 eV, whereas the peak in the Sn 4d spectrum for SnS₂ occurs at 26.7 eV. The presence of two maxima as observed for SnS could therefore stem from some amount of SnS₂ at the surface of the SnS particles, as indicated by the peak deconvolution in Fig. 3a. However, the splitting of the binding energy from electrons in the 4d_{3/2} and 4d_{5/2} orbitals could not be resolved in the spectra.

The S 2p spectra for SnS and SnS₂ are shown in Fig. 3b and 3c, respectively. The resulting peaks were fitted using two orbital energy levels, corresponding to 2p_{1/2} and 2p_{3/2}. After the peak deconvolution, the two peaks were separated by approx. 1.3 and 1.4 eV for the SnS and SnS₂ samples, respectively, which corresponds fairly well to literature data for metal sulfides [53]. The fitted binding energies of the main features of Sn and S for the SnS and SnS₂ samples are summarised in Table 3. According to the element quantification, the SnS₂ sample showed stoichiometric purity with a molar Sn:S ratio of 1:2. However, the SnS sample, which should have a molar Sn:S ratio of 1:1, exhibited an experimental ratio of 1:1.25 ratio. This supports our assumption of

Table 3

Fitted binding energies of Sn valence spectra and S 2p spectra with Sn to S atomic

Material	Sn 4d	S 2p _{1/2}	S 2p _{3/2}	Sn/S-ratio
SnS	25.7	162.9	161.6	1: 1.25
SnS ₂	26.9	163.9	162.5	1: 2

**Fig. 3.** XPS of a) Sn 4d spectra of SnS and SnS₂ and S 2p spectra of b) SnS and c) SnS₂.

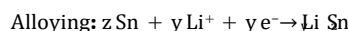
the presence of SnS_2 impurities at the surface of the SnS particles. However, since the XRD analysis did not indicate any impurities, we assume that there was no bulk oxidation of the sample to SnS_2 . Regardless, the results of the XPS analysis indicate the comparative difficulty in synthesizing phase-pure SnS , further emphasizing the need to modify the synthesis procedure as reported by Gou et al. [49] via 1) adding concentrated HCl to the SnCl_2 aqueous solution in order to re-dissolve the hydroxy-chloride complex, and 2) conducting the reaction in an H_2S -rich atmosphere to avoid the oxidation of Sn^{2+} ions to Sn^{4+} , which can quickly occur due to the exposure to oxygen.

SEM was performed on the as-prepared electrodes to characterize the particle morphologies and distribution of the C45 conductive additive prior to the electrochemical tests. The SEM images of uncycled SnS and SnS_2 electrodes are shown in Fig. 4a and b, respectively. According to the micrographs, the electrode processing destroyed the initial heterogeneous morphology of the powder samples, and in both cases, the primary particles of active material lost their regular hexagonal shape, adopted irregular morphologies, and tended to agglomerate. The PXRD patterns of pre-cycled electrodes are presented in the supplementary information (Fig. S3). According to the data, no phase transformations of the SnS and SnS_2 active electrode materials were observed to occur as a result of the electrode processing.

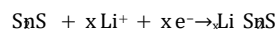
3.2. Electrochemical investigations

The electrochemical investigations were performed in half-cells in 2016-coin cell geometry with Li metal as the counter-electrode. Thus, the discharge reaction corresponds to the lithiation of the tin sulfides, which would occur during the charge reaction in a classical full-cell configuration. The electrodes containing SnS and SnS_2 as the active electrode materials were cycled for 100 cycles using a current rate of 100 mA g^{-1} in the voltage range from 0.01 to 1 V vs Li/Li^+ . The voltage profiles measured for the SnS and SnS_2 working electrodes at the 1st, 2nd, 10th, 50th and 100th discharge and charge cycles are presented in Fig. 5a and b, respectively.

The work of Cupid et al. [54] explored the thermodynamics of the lithiation of SnS_2 and SnS electroactive materials and presented calculations showing their lithiation pathways and equilibrium phase formation during the reaction with Li . According to this thermodynamic assessment, the full lithiation of SnS and SnS_2 should result in the formation of $\text{Li}_{17}\text{Sn}_4$, Sn and Li_2S with a first discharge capacity of 1111 and 1209 mAh g^{-1} , respectively. During lithiation, both SnS and SnS_2 are expected to exhibit the conversion and alloying reactions according to the equations:



In the conversion reaction, the tin sulfide compound reacts with Li to yield Li_2S and Sn . Further lithiation triggers the alloying reaction between Sn and Li , during which various Li-Sn phases are formed. However, in the case of SnS_2 , an initial intercalation reaction occurs prior to the conversion mechanism according to the equation:



as the 4+ valence state of Sn can be reduced to 2+, during which the Li ions can be intercalated into the SnS crystal structure to form Li_xSnS compounds. Although the Li ions preferably occupy inter-layer 1b Wyckoff positions (octahedral vacancies) in SnS_2 , they can also occupy the inter- and intra-layer 2d positions (tetrahedral vacancies) [55].

In our work, SnS yielded a specific discharge capacity of 1117 mAh g^{-1} in the first discharge vs Li/Li^+ , whereas the first discharge capacity of SnS_2 was 1248 mAh g^{-1} . However, in both cases, a large portion of the initial discharge capacity was lost due to the irreversibility of the conversion reaction, resulting in first cycle coulombic efficiencies of 46 and 39 % for SnS and SnS_2 , respectively. On the second discharge in the voltage window between 0.01 and 1 V vs Li/Li^+ , SnS exhibited a reversible capacity of 448 mAh g^{-1} (the theoretical value is 783 mAh g^{-1}), whereas the reversible capacity of SnS_2 was 460 mAh g^{-1} (theoretically 645 mAh g^{-1}). It should be mentioned that higher charge capacities could be attained if voltage cut-offs higher than 1.0 V vs Li/Li^+ were used. However, a cut-off voltage of 1.0 V vs Li/Li^+ was selected for our investigations, as it is realistic for the potential application of SnS and SnS_2 as anodes vs conventional cathode materials (e.g., LiFePO_4 with the olive structure, $\text{LiNi}_x\text{Mn}_y\text{Co}_{1-x-y}\text{O}_2$ with the layered structure, $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_2$ with the spinel structure) in LIBs.

The as-prepared electrodes were also tested by cyclic voltammetry at a scan rate of 0.2 mVs^{-1} in the voltage window between 0 and 3 V vs Li/Li^+ . The typical cyclic voltammograms for SnS and SnS_2 are presented in Fig. 5c. The voltammogram of SnS shows three distinguishable peaks at ~ 2.3 , 1.3 and 0.4 V vs Li/Li^+ in the first cathodic sweep, whereas the voltammogram of SnS shows only two peaks at ~ 1.4 and 0.5 V vs Li/Li^+ . The first cathodic peak at ~ 2.3 V vs Li/Li^+ for SnS_2 is associated with the intercalation of Li ions into its crystal lattice, whereas the second and third peaks correspond to the conversion and alloying reactions, respectively. Since no peaks were recorded in the first cathodic sweep of SnS at potentials higher than 1.4 V vs Li/Li^+ , the cyclic voltammetry measurements confirmed that no Li ions are intercalated into the SnS crystal structure. This is expected as the oxidation state of Sn in SnS is 2+, and a reduction of Sn^{2+} would result in the formation of metallic Sn and the onset of the conversion reaction of SnS to Li_2S and Sn . In the anodic sweep, one major peak can be distinguished at ~ 0.7 V and ~ 0.6 V vs Li/Li^+ for SnS and SnS_2 , respectively, corresponding to the de-alloying reaction of the Li_xSn_y phases. At higher potentials of ~ 1.5 V vs Li/Li^+ , a shallow peak can be observed in the first anodic sweep for

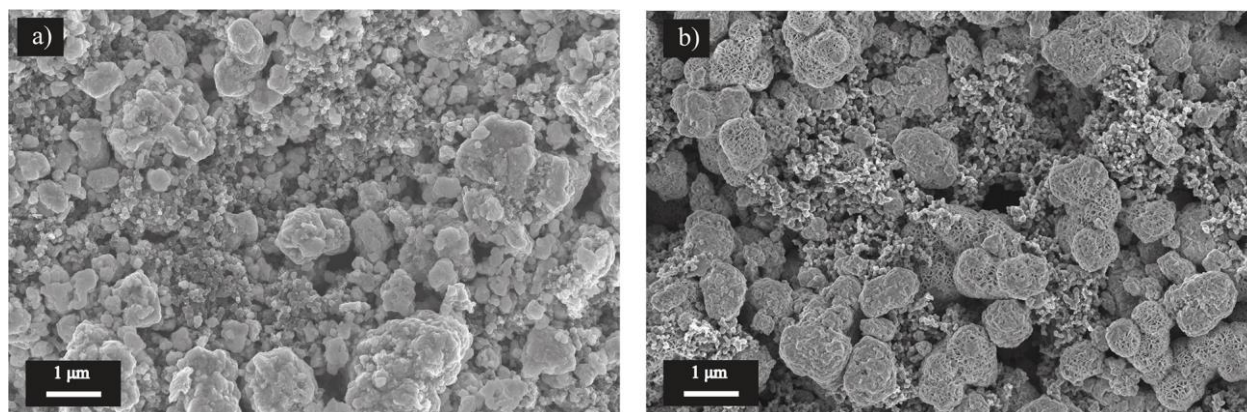


Fig. 4. SEM images of as-prepared a) SnS and b) SnS_2 electrodes.

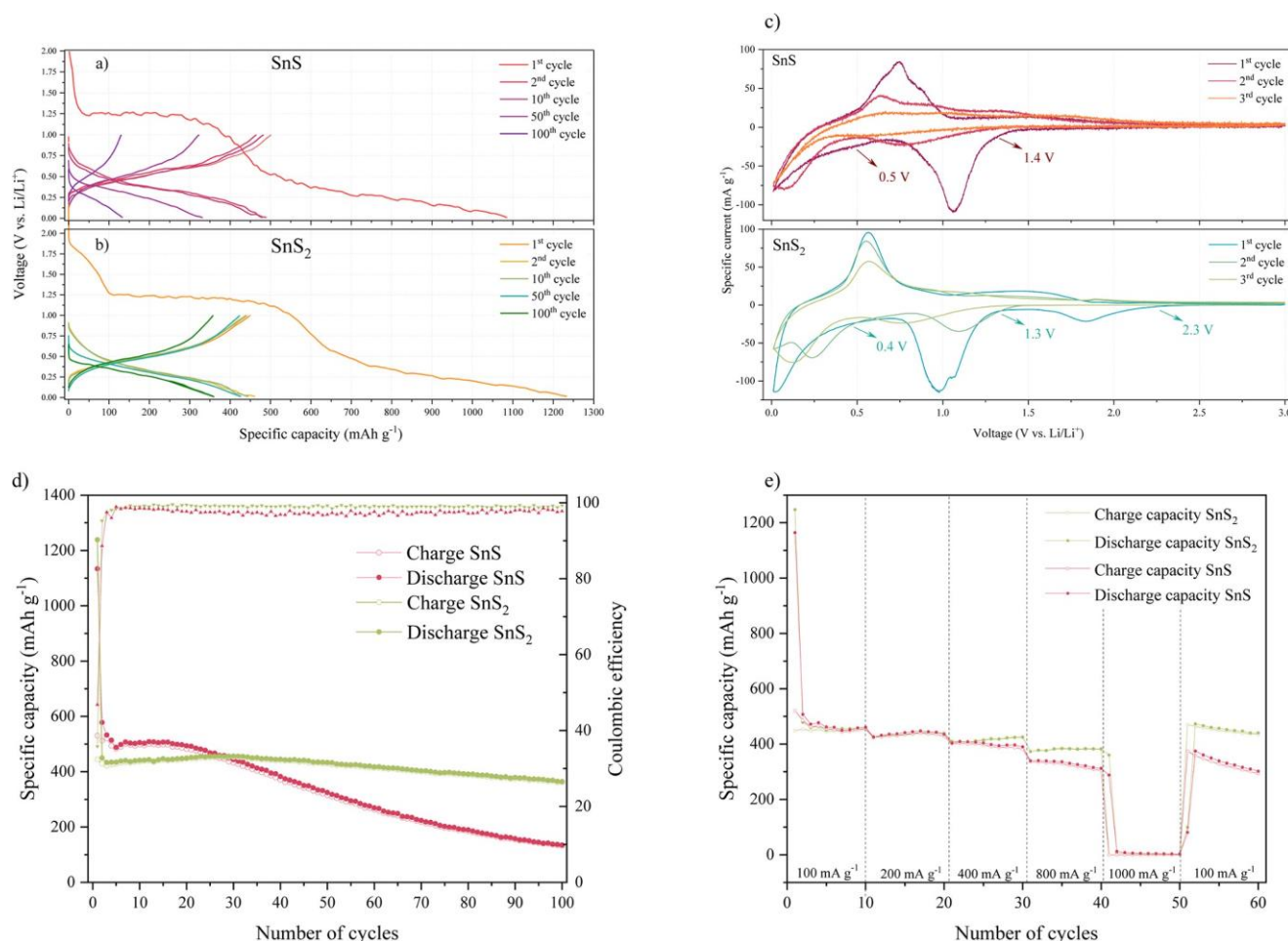


Fig. 5. The galvanostatic cycling data of a) SnS and b) SnS₂ electrodes presented with voltage profiles of the 1st, 2nd, 5th, 10th, 50th and 100th cycles. The cycling was conducted in a voltage window from 0.01 to 1 V vs Li/Li⁺ with an applied specific current of 100 mA g⁻¹. c) Cyclic voltammograms of SnS and SnS₂. The measurements were conducted in the voltage range from 0 to 3 V vs Li/Li⁺ at a scanning rate of 0.2 mV s⁻¹. d) Specific capacity versus cycle number with calculated coulombic efficiency for both SnS (red) and SnS₂ (green). e) Rate capability tests at sequential discharge rates of 100, 200, 400, 800, and 1000 mA g⁻¹ and back to 100 mA g⁻¹ for 10 cycles at each rate.

SnS and SnS₂, but this effect is absent in all other anodic scans. Although this shallow peak may be associated with the oxidation of Sn to a characteristic tin-sulfide, it ultimately confirms that the conversion reaction to Li₂S and Sn is highly irreversible for both SnS and SnS₂, as it does not appear in successive scans.

The specific capacities, along with the coulombic efficiency of the SnS and SnS₂ active electrode materials, recorded during 100 discharge and charge cycles are presented in Fig. 5d. With a specific capacity of 369 mAh g⁻¹ after 100 cycles, SnS₂ performed better than SnS, which exhibited, at most, a third of that capacity with only 133 mAh g⁻¹. After 100 cycles, SnS lost ~70 % of its initial reversible capacity, which is in accordance with existing data in the literature. Huang et al. [24] also investigated pure SnS as an anode material for LIBs. They cycled their electrodes in the voltage window between 0 and 3.0 V vs Li/Li⁺ and reported a capacity retention of only 8.4 % after 100 cycles at a current rate of 100 mA g⁻¹. According to their work, the final capacity of the SnS electrode was 83.2 mAh g⁻¹. They were only able to improve the performance of SnS via an *in-situ* coupling of SnS with nitrogen-doped porous carbon nanosheets. With this approach, a reversible capacity of 851.1 mAh g⁻¹ could be attained after 200 cycles at the same current rate.

SnS₂ lost only ~20 % of its practical reversible capacity, going from 460 to 369 mAh g⁻¹. In one of the more recent works, Huang et al. [20] also investigated the electrochemical performance of SnS₂. They showed a reversible capacity of 400.3 mAh g⁻¹ after only 60 cycles in the voltage

window between 0 and 2.5 V vs Li/Li⁺ at a specific current of 200 mA g⁻¹. They could only improve this performance by using the hydrothermal method to deposit SnS₂ onto carbon paper, thereby designing binder-free SnS₂ electrodes. After 60 cycles, a discharge capacity of 2073.8 mAh g⁻¹ could be attained, although a mechanism which explains this larger than expected capacity increase was not given.

Although SnS₂ exhibits better capacity retention than SnS, the electrochemical performance of both materials is poorer than that of graphite-based electrodes. This is due to the high irreversible capacity losses on the first cycle due to the conversion mechanism, as well as the volume expansion of the Sn, which leads to electrochemical performance decay. However, Fig. 6 shows that the as-prepared SnS₂ electrodes exhibit better capacity retention than electrodes prepared using pure Sn as the active anode material as observed from investigations in the literature [56–60]. For example, electrodes fabricated using pure Sn nanoparticles from Zhu et al. [56], and Seo et al. [57], as well as those prepared from bare Sn powder from Wang et al. [60] show rapid capacity losses in the first few cycles. However, in the works of Guo et al. [58,59], the capacity retention of hollow Sn nanospheres is better than that of pure Sn and SnS over 100 cycles but worse than that of SnS₂ presented in this work.

In order to examine the electrochemical behavior of SnS and SnS₂ at different specific discharge currents, rate capability tests were performed on the electrodes at sequential discharge rates of 100, 200, 400, 800, and 1000 mA g⁻¹ and back to 100 mA g⁻¹ for 10 cycles at each rate

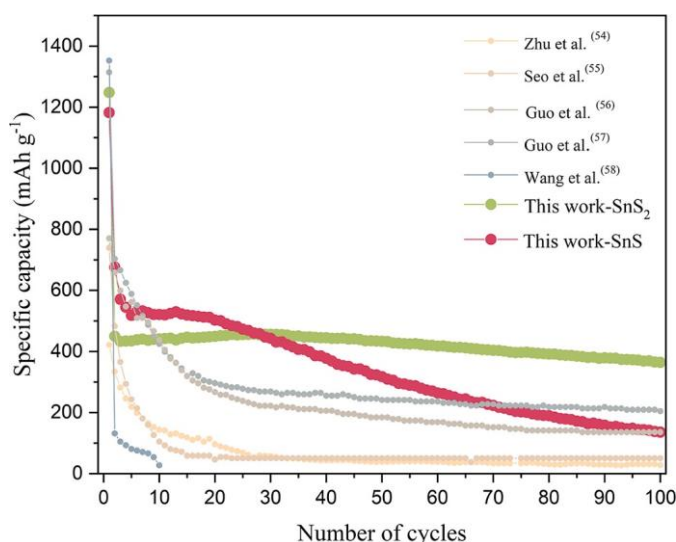


Fig. 6. Comparison of cycling performance of as-prepared SnS and SnS₂ and pure Sn available in literature.

(Fig. 5e). In all cases, a constant specific charge current of 100 mA g⁻¹ was used, and cycling was performed in the voltage window between 0.01 and 1.0 V vs Li/Li⁺. The first discharge capacity at a current rate of 100 mA g⁻¹ was found to be 1146 and 1247 mAh g⁻¹ for SnS and SnS₂, respectively. At the end of the 10th cycle, SnS and SnS₂ exhibited capacities of 469 and 457 mAh g⁻¹, respectively. Furthermore, after every successive 10th cycle, SnS yielded capacities of 447 mAh g⁻¹ (specific current: 200 mA g⁻¹), 420 mAh g⁻¹ (specific current: 400 mA g⁻¹), 358 mAh g⁻¹ (specific current: 800 mA g⁻¹) and 3 mAh g⁻¹ (specific current: 1000 mA g⁻¹). The capacities yielded by SnS₂ at the same specific currents are: 438 mAh g⁻¹ (specific current 200 mA g⁻¹), 425 mAh g⁻¹ (specific current: 400 mA g⁻¹), 382 mAh g⁻¹ (specific current: 800 mA g⁻¹), and only 1 mAh g⁻¹ at 1000 mAh g⁻¹. After the current rate was reset to the initial value of 100 mA g⁻¹, SnS exhibited a discharge capacity of 301 mAh g⁻¹ and SnS₂ a discharge capacity of 440 mAh g⁻¹. For a better overview, the yielded discharge and charge capacities after 10 cycles at each current rate are presented in Table 4.

The results of the rate-capability testing showed the superposition of two effects. One is the long-term capacity fading of the active anode materials, whereas the other is the capacity of the material delivered at a specific current rate. According to Fig. 5d, SnS was stable only between 0 and 30 cycles, whereas SnS₂ was stable up to the 100th cycle. Therefore, the last 10 cycles at 100 mA g⁻¹ for the rate capability testing of SnS showed lower capacities than those for SnS₂ since the measurement already exceeded the 30-cycle stability limit for SnS. However, the results still generally show that SnS₂ performs better compared to SnS.

After the 1st, 10th, 20th, 50th and 100th charge cycle at a specific current of 100 mA g⁻¹, the cells were opened, and the SnS and SnS₂ working electrodes were extracted and washed with dimethyl-carbonate

Table 4 Capacities yielded during cycling at different current rates. The capacities indicated are the capacities after 10 cycles at respective current rate.

Current rate (mA g ⁻¹)	SnS		SnS ₂	
	Discharge capacity (mAh g ⁻¹)	Charge capacity (mAh g ⁻¹)	Discharge capacity (mAh g ⁻¹)	Charge capacity (mAh g ⁻¹)
100	469	463	457	454
200	447	439	438	440
400	420	413	425	423
800	358	351	382	381
1000	3	0	1	0

solvent to prepare them for *post-mortem*, *ex-situ* XRD and SEM measurements to investigate the phase and morphological evolution of the electrodes during cycling. The XRD patterns, along with the Rietveld refinement of the measured data and the SEM images of SnS and SnS₂, are shown in Figs. 7 and 8, respectively. All measured PXRD patterns of the SnS and SnS₂ electrodes show a broad peak at 2θ ~ 20° (indicated by the dotted red line), which corresponds to the polycarbonate dome used to ensure an inert atmosphere during the measurements. Peaks attributed to the Cu-foil electrode substrate were recorded at 2θ = 43.4, 50.5, 74.2, 90.0 and 95.3° and could be observed in all *ex-situ* XRD patterns.

The peak attributed to the dome is indicated by the red dotted line, whereas those attributed to the Cu substrate are indicated by black lines.

Apart from the reflections originating from the polycarbonate dome and Cu substrate, the XRD pattern of the SnS electrode after the first charge cycle revealed several other reflections. The products of the conversion reaction of SnS to Sn and Li₂S could be detected with reflections at 2θ ≈ 31, 32, 44, 45, 55, 63, 65, 80° for Sn and reflections at 2θ ≈ 24, 40° for Li₂S. As the cycling continued, the peaks associated with the Sn and Li₂S phases broadened, indicating the amorphization of the electrode active material particles. After 100 cycles, the peaks were barely present. In all cases, the Li₁₇Sn₄ phase was detected in the charged state of the electrodes with two reflections at 2θ ≈ 24, and 40°, suggesting a sluggish Li-ion diffusion within the electrode. The SEM image of the electrode after the first charge cycle showed highly agglomerated particles with isolated chain-like Sn particles. Over the course of cycling, the morphology of the particles at the electrode surfaces remained similar, and any differences between the SEM images could be attributed to the fact that different positions from different electrodes were analyzed. Details of the Rietveld analysis for both SnS and SnS₂ are presented in the supplementary info (Table S1).

Contrary to XRD patterns of the SnS electrodes, in which characteristic reflections for Sn and Li₂S could be identified, there were no prominent peaks for Sn and Li₂S in the measured XRD patterns of the SnS₂ electrodes. However, the peak associated with the Li₁₇Sn₄ phase at 2θ ≈ 24° was observed and became more pronounced by the 100th cycle. The morphology of the electrodes did not undergo any significant changes influenced by cycling. After the first cycle, a film-like layer was formed on top of the particles after contact with the electrolyte. However, in all cases, the particle agglomerates were retained, and no cracking could be observed, neither in the active material particles nor in the SEI layer.

During the delithiation/ lithiation, tin particles experience extensive volume expansion and contraction (Sn particles can expand for up to 270 % [61–63]). This volume expansion occurs due to changes in the chemical composition and subsequent formation of several Li-Sn alloys, which have different crystal structures and densities. To determine the dimensional changes of the SnS and SnS₂ electrodes during lithiation and delithiation, electrochemical *in-situ* dilatometry measurements were conducted. The results of the dilatometry measurements are presented in Fig. 9. The relative dimensional change of the working electrode is expressed by normalized height changes according to the formula:

$$\text{Height change} = \frac{l - l_0}{l_0} \cdot 100 (\%), \text{ where } l \text{ is the displacement during the}$$

measurement and l_0 is the initial thickness of the electrode active layer. The initial thickness of the SnS electrode was 28 μm, whereas that of the SnS₂ electrode was 39 μm. The thickness difference between the two electrodes may be attributed to the difference in the particle size and the porosities of the electrodes. When comparing the SEM images of uncycled SnS and SnS₂ electrodes shown in Fig. 4a and b, respectively, it can be observed that the SnS particles were more densely packed than the SnS₂ particles. In fact, the calculated porosity of the SnS electrodes was ~ 59 %, whereas that of the SnS₂ electrodes was ~ 80 %. The details of the porosity calculations are presented in the supplementary information. After the first discharge cycle, in which several Li_xSn_{1-x} phases were formed, the SnS electrode exhibited a dimensional change of ~ +49 %, whereas that of the SnS₂ electrode was ~ +30 %. As the electrodes were

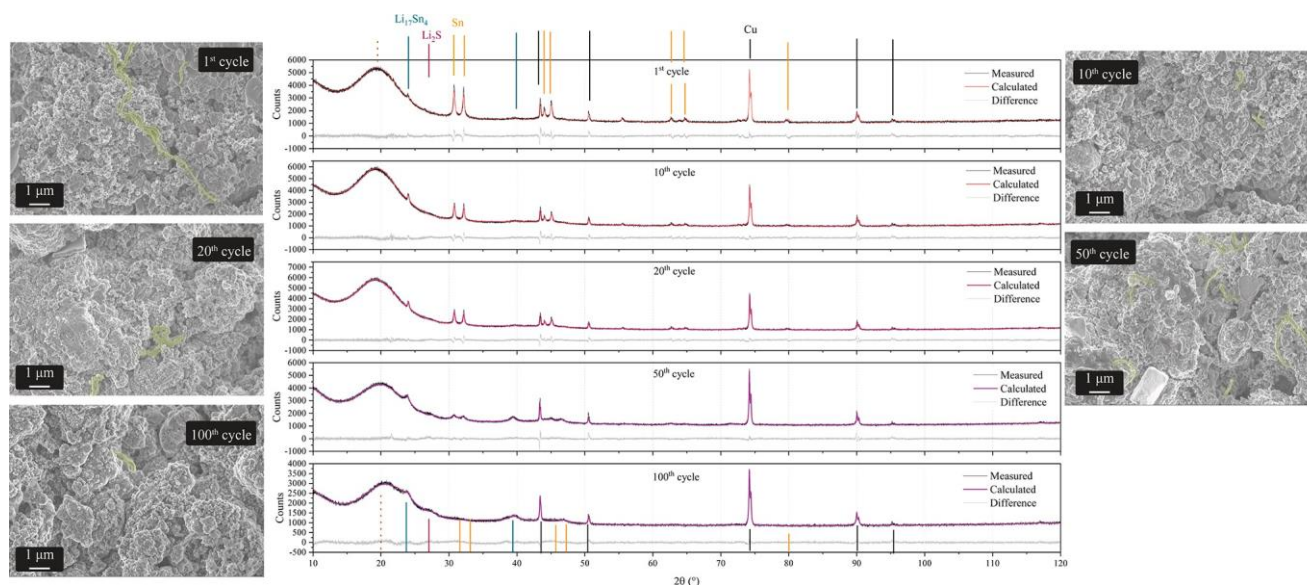


Fig. 7. Ex-situ XRD pattern of SnS electrodes after 1st, 10th, 20th, 50th and 100th charge cycles with corresponding Rietveld analyses and *ex-situ* SEM images.

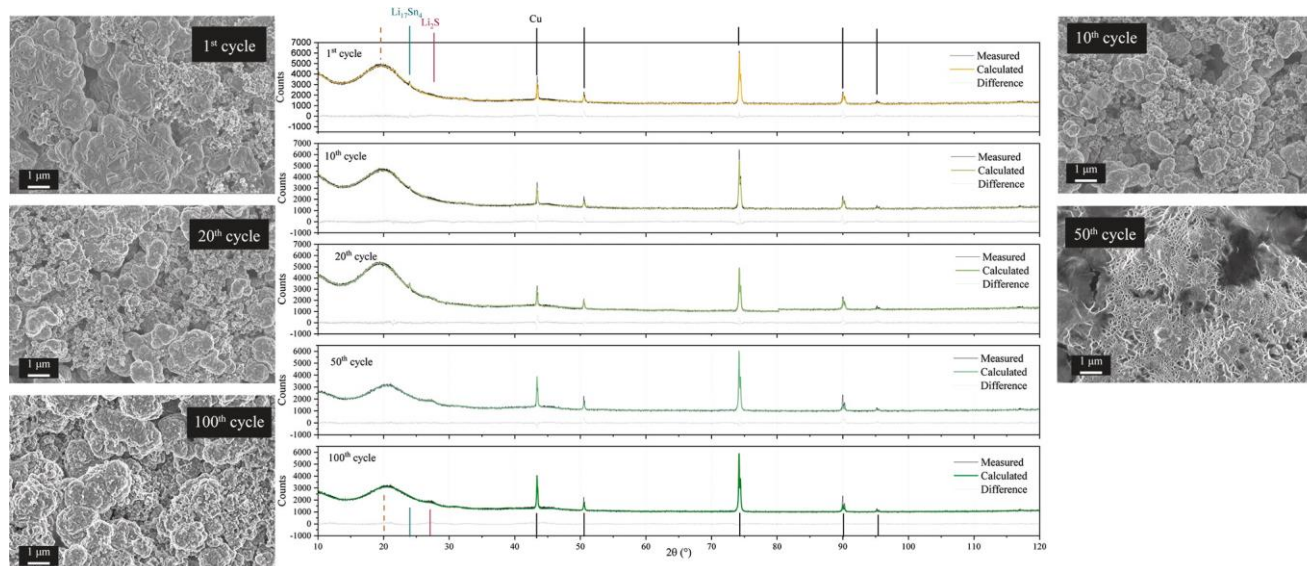


Fig. 8. Ex-situ XRD pattern of SnS₂ electrodes after 1st, 10th, 20th, 50th and 100th charge cycles with corresponding Rietveld analyses and *ex-situ* SEM images.

charged, they only partially contracted, resulting in 20 % of an irreversible length change for both SnS and SnS₂. The irreversible length change of the SnS₂ electrode remained stable over 20 cycles, whereas that of the SnS electrode stabilized at ~ 36 %. The in-situ dilatometry results also indicated that during the charge step, the length change of the SnS electrodes was ~50%, whereas that of the SnS₂ electrodes was ~ 30%.

Finally, the electrochemical impedance spectroscopy (EIS) technique was performed to determine the different contributors to the overall impedance occurring during cycling of the SnS and SnS₂ electrodes. The cells were cycled in the voltage window from 0.01 to 1 V vs Li/Li⁺ at a current rate of 100 mA g⁻¹ and at the end of the charge step of each cycle, impedance spectroscopy was performed. The experimental data were fitted using an equivalent circuit model presented in Fig. 10a. This type of circuit has already been reported for the analysis of EIS data measured on tin sulfides in the literature [64–68]. In this circuit model, R_s represents the internal resistance of the bulk materials in the cell, which originates from the current collector, separator, and electrolyte.

R_{SEI} is the resistance arising from the SEI and Li₂S layers, which are formed from electrolyte decomposition and the conversion reactions of the tin-sulfides, respectively. The capacitive characteristic of the electrical double layer at the SEI-electrolyte interface is represented by the constant phase element CPE_{SEI}, as its behaviour deviates from that of an ideal capacitor. R_{CT} is the charge transfer resistance inside the electrode, which is closely linked to the kinetics of the electrochemical reaction. Since the behaviour of the electric double layer at the electrode-SEI interface is non-ideal due to the surface roughness and electrode porosity, the capacitance of this layer is represented by a constant phase element CPE_{anode}. Lastly, the Warburg element was included to represent the one-dimensional diffusion of the Li⁺ ions through the planar electrode bound on one side.

The Nyquist plots of the first ten charge cycles of the SnS and SnS₂ electrodes are shown in Fig. 10b. The first ten cycles were chosen for the EIS investigations, as they are within the stability limits of SnS (approximately 30 cycles) and SnS₂ (approaching 100 cycles), enabling an EIS analysis of the fundamental phase-change reactions without

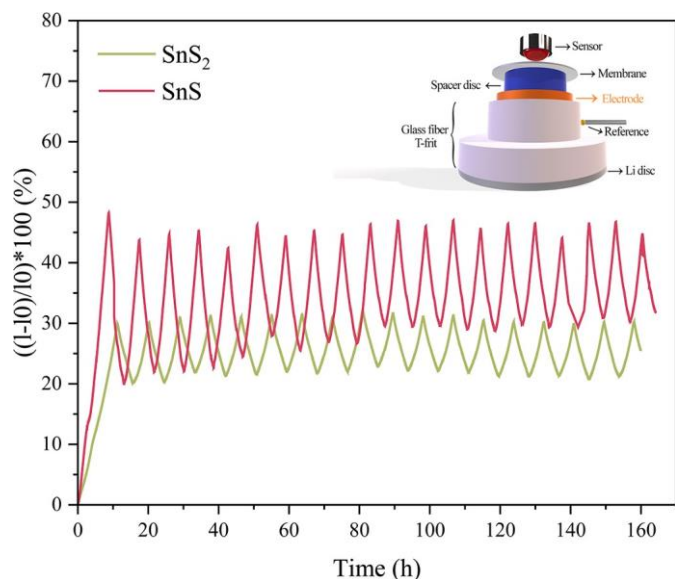


Fig. 9. Dimensional changes of the SnS (red line) and SnS₂ (green line) electrodes developed during 10 discharge and charge cycles.

having to consider long-term degradation effects of the electrodes. The Nyquist plot of SnS consists of one semicircle in the high frequency region, which is usually associated with the formation of the SEI layer. The second semicircle in the middle frequency region is due to the impedance of a reaction involving charge transfer at the interface between the electrolyte and the active material. The straight line with a slope in the low frequency region is a response to diffusion phenomena within the electrodes. Over the 10 cycles, the diameter of the first semicircle increased from $\sim 117 \Omega$ after the first cycle to $\sim 120 \Omega$ after the 10th

cycle. The second semicircle also increased, and the degree of slope for the diffusion phenomena was less than 45° , hence using a CPE contribution for fitting due to the semi-infinite diffusion layer influenced by porosity in the electrodes. The results for SnS₂ show only one semicircle whose diameter increased from $\sim 40 \Omega$ after the first cycle to $\sim 54 \Omega$ after the 10th cycle and a sloped line with only a vague hint of a second semicircle at the 10th cycle.

In Fig. 10c, the ohmic resistance, impedance from the SEI layer and charge transfer resistance as a function of cycle number are presented. The measured ohmic impedances (R_s) were constant for both SnS and SnS₂ electrodes within experimental error. The impedance associated with the SEI layer in the SnS and SnS₂ electrodes was stable; however, R_{SEI} was significantly higher for the SnS electrode. Similarly, the charge transfer impedance R_{CT} was significantly higher for SnS than for SnS₂, although in both cases, the value remained relatively constant over the 10 cycles. The EIS data after the first charge cycle obtained in this study were compared to those available in the literature and presented in Table 5. Our measured R_s data for SnS (6.5Ω) and SnS₂ (1.9Ω) are in agreement with those in the literature (5.9Ω [13] for SnS and 2.1 [67]– 6.2Ω [68] for SnS₂). Our R_{SEI} value for SnS is comparable to that of Huang et al. [24], but higher than that of Lu et al. [13]. Conversely, our R_{CT} value for SnS is between that of Huang et al. [24] and Lu et al. [13]. The differences in the R_{CT} values may be loosely attributed to the microstructures of the SnS electroactive materials that were investigated. Lu et al. [13] prepared SnS nanobelts with preferred, one-dimensional diffusion pathways, which may improve the kinetics of the electrochemical reaction and lead to lower R_{CT} values, whereas Huang et al. [24] synthesised spherical SnS particles which may be larger than those investigated in this work, thereby resulting in higher R_{CT} values due to the slower kinetics.

For SnS₂, our R_{SEI} value of 20.2Ω is within the range of those reported in the literature (9.8 [66] – 53.6 [67] Ω), whereas our R_{CT} value of 12.2Ω is lower. This may also be attributed to the differences in the microstructures of the SnS₂ electroactive materials. Lu et al. [64]

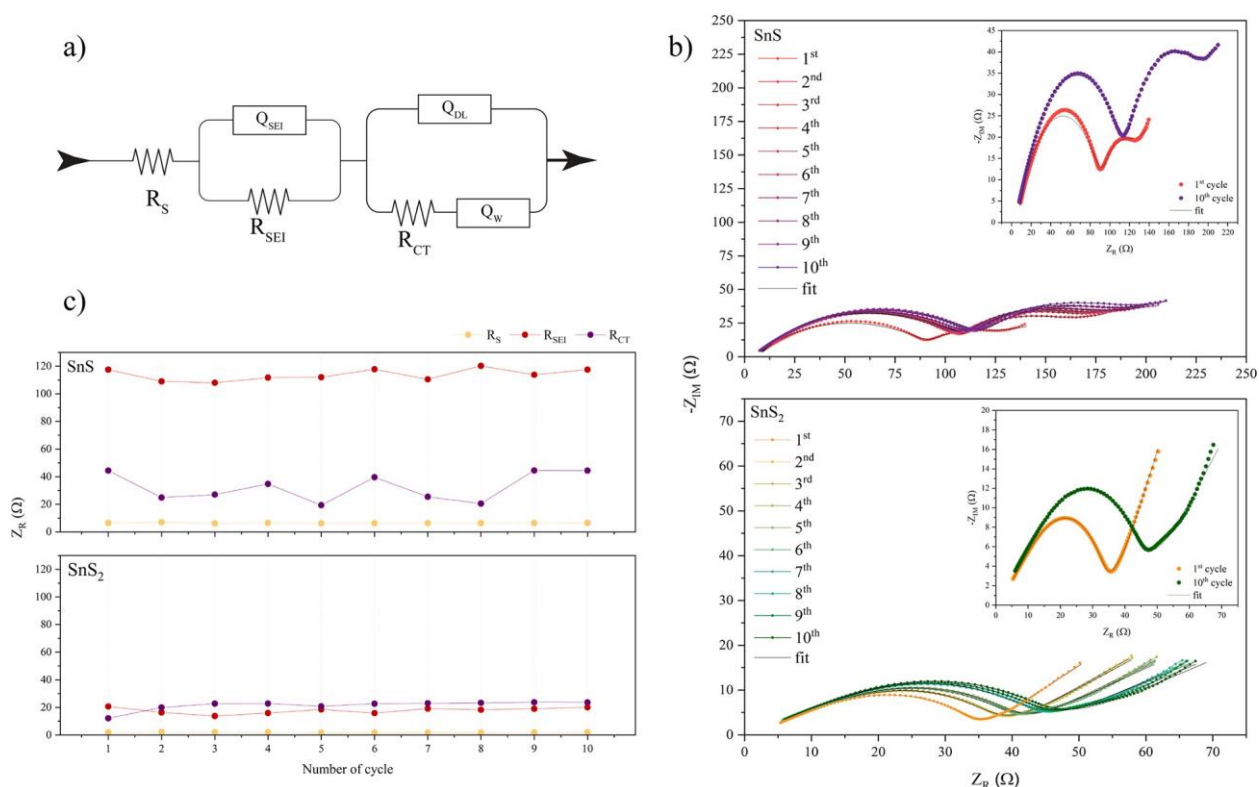


Fig. 10. a) The equivalent circuit used to fit the experimental impedance data. b) Nyquist plots of SnS and SnS₂ electrodes measured after each charge step for the first 10 cycles. c) Different contributors to the overall impedance as a function of number of cycles.

Table 5

Compiled resistance data for the first cycle for both SnS and SnS₂ along with data available in the literature. Yin et al. [67] prepared SnS₂ electrodes with sodium alginate^a, carboxymethyl cellulose^b, polyacrylic acid^c, and carboxymethyl cellulose—poly acrylic

Study	SnS			SnS ₂		
	R _s Ω	R _{SEI} Ω	R _{CT} Ω	R _s Ω	R _{SEI} Ω	R _{CT} Ω
Present work (1 st cycle)	6.5	117.5	44.4	1.9	20.7	12.2
Lu et al. [13]						
Huang et al. [24]	5.9	3.9	16.6			
Lu et al. [64]				NR	NR	124.6
Wang et al. [65]				NR	NR	
Tang et al. [66]				NR	9.8	652
Yin et al. [67]						
				2.5	53.6	41.6 ^a
				2.9	27.9	40.4 ^b
				2.1	67.1	58.1 ^c
Chen et al. [68]						

*NR = not reported

prepared 100 nm, well-defined nanoplates, Wang et al. [65] synthesized SnS₂ flower-like structures with an average diameter of 2 μm, and Tang et al. [66] produced pristine SnS₂ nanoplates, which were agglomerated to secondary particles with diameters between 600–800 nm. On the other hand, the SnS₂ samples from Yin et al. [67] consisted of agglomerates of flake-like particles, which themselves exhibited a size distribution of 5–10 nm. (Chen et al. [68] did not present electron microscopy images of their samples.) Yin et al. [67] used different binders (sodium alginate^a, carboxymethyl cellulose^b, poly acrylic acid^c, and carboxymethyl cellulose—poly acrylic acid^d) to prepare their electrodes, and attribute the differences in their R_{CT} values, which range from 25.5 Ω for poly acrylic acid to 41.6 Ω for sodium alginate, to the effects of the binder. It appears that our heterogenous microstructure consisting of nanoplates arranged in flower-like structures (100–250 nm) and irregularly shaped nanoparticles with a size of 50–100 nm may lead to faster kinetics of the electrochemical reaction, resulting in lower R_{CT} values that reported in the literature. Indeed, our R_{CT} value of 12.2 Ω is most similar to that of Yin et al. [67] (25.5 to 41.6 Ω), who also synthesized flake-like SnS₂ particles which agglomerate to nanospheres during electrode processing and cycling. The EIS data for all subsequent cycles can be found in the supplementary information in Table S4.

The cycling data presented in Fig. 5 clearly show that SnS₂ electrochemically outperformed SnS. Furthermore, SnS₂ showed improved electrochemical performance when compared to pure Sn electrodes from data taken from the literature [56–60]. Based on the experiments and observations, several effects and mechanisms may contribute to the better performance of SnS₂ electrodes compared to SnS (and pure Sn). These are listed and discussed below:

I) Stoichiometrically, the atomic ratio between S and Sn in SnS₂ is higher than that in SnS. Therefore, the conversion reaction between SnS₂ and Li should yield more Li₂S when compared to a similar reaction between SnS and Li. Furthermore, we found that the volume expansion of tin sulfide electrodes could be correlated to the ratio of S to Sn. The results of *in-situ* dilatometry data showed that electrodes with SnS₂ as an active material exhibited less reversible and irreversible dimensional changes than those for SnS (Fig. 9).

II) Due to the 4+ oxidation state of Sn in SnS₂, as well as its CdI₂-type structure in which the Sn⁴⁺ ions are coordinated to six S²⁻ ions in octahedral geometry (see Fig. 1), there are interstitial positions between the edge-sharing Sn-S octahedra layers in the crystal lattice, which can be occupied by Li ions during intercalation and reduction of Sn⁴⁺ to Sn²⁺ to form the Li_xSnS₂ solid solution phase. Therefore, when the conversion reaction to Li₂S and Sn is triggered, the Li ions are already located inside the Li_xSnS₂ crystal lattice, resulting in a distribution of Li₂S and Sn on an atomic level. On the other hand, in the case of SnS, since Li is not intercalated into the SnS crystal structure, the conversion reaction must

necessarily take place at the particle surfaces, with a reaction front which diffuses into the particles as lithiation proceeds. In fact, these mechanisms explain why crystalline Sn was observed in the PXRD pattern of the SnS electrode after 20 cycles (Fig. 7), whereas even after the 1st cycle, crystalline Sn could not be identified in the PXRD pattern of the SnS₂ electrode (Fig. 8). Specifically, since the conversion reaction occurs on an atomic level within the lithiated SnS₂ crystal lattice, the Sn atoms cannot display long-range ordering, as this is interrupted by Li₂S. Similar behavior has been observed for other anode materials such as SiB₃, SiO, CaSi₂, and NiSi₂ [69]. On the other hand, when SnS is lithiated, the S atoms can diffuse out of the crystal lattice to create an outer Li₂S layer, and the remaining chains of Sn atoms crystallize to β-Sn along the crystallographic *a*-axis (Fig. 1a), thereby resulting in a chain-like Sn-morphology, which was interestingly observed in the SEM images of the cycled electrodes (see Fig. 7).

The results of the EIS experiments also support these hypotheses. Theoretically, the amount of Li₂S formed should be higher for SnS₂ than for SnS. This should result in larger charge transfer and SEI resistances for the SnS₂ electrodes. However, the EIS data in Fig. 10 show that the charge transfer and SEI resistances of the SnS electrodes are higher than that of SnS₂. This phenomenon is most likely a result of the formation of Li₂S on the surface of SnS particles, which hinders the electronic and ionic transport of Li⁺ ions at the particle/electrolyte interface and also increases the SEI resistance. On the other hand, due to the postulated atomic-level distribution of Li₂S in the SnS₂ electrodes after the conversion reaction of the lithiated Li_xSnS₂ crystal lattice, there is less Li₂S at the particle surfaces to hinder Li⁺ transport from the electrolyte to the particles. This phenomenon also decreases the SEI resistance. A schematic highlighting the differences in the lithiation mechanisms of SnS and SnS₂ as proposed in this work is shown in Fig. 11 below.

4. Conclusion

SnS and SnS₂ anode active materials were prepared via the precipitation reaction using SnCl₂·2H₂O and SnCl₄·5H₂O precursors, respectively. The electrochemical properties of the as-prepared materials were compared to each other, and it was shown that SnS₂ outperforms SnS. After 100 cycles in the voltage window between 0.01 and 1 V vs Li/Li⁺, SnS exhibited a capacity of only 133 mAhg⁻¹, whereas that of SnS₂ was 369 mAhg⁻¹. This work shows that these results can be closely correlated to the formation of Li₂S and its distribution within the electrode active materials. Firstly, due to the higher ratio of S to Sn in SnS₂, the conversion reaction yielded a higher amount of Li₂S, which may better serve to mitigate the volume expansion of Sn during the successive lithiation steps. Secondly, since lithium can be intercalated into the crystal structure of SnS₂ prior to the conversion reaction, the Li₂S is more evenly distributed on an atomic scale and, therefore can more effectively accommodate the volume changes of the Sn atoms during lithiation. As demonstrated in this work, since SnS₂ has several advantages over SnS as an anode active material for LIBs, it may be more beneficial to focus future research efforts on improving the understanding of the structure-performance-property relationships of SnS₂ for such applications.

CRediT authorship contribution statement

Albina Glibo: Conceptualization, Methodology, Data curation, Writing – original draft. **Nicolas Eshraghi:** Data curation, Writing – review & editing. **Yuri Surace:** Data curation, Writing – review & editing. **Andreas Mautner:** Data curation, Writing – review & editing. **Hans Flandorfer:** Conceptualization, Methodology, Writing – review & editing. **Damian M. Cupid:** Conceptualization, Methodology, Writing – review & editing.

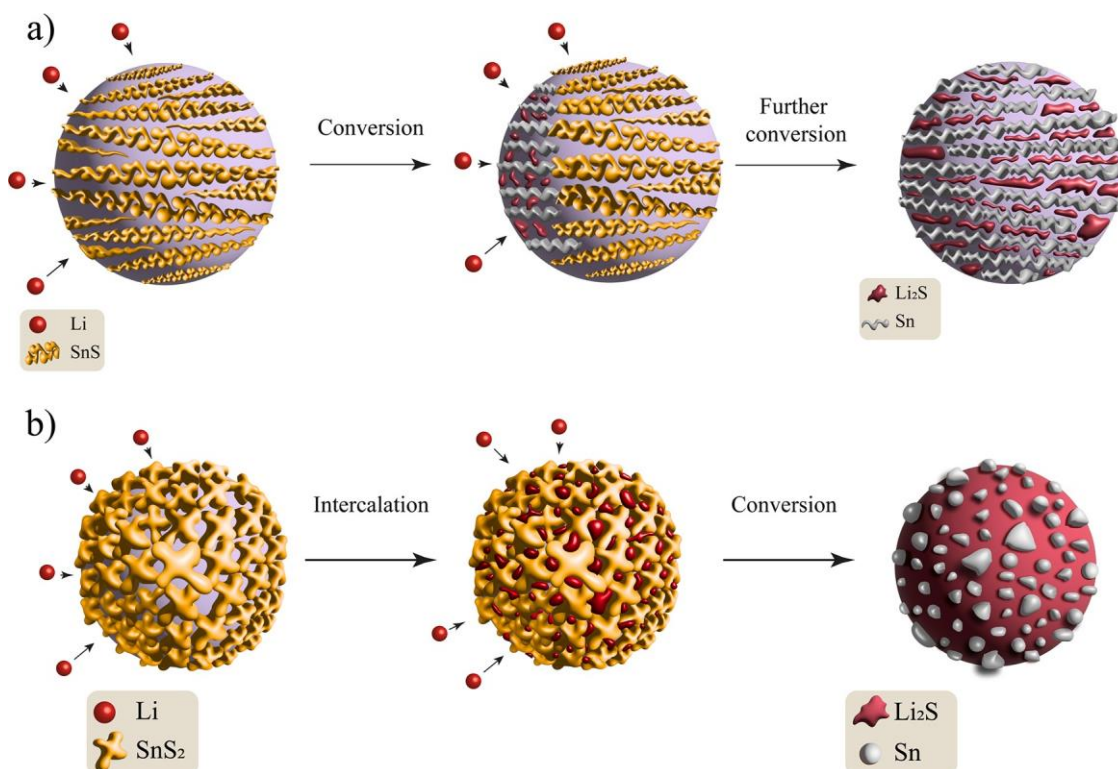


Fig. 11. Schematic representation of the lithiation of a) SnS and b) SnS₂.

Declaration of Competing Interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests
Damian Cupid reports financial support was provided by Austrian Research Promotion Agency

Data availability

Data will be made available on request.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.electacta.2022.141725.

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5.3. Correlation between microstructure, thermodynamic stability and electric work of tin sulfide active anode materials for Li-ion batteries

Journal of Alloys and Compounds
Correlation between microstructure, thermodynamic stability and electric work of tin sulfide active anode materials for Li-ion batteries
 --Manuscript Draft--

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Abstract:	The precipitation and hydrothermal synthesis methods were utilized to prepare phase pure SnS and SnS ₂ materials with different degrees of crystallinity, particle sizes, and morphology. The crystallite size, morphology, and phase composition of the as-synthesised materials were determined. The limiting molar enthalpies of solution of sulphur, the as-prepared materials, and that of a commercially available, macro-crystalline SnS ₂ in tin were established by drop calorimetry and subsequently, the enthalpies of formation were derived. The obtained enthalpies of formation of SnS range from -48.8 to -52.8.2 kJ mol ⁻¹ of atoms and for SnS ₂ from -50.2 to 51.0 kJ mol ⁻¹ of atoms, which aligns well with existing literature results. For SnS, a trend towards less exothermic enthalpy of formation with decreasing crystallite size was observed. The obtained data of the as-prepared SnS ₂ materials did not clearly show such a trend and were further compared to that from commercially available, macro-crystalline SnS ₂ . The obtained enthalpy of formation was even less exothermic compared to as-prepared SnS ₂ materials. After ball-milling of macro-crystalline SnS ₂ its formation enthalpy was the most exothermic of all SnS ₂ samples. An explanation of these unexpected results is given based on the energetics of crystallite size versus particle shape and size. Furthermore, the as synthesized and purchased materials were subjected to electrochemical discharge tests, and from the resulting voltage (as a function of x in Li _x SnS and Li _x SnS ₂) curves, the electrochemical work of the lithiation reactions was derived.
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Correlation between microstructure, thermodynamic stability and electric work of tin sulfide active anode materials for Li-ion batteries

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Abstract

The precipitation and hydrothermal synthesis methods were utilized to prepare phase pure SnS and SnS₂ materials with different degrees of crystallinity, particle sizes, and morphology. The crystallite size, morphology, and phase composition of the as-synthesised materials were determined. The limiting molar enthalpies of solution of sulphur, the as-prepared materials, and that of a commercially available, macro-crystalline SnS₂ in tin were established by drop calorimetry and subsequently, the enthalpies of formation were derived. The obtained enthalpies of formation of SnS range from -48.8 to -52.8.2 kJ mol⁻¹ of atoms and for SnS₂ from -50.2 to 51.0 kJ mol⁻¹ of atoms, which aligns well with existing literature results. For SnS, a trend towards less exothermic enthalpy of formation with decreasing crystallite size was observed. The obtained data of the as-prepared SnS₂ materials did not clearly show such a trend and were further compared to that from commercially available, macro-crystalline SnS₂. The obtained enthalpy of formation was even less exothermic compared to as-prepared SnS₂ materials. After ball-milling of macro-crystalline SnS₂ its formation enthalpy was the most exothermic of all SnS₂ samples. An explanation of these unexpected results is given based on the energetics of crystallite size versus particle shape and size. Furthermore, the as synthesized and purchased materials were subjected to electrochemical discharge tests, and from the resulting voltage (as a function of x in Li_xSnS and Li_xSnS₂) curves, the electrochemical work of the lithiation reactions was derived.

1. Introduction

In recent years, the tin sulfide family of materials, which includes stable binary compounds such as SnS, Sn₂S₃, and SnS₂, has attracted significant attention as materials for energy storage and conversion applications. SnS is particularly interesting as an absorber material for photovoltaic (PV) devices, due to its optical band gap energy of 1.08 eV [1] and high optical absorption coefficient for photons with energies greater than 1.3 eV [2]. SnS₂ is deemed to be an excellent photocatalyst for hydrogen generation [3],[4] owing to its band gap energy in the range between 2.18 - 2.44 eV. Furthermore, both SnS₂ and SnS have been the subject of investigations as anode active materials for lithium-ion batteries (LIBs) due to their high theoretical capacities of 1111 and 1209 mAhg⁻¹, respectively. However, more relevant for electrochemical energy conversion and storage applications is the theoretical reversible capacity of 755 mAhg⁻¹ for SnS and 645 mAhg⁻¹ for SnS₂. Both reversible capacities are at least double that of the conventionally used graphite (372 mAhg⁻¹) [5]. In addition to their optical and electrochemical properties, SnS and SnS₂ can be readily synthesised as one-dimensional, two-dimensional, or even three-dimensional open framework structures due to the versatile coordination geometry of tin and sulphur [6]. Furthermore, since tin and sulphur are non-toxic and abundant in the Earth's crust, both SnS and SnS₂ are considered environmentally friendly and sustainable materials, which are currently not on the list of critical raw materials.

SnS is known to form two stable modifications: the low temperature (LT) orthorhombic α -SnS with GeS-type structure (space group *Pnma*) and the high temperature (HT) orthorhombic β -SnS with TII-type structure (space group *Cmcm*). The crystal structure of α -SnS can be considered as distorted cubic ZnS-type structure (both, cubic and hexagonal ZnS structures exhibit tetrahedral mutual coordination of Zn and S). In the α -SnS crystal lattice, however, the Sn²⁺-ion is coordinated to only three sulphur ions, and the Sn 5s² lone pair of electrons “occupies” the remaining orbital in hypothetical tetrahedral geometry stemming from the ZnS-type structure [7], see Figure 1a. The 5s lone pair distorts the hypothetical cubic ZnS-type structure resulting in an orthorhombic structure of the compound. Via displacement of the Sn atoms along the [1 0 0] direction and decreasing the axial ratio a/c , α -SnS can be transformed into β -SnS. The second-order transition temperature between α - and β -SnS is 878 K and is defined as the temperature at which $a/c = 1$ [8].

SnS₂ adopts the CdI₂-type structure with a trigonal unit cell and *P-3m1* space group. However, many polytypes are known, which are formed by multiplication of the *c*-axes due to the presence of stacking variants along the

[0 0 1] direction [9]. In the CdI_2 -type structure (Figure 1b), Sn^{4+} ions are coordinated to six S^{2-} ions in an octahedral geometry. Similar to ZnS , which is considered to be a compound displaying bonding that is on the transition between ionic and covalent, tin sulfides exhibit features of both bonding types (the electronegativity is 1.7 for both Zn and Sn, according to Allred and Rochow). In SnS , the coordination number of 3 indicates that Sn and S atoms are bonded covalently within the (Sn-S)-layers, whereas the interlayer bonding is based on ionic interactions³. In SnS_2 , the (S-Sn-S) layers are based on SnS_6 -octahedra, which are linked to each other via surfaces; see Figure 1b. The coordination number of 6 and the higher charge density of the Sn^{4+} ion compared to the Sn^{2+} rather indicate an ionic character of the intralayer bonding; however, the interlayer bonding, where pure sulphur layers face each other, is much weaker and only based on van der Waals interactions.

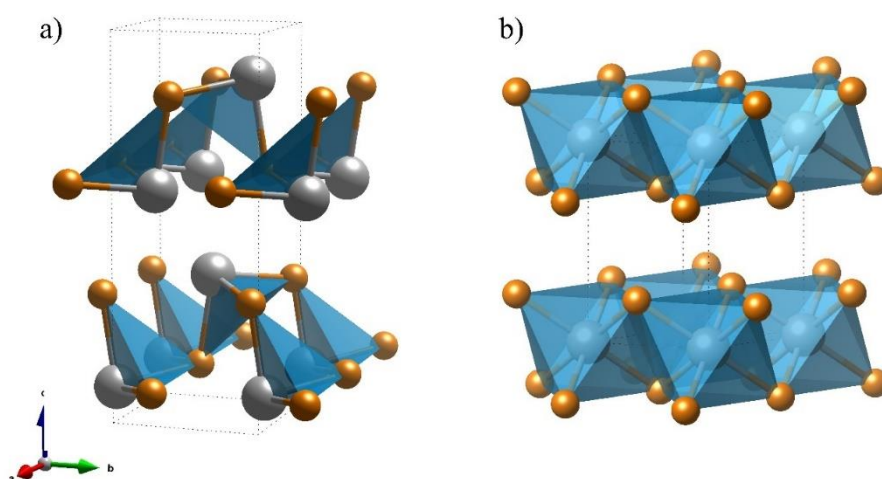


Figure 1. Scheme of the crystal structure of a) LT α -SnS state and b) SnS_2

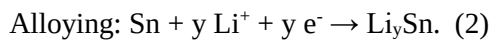
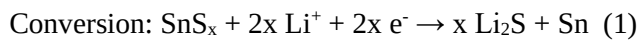
According to literature, SnS has been synthesised as powders and single crystals via wet chemistry methods, the mechanochemical method [10], melt mixing [11] and crystal growing [12]. SnS can also be fabricated as thin films for photovoltaic applications using chemical and physical deposition techniques. Chemical deposition syntheses reported in the literature include bath [13], electrochemical [14], chemical vapour [15], atomic layer deposition [16] and spray pyrolysis [17] methods. The physical methods include thermal evaporation [18], sputtering [19] and sulfurization [20].

³ The term layer is meant here in the crystallographic sense, in the physical-chemical sense SnS is not a layered structure.

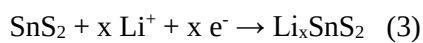
SnS₂ has also been synthesised using several methods, including liquid-solid phase reaction [21], ionothermal synthesis [22], sonochemical method [23], hydrothermal and solvothermal [24][25][26][27] methods as well as other wet chemical methods [23][24].

Previously, we published a study in which the electrochemical performance of well-defined, nanocrystalline SnS₂ was compared to that of partially amorphous SnS₂ [28]. In another study, the electrochemical performance of partially amorphous SnS and SnS₂ were compared to each other [29]. Both studies conclude that partially amorphous SnS₂ performs better than both nano-crystalline SnS₂ and partially amorphous SnS. Furthermore, the studies emphasised the importance of Li₂S, formed via the conversion reaction during the lithiation of SnS and SnS₂, respectively, and its positive impact on the capacity fade during repeated lithiation and delithiation of SnS and SnS₂ materials.

During lithiation, both SnS and SnS₂ are expected to exhibit the conversion and alloying reactions according to the equations:



In the conversion reaction, a tin sulfide compound reacts with Li to yield Li₂S and Sn. Further lithiation triggers the alloying reaction between Sn and Li, forming various Li-Sn phases with Li_{4.4}Sn being the last plausible phase. However, in the case of SnS₂, prior to the conversion reaction, an intercalation reaction occurs, according to the equation:



Li-ions are intercalated into the SnS₂ crystal structure between the SnS₆-octaheder layers to form metastable Li_xSnS₂ phases. The intercalation is accompanied by the reduction of Sn from the 4⁺ to 2⁺ valence state up to a maximum of x=1.5 [30]. The main role of Li₂S is to absorb the mechanical stress occurring due to the volume changes of the tin particles on alloying with Li. The volume expansion is a consequence of the formation of various Li-Sn compounds with different densities. The intercalation of Li-ions prior to conversion in the case of SnS₂ leads to a better distribution of Li₂S around Sn particles than in SnS, where whiskers of pure tin are formed.

Nano-crystallinity can be considered as a transition state from macro-crystallinity to the amorphous modification. Nano-crystalline and amorphous materials are metastable since crystallisation, reduction of grain boundary surfaces, and decreasing defect concentrations are exothermic processes. Thus, the enthalpy of formation of nano-crystalline/amorphous modifications should be less negative than that of the macro-crystalline substance. This could be proven in previous works where the enthalpy of solution of nano-crystalline Co [31], Cu, and Ni [32] in a metal bath was determined and compared to their respective bulk materials. Such data are essential for the thermodynamic modelling and description of all processes where nano-crystalline/amorphous materials are applied or formed.

The experimentally derived, electric work of the complete lithiation reaction derived from the integration of voltage curves (cell voltage versus mole of Li) usually deviates significantly from the calculated equilibrium Gibbs energy values. Insufficient diffusion, metastable compound formation, mechanical strain, and the presence of nano-crystalline or amorphous products can lower the electric work. In contrast, nano-crystalline or amorphous educts, parasitic lithiation reactions, and SEI formation can enhance the electric work.

In this work, two aspects are considered. Firstly, the energetic differences between SnS, SnS₂, (both prepared by precipitation and hydrothermal syntheses) and purchased, macro-sized SnS₂ (MKNano), were assessed by measuring their enthalpies of formation via drop solution calorimetry in a tin bath. Secondly, the materials were electrochemically discharged at slow current rates to subsequently extract the Gibbs free energy of the lithiation reactions. This work attempts to quantify the influence of crystallinity on thermodynamic stability, which is linked to the electrical work which is performed in the first-cycle discharge reactions. Furthermore, the stability of the starting active materials is correlated to the overall energy output of the lithiation reactions. The purity and crystallinity of the four substances were characterised using powder XRD, SEM and TEM. For comparison, the same techniques were applied to a commercially available macro-crystalline SnS₂ powder, (both as purchased and ball milled) which were proven to be phase pure by XRD.

The most accurate method to determine enthalpy values is calorimetry. To our best knowledge, the enthalpy of formation of α -SnS and SnS₂ has not yet been determined by direct reaction or solution calorimetry, only by indirect reaction calorimetry based on the reaction $\text{SnS}_x + \text{Zn} \rightarrow x \text{ZnS} + \text{Sn}$ [33], see also section 2. The latter method can be considered as inaccurate, since there are two modifications of ZnS (sphalerite and wurtzite), which are both formed during indirect reaction calorimetry. To calculate the formation enthalpies of

the tin sulfides, the formation enthalpies of both ZnS modifications and their relative quantities in the product must be known. Those relative quantities could only be determined approximately by powder XRD measurements and Rietveld refinements [33].

In our work, we therefore present the first accurate measurement of the enthalpy of the formation of SnS and SnS₂, applying drop solution calorimetry. Furthermore, in this work, the limiting enthalpy of solution (and mixing) of sulphur in tin was experimentally determined for the first time.

2. Literature data

A comprehensive compilation of thermodynamic data for solid tin sulfides was given by Gamsjäger et al. [34]. Various techniques were utilised to determine the enthalpy of formation of α -SnS and SnS₂, including transpiration methods, emf, Knudsen effusion cell experiments, and indirect reaction calorimetry. The experimental results given in this compilation range from -42 to -55 kJ/mol of atoms for α -SnS. There is only one experimental work based on calorimetry (indirect reaction method) from Morozova et al. [33], where α -SnS was reacted with Zn to yield ZnS and Sn (indirect reaction, as described above). The result is -55 ± 2.5 kJ/mol of atoms. For SnS₂, the experimental values range from -41 to 57 kJ/mol of atoms as reported in [34]. Also, for the enthalpy of formation of SnS₂, there is only one result from indirect reaction calorimetry, with a value of -41 kJ/mol of atoms [33]. Theoretical calculations have also been performed based on different variants of DFT methods to calculate the enthalpies of formation of the tin sulfides. The results are -51.4 kJ/mol of atoms [35] and -49.7 kJ/mol of atoms [36] for α -SnS. For SnS₂, -45.5 kJ/mol of atoms [35], -43.7 kJ/mol of atoms [36], and -54.0 kJ/mol of atoms [37] have been reported according to the DFT calculations.

3. Experimental

3.1. Materials

All chemicals used in this work are of analytical grade and were not subjected to further purification steps. They are listed in Table 1.

Table 1. The summary of all the materials used for the synthesis of the materials and drop solution calorimetry

Material	Vendor	Purity	State	Role
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SnCl ₂ ·2H ₂ O	Sigma Aldrich	≥ 99.99%	Powder	Reactant, source of Sn
SnCl ₄ ·5H ₂ O	Alfa Aesar	98 %	Powder	Reactant, source of Sn
Thioacetamide (TAA)	Alfa Aesar	99 %	Powder	Reactant, source of S
Conc. HCl	Honeywell	/	Liquid	Solvent
Sn	Dentaurum	99.9%	Foil, 100 µm thickness	tin crucibles
Sn	Smart elements	99.999 %	granules	tin bath
SnS ₂	MK-Nano	99+%	Powder, 3 µm	reference material
Carbon black C45	Imerys	/	Powder	Conductive additive
Polyvinylidene fluoride (PVDF)	Solvay	/	Powder	Binder
N-methyl-2- pyrrolidone (NMP)	Sigma Aldrich	99%	Liquid	Solvent
1M solution of LiPF ₆ in 3:7 weight mixture of ethylene carbonate and ethyl methyl carbonate with 2 wt% of vinylene carbonate	Soulbrain	/	Liquid	Electrolyte

Li metal	PI-KEM	99.9 %	Bulk	Counter/reference electrode
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3.2. Syntheses procedure

Synthesis of SnS and SnS₂ via precipitation reaction

To synthesize SnS, the reactants SnCl₂·2H₂O and thioacetamide (TAA) were weighted in a molar ratio of 1:1. In separate beakers, 0.9 g of SnCl₂·2H₂O (4 mmol) and 0.3 g of TAA (4 mmol) were dissolved in 20 mL of deionised water. 15 mL of concentrated HCl was added to the aqueous SnCl₂ solution, which was subsequently poured into the aqueous TAA solution. The final solution was transferred into a round bottom Schlenk flask with a volumetric capacity of 150 mL. The ground glass joint of the flask was capped with a stopcock, and the sidearm was connected to a rubber tube immersed in a 1M NaOH solution. This not only prevents the build-up of pressure in the flask but also the release of H₂S gas into the atmosphere. Such a setup is required since, in the presence of air, Sn²⁺ ions can be easily oxidised to Sn⁴⁺ in aqueous solutions. The reaction was heated to 60 °C by submerging the reaction flask into an oil bath which was heated via a hot plate. The reaction was kept at 60 °C for 3 h with light stirring. Subsequently, the flask was taken out of the bath and let to cool down to room temperature.

The synthesis of SnS₂ was performed similarly to that of SnS. However, in this case, SnCl₄·5H₂O was used as an Sn source. 0.701 g of SnCl₄·5H₂O (2 mmol) was dissolved in 8 mL of concentrated HCl, and 0.301 g of TAA (4 mmol) was dissolved in 20 mL of deionised water. The SnCl₄ + HCl solution was poured into the aqueous TAA solution, which was then transferred into a round-bottom flask with a volumetric capacity of 150 mL. Due to the formation of H₂S gas, the exhaust was directed to a 1M NaOH solution via a rubber tube. The flask was placed in an oil bath heated to 80 °C with a heating plate, and the flask's content was stirred lightly. As the temperature of the oil bath reached 70 °C, the transparent solution of SnCl₄+HCl+TAA acquired a yellow colour, and at 80 °C, the thick opaque yellow precipitate was observed. The flask was taken out of the oil bath and let to cool down to room temperature.

After both procedures, the separation of the precipitates and liquid was done by vacuum filtration using a Büchner flask and borosilicate glass funnel with a built-in porous filter plate (with a pore diameter of 1-1.6

μm). The products were washed three times with water and ethanol before they were dried for 4 h at 60 °C in a vacuum furnace. From now on, SnS and SnS₂ synthesized via precipitation reaction are referred as PR-SnS and PR-SnS₂, respectively.

Synthesis of SnS and SnS₂ via hydrothermal method

In the synthesis procedure for SnS, SnCl₂ (anhydrous) and TAA were used as sources of Sn and S, respectively, and were weighed in a 1:1 molar ratio. 5.271 g of SnCl₂ (28 mmol) and 2.089 g of TAA (28 mmol) were dissolved in 25 ml of deionised water in separate beakers. 15 mL of conc. HCl was added to the aqueous solution of SnCl₂ before adding the TAA solution. The resulting solution was transferred into a 100 ml Teflon vessel of a steel autoclave. Subsequently, the autoclave was heated at 180 °C for 2 h. After 2 h, the autoclave was removed from the furnace and cooled to room temperature.

For the synthesis of SnS₂, SnCl₄ · 5H₂O and thioacetamide (TAA) were used as sources of tin and sulphur, respectively. In the first step, 3.26 g of SnCl₄ · 5H₂O (9 mmol) and 1.0 g of TAA (13 mmol) for a molar ratio of 1:1.48 were weighed. SnCl₄ · 5H₂O was dissolved in 8 mL of conc. HCl, whereas TAA was dissolved in deionised water (52 mL). The SnCl₄ · 5H₂O + HCl solution was poured into the TAA solution and stirred for approx. 1 min before the final solution was transferred into a 100 mL Teflon-lining of a steel autoclave. The autoclave was placed in a furnace for 24 h at 120 °C. After 24 h, the autoclave was taken out and let to cool down to room temperature.

After both reactions, the precipitates were filtered via vacuum filtration using a Büchner flask and borosilicate glass funnel with a built-in porous filter plate (with a pore diameter of 1-1.6 μm). After filtration, the product was washed with water and ethanol three times before it was dried for 4 h at 60 °C in a vacuum furnace. From now on, SnS and SnS₂ synthesized via hydrothermal method are referred as HM-SnS and HM-SnS₂, respectively.

Ball milling of purchased SnS₂

A part of this study was to compare the results of the enthalpy of formation and Gibbs free energy of the lithiation reaction of the as-prepared tin sulfide materials with phase pure, commercially available SnS₂. The purchased SnS₂ was ball milled using an airtight closed ZrO₂ milling bowl in the combination with ZrO₂ balls. Powder and balls were weighted in mass ratio of 1:20 and during milling the rotation speed of 200 revolutions

per minute (rpm) was applied, for a total milling time of 10 hours. After each 15 min of milling, a pause of 30 min was introduced in order to reduce thermal effects. The milling was performed in an Argon atmosphere. After milling, the bowl was opened in ambient conditions.

From now on, SnS₂ purchased from MKNano is referred as MKN-SnS₂ and the ball milled sample as MKN-SnS₂-BM.

3.3. Characterisation techniques

Powder x-ray diffraction (PXRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM)

The purity of the products was investigated via powder X-ray diffraction using a Bruker D8 diffractometer ($\theta/2\theta$ -geometry) with a copper radiation source (40 kV / 40 mA) and a Ni-filter. Using petroleum jelly, the powder samples were fixed onto a silicon mono-crystal sample holder. Signals were detected by a Lynxeye strip detector covering $\pm 1.5^\circ$ in 2θ simultaneously. The obtained patterns were evaluated based on Rietveld-refinements using Topas4[®] software. Rietveld analysis was used to identify the phases in all samples; however, the absolute uncertainty in the given weight percentages of the identified phases can be up to 3 %.

The sample morphology and growth of the particles were investigated by scanning electron microscopy (SEM) using a Carl Zeiss Supra 40 scanning electron microscope with Everhart–Thornley (ETD) and Through-Lens (TLD) detectors with primary electron-beam energy of 5 keV.

Transmission electron micrographs were collected at 200 keV on a CM200 transmission electron microscope (TEM, Philips, Amsterdam, the Netherlands) with a LaB6 electron source. A 512×1024 pixel JUNGFRÄU detector with a 320 μm thick silicon sensor and a pixel size of (75 μm) was used.

3.4. Drop solution calorimetry

The drop solution calorimetry measurements were performed using a Calvet-type twin calorimeter with two thermopiles, including more than 230 thermocouples each. To ensure isoperibolic conditions, a large wire wound resistance furnace surrounds the two calorimeter cells. A self-constructed auto-sampler with a capacity of 30 drops was installed to execute drops in inert atmosphere. The equipment was controlled by a self-written

software based on LabVIEW. The data were evaluated using the HIQ program. A more detailed description of the device and method is given by Flandorfer et al. [38]. The drop-solution calorimetry technique was used to determine the enthalpy of formation of the as-synthesized SnS and SnS₂ samples. Accordingly, the limiting partial enthalpies of solution of pure S and the various SnS and SnS₂ samples in Sn were measured.

The respective samples were dropped into the tin bath to achieve a maximum concentration of approx. 5 at.% of the bath. Since the dropped substances (S, SnS, and SnS₂) were powders and are generally much less dense than Sn, they were wrapped in small containers made of Sn sheets, which were previously washed in acetone in an ultrasonic bath. With this method, all the powder samples were dropped directly into the Sn bath and were completely immersed and dissolved quickly. There is also no need to press the powders, which ensured that the crystallite sizes of the as-synthesized powders were maintained. The auto-sampler was loaded with 10-15 sample drops (S, SnS, or SnS₂ in Sn containers) and 5 pieces of NIST standard α -Al₂O₃ to evaluate the calorimeter constant, see below. Each drop was performed from ambient temperature (T_0) into the calorimeter chamber at 1073 K (T_c), where a boron nitride crucible containing the molten Sn (~12 g of Sn) was positioned. The whole system was flushed three times with Ar (99.999 Vol.% purity) prior to the measurements and run under an Ar-flow of 50 mL min⁻¹. After stabilising the system at 1073 K for 12 hours, the drops were performed in 2400 s intervals to allow the heat flow signal to return to its baseline value. The heat flow acquisition interval was 0.5 s. The obtained signals were recorded, integrated, and energetically quantified using the calorimeter constant. To prove the reproducibility of the data, measurements were repeated at least one time.

The calorimeter constant was determined at the end of the measurement by dropping five pieces (approximately 50-90 mg each) of a NIST Standard sapphire into the tin bath in the calorimeter. Thereby, the integrated signal of the heat effect ($S^{T_0 \rightarrow T_c}$) in $\mu\text{V}\cdot\text{s}$ can be determined, which corresponds to the enthalpy increments of the reference material from the drop temperature (T_0) to the calorimeter temperature (T_c). The values ($\Delta_{T_0 \rightarrow T_c} H_{ref}$) for each drop were calculated using the polynomial provided by NIST. The calorimeter constant k [$\text{J}\cdot\mu\text{V}^{-1}\cdot\text{s}^{-1}$] was determined by applying the following equation

$$k = \frac{\Delta_{T_0 \rightarrow T_c} H_{ref} \cdot n_{ref}}{S^{T_0 \rightarrow T_c}} \quad (4)$$

and calculated using the average out of the five drops.

The calorimeter constant k and the measured signals ($S^{T_0 \rightarrow T_c}$) for each sample drop were used to calculate the measured enthalpy values (ΔH_{signal}) using the following equation:

$$\Delta H_{signal} = S^{T_0 \rightarrow T_c} \cdot k \quad (5)$$

The enthalpy increment of the pure element Sn was required to:

- 1) Subtract the enthalpy increment of the Sn sheet, which was used to construct the small containers for the drops, from the total measured enthalpy effect ΔH_{signal} . The enthalpy increment of the Sn sheet includes the energy needed to heat up and melt the Sn container during the drop. The remaining heat is considered as the enthalpy of solution, $\Delta_{sol}H_i$, of S, SnS, and SnS₂ in Sn.
- 2) the enthalpy of solution, $\Delta_{sol}H_{Sn}$, of Sn in Sn, which is required to calculate the enthalpy of formation of the respective tin sulfide.

On the other hand, the enthalpy increment of the pure element S was required to:

- 1) calculate the limiting enthalpy of mixing for S in Sn at infinite dilution at the calorimeter temperature T_c . This is derived from the measured limiting enthalpy of solution of S in Sn.

The enthalpy increments for the pure elements Sn and S from ambient temperature to the temperature of the calorimeter were calculated using the so-called Dinsdale polynomials:

$$H = a - c T - \sum (n - 1) d T^n \quad (6)$$

where a , b , c and d are the coefficients for the stable phase of the element at temperature T taken from the SGTE (Scientific Group Thermodata Europe) database for pure elements [39]. Since the masses of the dropped samples were miniscule compared to the mass of the Sn bath, the enthalpy of solution for each drop can be considered as the partial enthalpy of solution, $\Delta_{sol}\bar{H}_i$.

To determine the enthalpy of formation of a compound A_xB_y by drop solution calorimetry, the enthalpies of solution at infinite dilution of its constituent elements ($\Delta_{sol}\bar{H}_A$, $\Delta_{sol}\bar{H}_B$) and the compound $\Delta_{sol}\bar{H}_{ij}^\infty = \Delta_{sol}\bar{H}_{AxBy}^\infty$ at the respective temperature must be considered. The molar enthalpy of formation at the drop temperature, T_0 , can be calculated according to the equation:

$$H_{f, SnxSy}^{T_0} = x \cdot \Delta_{sol}\bar{H}_{Sn}^\infty + y \cdot \Delta_{sol}\bar{H}_S^\infty - \Delta_{sol}\bar{H}_{SnxSy}^\infty \quad (7)$$

Random experimental errors can occur due to sample weighing, the calibration procedure, and signal integrations. Systematic errors can occur as a result of calorimeter construction, the measurement setup, and so-called "chemical errors", *e.g.*, incomplete reactions, a reaction between molten metal and crucible, evaporation of molten metal, and the reaction between the vapour with quartz glass. We tried to rule out systematic errors. The various random errors were determined or estimated, and the total error of our results was calculated based on error propagation.

3.5. Electrochemical discharging

All electrochemical measurements were conducted on a coin-cell level, in two-electrode configuration in which Li metal served as both counter and reference electrode. To prepare the slurry for electrode coating, the as-synthesized materials were combined with carbon black C45 conductive additive and PVDF binder in a weight ratio of 80:10:10. NMP was used to dissolve PVDF powder, which was dried for 4 h at 60 °C prior to mixing with NMP. An appropriate amount of PVDF was weighed to produce a 6 wt.% PVDF in NMP solution. The slurry was mixed in a Thinky Inc. mixer in three intervals of 1 min mixing and 1 min of break, each. The slurry was casted onto a Cu current collector and dried in air at 60 °C. Several electrodes were subsequently punched into a disc form with a diameter of 15 mm and dried at 120 °C for 12 h in vacuum using a Büchi® glass oven. The electrodes were introduced into an Ar filled glove box where coin cells were constructed. Li metal (thickness 0.6 mm) was used as the counter electrode, a single PP/PE/PP Celgard 2325 membrane (polypropylene film, thickness 0.25 µm) was used as the separator and 75 µL of the 1 M electrolyte solution were added. The electrochemical measurements were carried on an Arbin potentiostat (LBT 96-channel battery tester), and the raw data were evaluated using the Origin2021G software. The constructed cells were discharged using constant current of C/200 from open circuit voltage value to 0.01 V. For SnS₂, the theoretical capacity of 1209 mAh g⁻¹ was used for the C-rate determination, whereas for SnS, a theoretical capacity of 1111 mAh g⁻¹ was adopted.

4. Results and discussion

4.1. Physio-chemical characterisation

The purity and crystallinity of the samples after synthesis was determined by PXRD. The PXRD patterns and corresponding Rietveld analysis of the SnS products, along with SEM images, are shown in Figure 2.

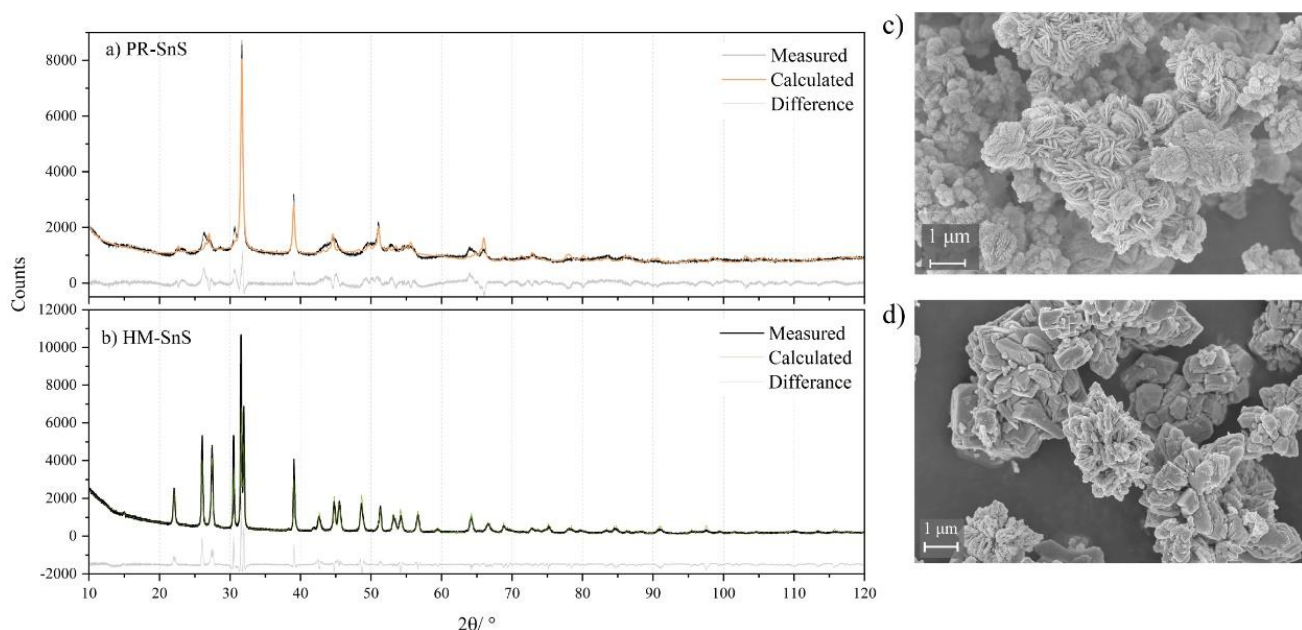


Figure 2. PXRD patterns and corresponding Rietveld analysis of a) PR-SnS and b) HM-SnS. SEM images of c) PR-SnS and d) HM-SnS.

According to the Rietveld analysis (Figure 2a), the precipitation reaction in which $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ was used as a source of Sn indeed yielded pure α -SnS (space group: $Pnma$). However, to fit the measured XRD pattern via the Rietveld refinement method, two α -SnS phases had to be used. An average crystallite size parameter of 45 nm was refined for one phase, whereas 10 nm was the average crystallite size of the other phase. This therefore indicates the existence of a well-crystallized portion and a portion with very low crystallinity, which could even be amorphous. The sample synthesized via the hydrothermal reaction was proven to be phase pure α -SnS with a defined average crystallite size of 75 nm. Both PR- and HM-SnS showed a preferred orientation in the $[1\ 1\ 1]$ direction. The details of the Rietveld analyses are presented in Table 2. The broader peaks and the merging of some peaks observed in the PXRD pattern of PR-SnS indicate a partially amorphous/nanocrystalline nature of the sample. On the contrary, HM-SnS shows narrower, sharp and well distinct diffraction peaks which are the indication of a well-crystallized

material. A considerable difference in morphology can also be observed between the two samples. PR-SnS is composed of 10-20 nm nano-sized primary particles agglomerated into μm -size secondary particles of irregular shape as well as platelets of $\sim 1\ \mu\text{m}$ in size; HM-SnS is made up of $> 1\ \mu\text{m}$ well-defined primary particles with irregular shape but distinct facets, indication of a higher degree of crystallization confirming XRD findings.

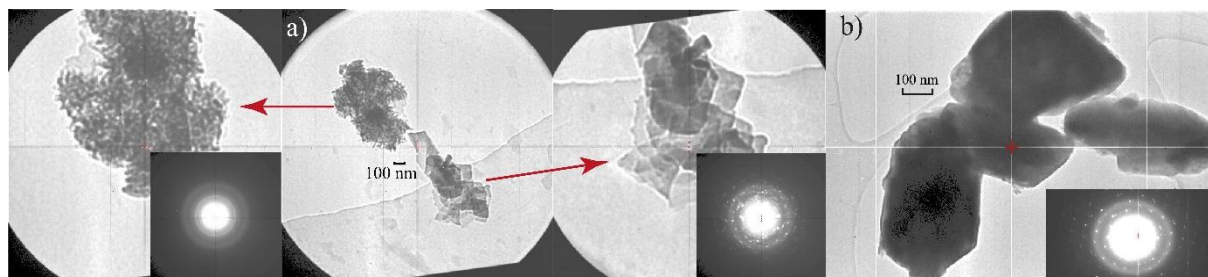


Figure 3. TEM micrographs of a) PR-SnS and b) HM-SnS

TEM micrographs of the PR-SnS sample, along with selected area electron diffraction (SAED) patterns, are shown in Figure 3a. The sample consisted of near-to amorphous and well-crystalline portions. The PR-SnS cluster on the left exhibited characteristic halo rings in the SAED pattern; distinct diffraction spots could not be observed, indicating that this part of the sample is practically amorphous. The cluster on the right showed a SAED pattern in which halo rings were present, as well as bright diffraction spots. The spots correspond to a polycrystalline material with a smaller number of crystals. Figure 3b presents TEM micrographs and corresponding SAED patterns of HM-SnS. Accordingly, the sample consists of small single crystals of 200-500 nm size indicated by the bright, distinct spots in the SAED pattern. These results agree with the PXRD and SEM data, showing that PR-SnS material is not fully crystalline with amorphous portions. In contrast, the HM-SnS sample has a higher degree of crystallinity and does not show an amorphous phase.

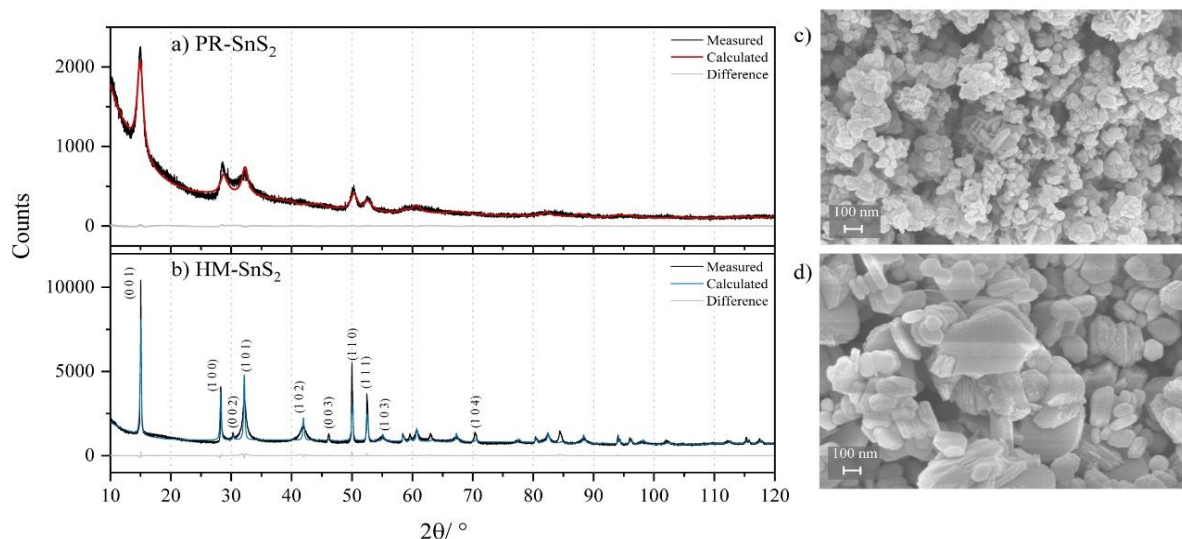


Figure 4. PXRD patterns and corresponding Rietveld analysis of a) PR-SnS₂ and b) HM-SnS₂. SEM images of c) PR-SnS₂ and d) HM-SnS₂.

The measured PXRD patterns of PR-SnS₂ and HM-SnS₂, along with their Rietveld analysis, are shown in Figures 4a and b, respectively. The results of the Rietveld refinements are presented in Table 2. The PR-SnS₂ product again shows a very low degree of crystallinity. The average crystallite size is 8 nm, whereas the high background indicates the presence of amorphous material. On the other hand, the product of the hydrothermal reaction shows a significantly higher degree of crystallinity, as indicated by the sharper and better-defined diffraction peaks. Those samples exhibited an average crystallite size of 60 nm. The measured XRD pattern of the HM-SnS₂ sample showed significantly broader peaks along the (1 0 l) crystallographic planes, implying the presence of stacking faults along the [1 0 l] directions. SEM images of PR-SnS₂ and HM-SnS₂ are presented in Figures 4c and 4d, respectively. The HM-SnS₂ sample consisted of primary nanosized platelets between 150 and 500 nm in size. On the other hand, the PR-SnS₂ sample was characterized by a nanoplates with dimensions smaller than 100 nm arranged in flower-like structures and close-to-spherical secondary particles.

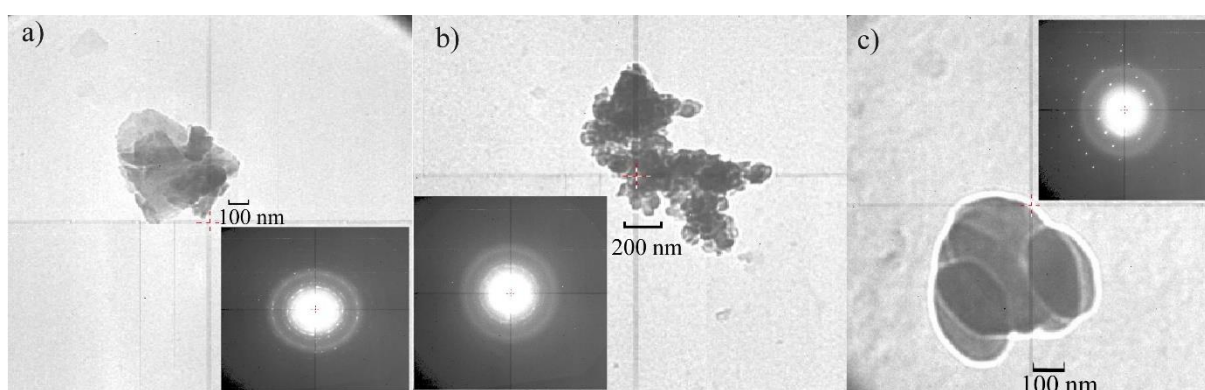


Figure 5. TEM micrographs of a) and b) PR-SnS₂ and c) HM-SnS₂ with corresponding SAED patterns

Further investigation of the crystallinity was done via TEM. Micrographs of PR-SnS₂ are shown in Figures 5a and b. Along with TEM micrographs, SAED patterns are presented. The sample was heterogeneous and consisted of a polycrystalline portion indicated by a characteristic ring pattern formed by distinct diffraction spots. The second selected cluster of the PR-SnS₂ sample presented in Figure 5b, on the other hand, showed a SAED pattern with halo rings and the absence of clearly distinct diffraction spots, resembling the ones expected from amorphous or highly nano-crystalline materials. A micrograph with the SAED pattern of HM-SnS₂ is presented in Figure 5c. The sample consists of smaller crystals of 200-300 nm size indicated by bright dots in the SAED pattern. The TEM micrographs and SAED patterns of both PR-SnS₂ and HM-SnS₂ follow the conclusions drawn for PXRD and SEM; PR-SnS₂ is partially amorphous, whereas HM-SnS₂ is a highly crystalline material.

The purchased MKN-SnS₂ and ball-milled MKN-SnS₂ were also subjected to PXRD and SEM. The XRD patterns and SEM images are shown in Figure 6. The results of refinements are included in Table 2.

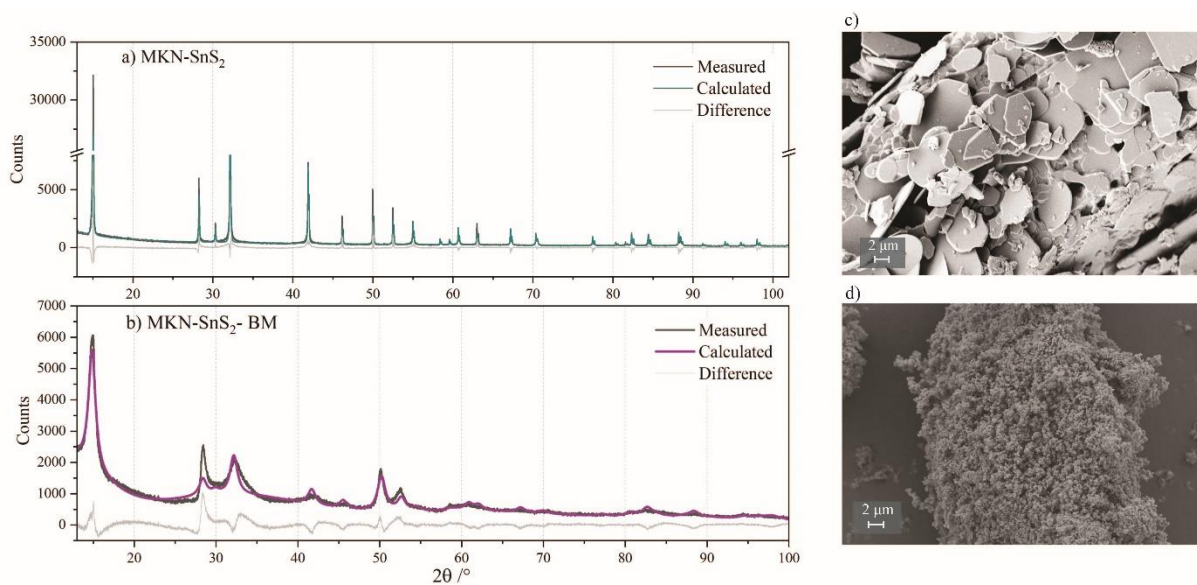


Figure 6. PXRD patterns and corresponding Rietveld analysis of a) MKN-SnS₂ and b) MKN-SnS₂-BM. SEM images of c) MKN-SnS₂ and d) MKN-SnS₂-BM.

Table 2. The details of the Rietveld refinement of XRD patterns of as-synthesized SnS and SnS₂ products and purchased SnS₂

Material	Conditions of the precipitation reaction	Phases/ Space group	Lattice Parameters [Å]	Cell Volume [Å ³]	Cryst allite size [nm]	R w p
PR-SnS	Sample after precipitation reaction at 60 °C with SnCl ₂ and TAA as sources of Sn and S, respectively	α -SnS/ <i>Pnma</i>	$a =$ 11.34±0.09	193.1(1)	45	8
			$b = 4.08 \pm$ 0.01			
			$c = 4.17 \pm$ 0.01			
			$a =$ 11.41±0.04			
			$b = 4.08 \pm$ 0.09	195.5(1)	10	9
			$c = 4.20 \pm$ 0.08			
			$a =$ 11.34±0.09			
			$b = 4.08 \pm$ 0.01			
			$c = 4.17 \pm$ 0.01			
			$a =$ 11.41±0.04			
HM-SnS	Sample after hydrothermal reaction at 180 °C with SnCl ₂ and TAA as sources of Sn and S, respectively	α -SnS/ <i>Pnma</i>	$a =$ 11.34±0.09	193.1(7)	75	6
			$b = 4.08 \pm$ 0.01			
			$c = 4.17 \pm$ 0.01			
			$a =$ 11.41±0.04			
			$b = 4.08 \pm$ 0.01			
PR-SnS ₂	Sample after precipitation reaction at 80 °C with SnCl ₄ ·5H ₂ O and TAA as sources of Sn and S, respectively	SnS ₂ / <i>P</i> - <i>3m1</i>	$a = 3.622$ ± 0.002	67.1(4)	8	9
			$c =$ 5.9109±0.0			
			$a = 3.622$ ± 0.002			
			$c =$ 5.9109±0.0			
			$a = 3.622$ ± 0.002			

HM-SnS ₂	Sample after hydrothermal reaction at 120 °C with SnCl ₄ ·5H ₂ O and TAA as sources of Sn and S, respectively		SnS ₂ / <i>P</i> -3 <i>m1</i>	<i>a</i> =	68.1(1)	60	.	1
	3.649±0.00			3				
	02			1				
	<i>c</i> =			3				
	5.9047±0.0							
	007							
MK-N-SnS ₂	purchased		SnS ₂ / <i>P</i> -3 <i>m1</i>	<i>a</i> =	68.0(1)	143	.	1
	3.6487±0.0			4				
	003							
	<i>c</i> =			8				
	5.8987±0.0			8				
	007							
MK-N-SnS ₂ -BM	Purchased/ ball-milled		SnS ₂ / <i>P</i> -3 <i>m1</i>	<i>a</i> =	68.6(4)	6	.	1
	3.638±0.00			1				
	6			4				
	<i>c</i> =			4				
6.98±0.04								

As expected, the refinements and SEM images clearly show that after MKN-SnS₂ was ball-milled at 200 rpm for 10 h, the crystallinity significantly decreased. The as-purchased MKN-SnS₂ exhibited an average crystallite size of 143 nm. The ball milling has significantly reduced the crystallinity, as indicated by the broader and poorer-defined diffraction peaks. Those samples exhibited an average crystallite size of approx. 6 nm.

4.2. Formation enthalpies of S, SnS, and SnS₂

To calculate the enthalpies of the formation of SnS and SnS₂ compounds applying drop solution calorimetry, the limiting partial enthalpies of solution of the respective compound in the tin bath, $\Delta_{\text{Sol}}\bar{H}_{\text{Sn}x\text{Sy}}^{\infty}$, $\Delta_{\text{Sol}}\bar{H}_{\text{Sn}}^{\infty}$, and $\Delta_{\text{Sol}}\bar{H}_{\text{S}}^{\infty}$ must be known. $\Delta_{\text{Sol}}\bar{H}_{\text{Sn}}^{\infty}$ is the enthalpy increment transforming solid Sn from ambient temperature to liquid Sn at calorimeter temperature. It can be directly calculated using the Dinsdale polynomials [39]. Reliable information on $\Delta_{\text{Sol}}\bar{H}_{\text{S}}^{\infty}$ at 1073 K was unavailable in the literature and therefore needed to be determined

experimentally. The results of the enthalpies of solution of S in the Sn bath at 1073 K are shown in Figure 7, indicating that the partial solution enthalpy varies roughly linearly with the mole fraction of S up to approx. 3 at.% S in Sn. Further drops show a clear, abrupt drop in the solution enthalpies, which gradually approach a constant value. This indicates a two-phase field, L + β -SnS, according to the published phase diagrams, e.g. Lindwall et al. [40]. The liquidus point of ~3 at.% at 1073 K well agrees with the calculated phase diagram in [40]. Furthermore, we see that the change in enthalpy at the liquidus phase boundary is about -55 kJ mol^{-1} of atoms, which should correspond to the enthalpy of formation of β -SnS from liquid sulphur and liquid tin. Converted to solid sulphur and solid tin as the reference state, this would be -50 kJ mol^{-1} of atoms, which agrees quite well with the literature results for α -SnS, see section 2. It is not expected that α -SnS and β -SnS exhibit significantly different heats of formation.

The limiting partial enthalpy of solution of S in the Sn bath at infinite dilution, $\Delta_{\text{sol}}\bar{H}_S^\infty$, can be determined by a linear extrapolation of the values within the purely liquid phase to $x_{\text{sulphur}} = 0$. $\Delta_{\text{sol}}\bar{H}_S^\infty$ was determined to be $-17.0 \pm 1.3 \text{ kJ mol}^{-1}$ from three different runs. To our knowledge, this work is the first to report on the experimentally determined limiting molar enthalpy of solution of S in Sn. The given error corresponds to the standard error of the linear data fit. The enthalpy increments $\Delta H = H_{(S(l), TC)} - H_{(S(s), TO)}$, derived from the Dinsdale polynomials [32], were used to calculate the partial limiting enthalpy of mixing of S in Sn. $\Delta_{\text{Mix}}\bar{H}_{S \text{ in Sn}}^\infty$ was found to be $-43.3 \pm 1.3 \text{ kJ mol}^{-1}$, thus confirming the pronounced exothermic mixing behaviour reported in the literature, e.g. in Lindwall et al. [40].

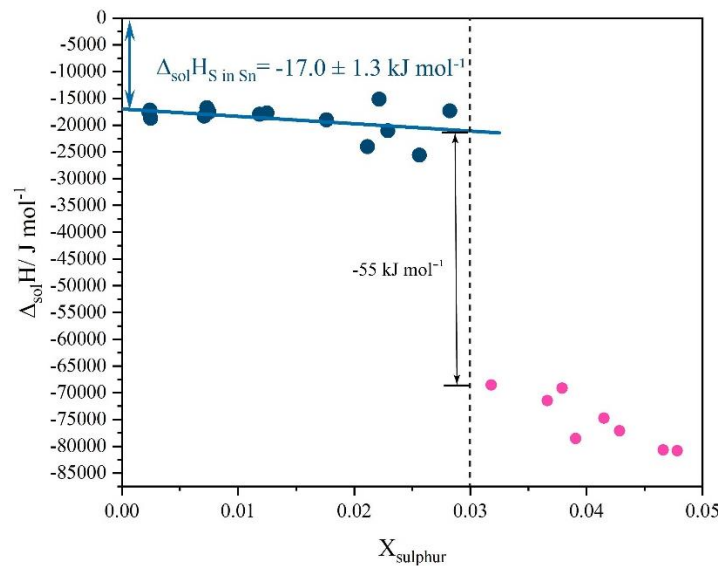


Figure 7. Limiting enthalpy of solution of sulphur at 1073 K of sulphur in tin

The measured values of the partial enthalpy of solution of PR-SnS and HM-SnS in Sn at 1073 K are shown in Figures 8a and 8b, respectively. Accordingly, the limiting partial enthalpy of solution of PR-SnS in Sn is $58.9 \pm 0.9 \text{ kJ mol}^{-1}$, whereas that of HM-SnS in Sn is $54.8 \pm 0.9 \text{ kJ mol}^{-1}$.

The measured partial enthalpy of solution values of PR-SnS₂ and HM-SnS₂ in Sn at 1073 K are shown in Figures 9a and 9b, respectively. Accordingly, the limiting partial enthalpy of solution of PR-SnS₂ in Sn is $48.9 \pm 1.4 \text{ kJ mol}^{-1}$, whereas that of HM-SnS₂ in Sn is $48.4 \pm 0.9 \text{ kJ mol}^{-1}$.

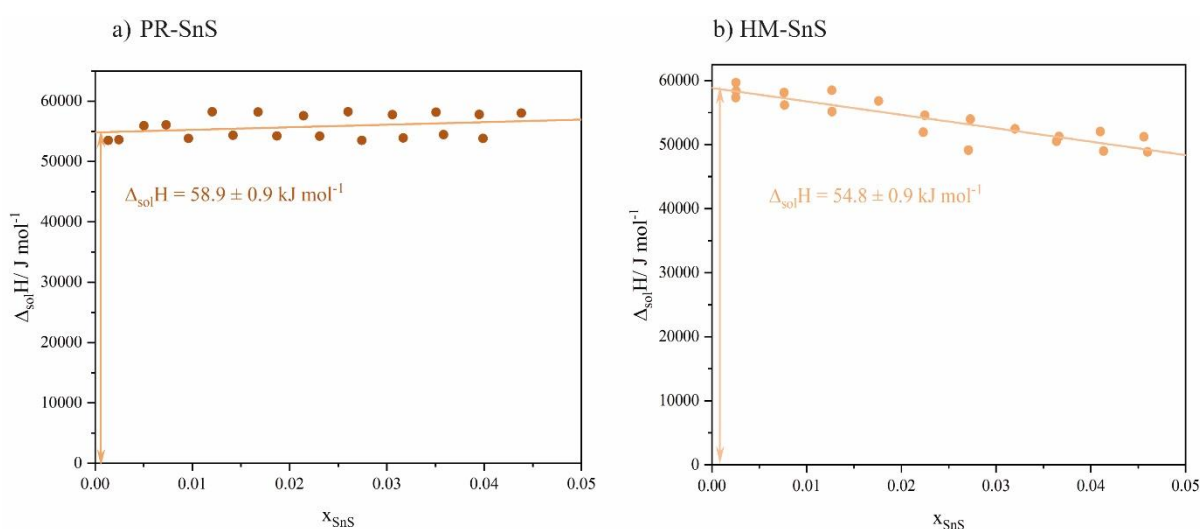


Figure 8. The limiting enthalpy of solution of a) PR-SnS and b) HM-SnS at 1073 K in tin

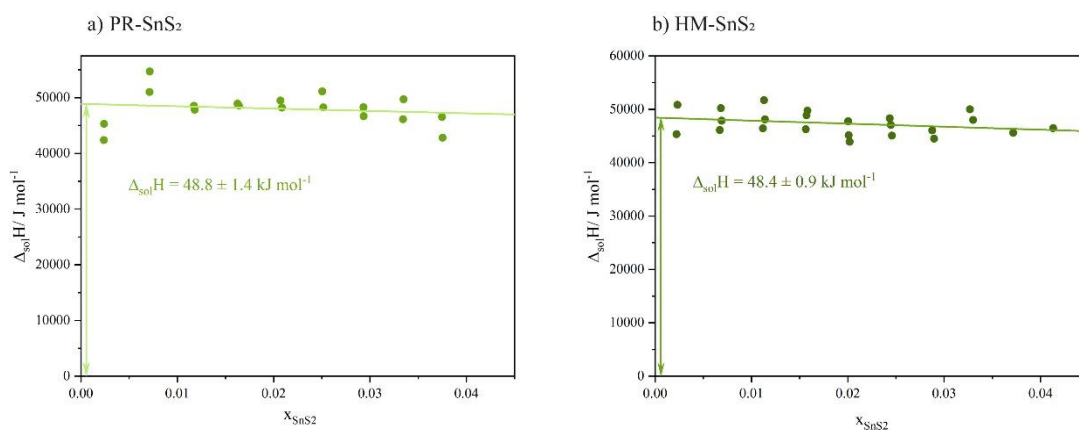


Figure 9. The limiting enthalpy of solution of a) PR-SnS₂ and b) HM-SnS₂ at 1073 K in tin

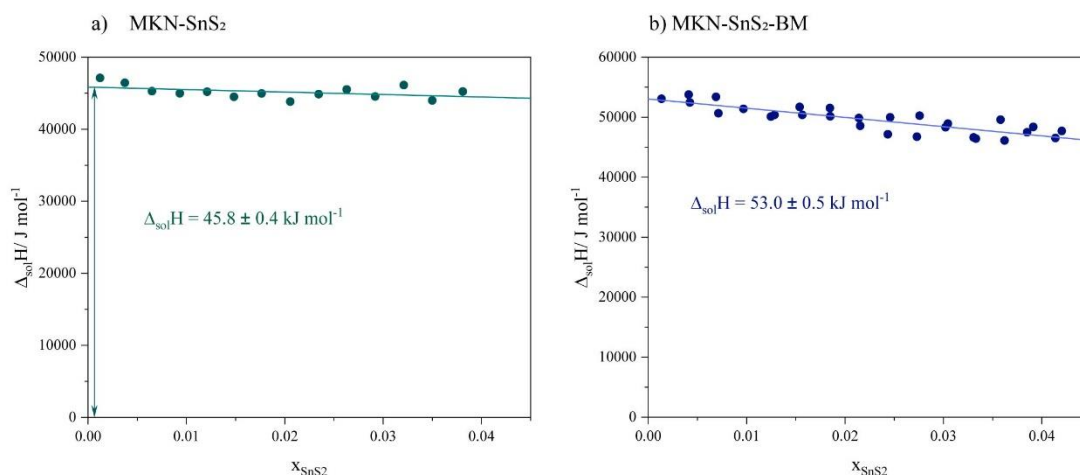


Figure 10. The limiting enthalpy of solution of a) pristine and b) ball-milled MKN- SnS_2 at 1073 K in tin

The commercially available, macro-crystalline MKN- SnS_2 sample was also dropped into the liquid tin. The results of those experiments can be seen in Figure 10. The resulting limiting partial enthalpy of solution is $45.8 \pm 0.4 \text{ kJ mol}^{-1}$. The limiting partial enthalpy of solution of MKN- SnS_2 -BM was also measured, and it was determined to be $53.0 \pm 0.5 \text{ kJ mol}^{-1}$. At the time of performing experiments, phase pure SnS was not commercially available as all commercially available products showed significant Sn_2S_3 impurities.

The determined limiting partial enthalpy of solution of sulphur and those of the as-prepared tin sulphides were subsequently used to calculate the enthalpy of formation of the respective materials according to equation (7) shown in section 3.4. The calculated values of the standard formation enthalpy $\Delta_f H^\circ$ for all materials investigated in this study are presented in Table 3. The given error was evaluated by error propagation calculation.

The enthalpy of formation ($\Delta_f H^\circ$) of SnS and SnS_2 were previously reported in numerous publications, both experimentally determined using various techniques and from calculations, see section 2. The available data have been compiled and well-assessed by Gamsjäger et al. [34]. The experimental results for α -SnS range from -42 to -55 kJ per mole of atoms, and those for SnS_2 range from -41 to -57 kJ per mole of atoms. Interestingly, the values related to one mole of atoms are in the same range for both compounds. The stronger intralayer bonding in SnS_2 seems to outweigh the stronger interlayer bonding in SnS, as it was discussed in section 1.

All experimental results of this study are within the range of literature values. The nanocrystalline or amorphous states are metastable and do not represent thermodynamic equilibrium (see section 1). Therefore, endothermic enthalpy contributions are expected. Those contributions can be related to the increased interfacial energy, defect concentration (for the nanocrystalline state), and reduced lattice energy (for the amorphous state). As a result, a material with a smaller crystallite size would be less stable and exhibit a less negative enthalpy of formation. In the case of SnS, this is indeed observed. The partially amorphous PR-SnS (maximum crystallite size of 45 nm) has a smaller crystallite size, so that the measured enthalpy of formation of $-48.8 \text{ kJ mol}^{-1}$ is less negative compared to HM-SnS (average crystallite size of 75 nm) with $-52.8 \text{ kJ mol}^{-1}$. However, regarding errors, the difference of 4 kJ mol^{-1} is hardly significant but falls within the expected range; (see section 1, [31], [32]).

On the other hand, a considerable difference in the enthalpy of formation between precipitated (crystallite size of 8 nm) and hydrothermally synthesized (crystallite size of 60 nm) SnS_2 was not observed. In that case, there is no dependency between formation enthalpy and crystallite size. For comparison, the enthalpy of formation of a commercially available SnS_2 material with an average crystallite size of 143 nm was determined. The result of $-47.6 \text{ kJ mol}^{-1}$ is even less negative than that for PR- SnS_2 and HR- SnS_2 . This is surprising since the nano-crystalline state is less stable than the macro-crystalline state, and one would expect a more negative enthalpy of formation for the later one. The texture of the purchased SnS_2 powder sample is somewhat peculiar– it shows large platelets in the SEM image, what is also confirmed by a very strong preferred orientation along the [001] direction as detected by PXRD analysis, see Figure 6. The energetic state of a solid powder is not only influenced by its crystallite size but also by the extent of agglomeration as well as the size and shape of its particles. The equilibrium particle size is the result of a balance between bulk energy, which lowers with r^3 , and the surface energy, which rises with r^2 , where r is the radius of a spheric particle in this model [41]. Large particles that deviate significantly from a spherical shape can be deemed unstable. In order to demonstrate this, the commercially purchased MKN- SnS_2 material was subjected to ball milling, as discussed in Chapter 3.2. Through this process, the average crystallite size was reduced from 143 to 6 nm, resulting in smaller and more spherical particles, as depicted in Figure 6. Importantly, the enthalpy of formation exhibited a notable increase in negativity after ball milling, approximately by 7.1 kJ mol^{-1} . Directing the focus towards PR- SnS_2 and HM- SnS_2 , it was observed that both materials exhibited comparable enthalpies of

formation although PR-SnS₂ had a smaller crystallite size whereas HM-SnS₂ had a larger particle size, see Table 2 and Figure 4. This finding suggests that the particle size exerts a substantial influence on the stability of a powdered material and may overshadow the influence of the crystallite size.

In conclusion, it is evident that particles with larger sizes and significant deviations from spherical shape tend to exhibit instability. The reduction in particle size, achieved through ball milling, resulted in a more negative enthalpy of formation even so the crystallite size was strongly reduced. Furthermore, the enthalpies of formation for PR-SnS₂ and HM-SnS₂, despite their differences in crystallite size, were found to be comparable.

These thermodynamic considerations are only plausible if the entire amount of powder dropped into the Sn-bath has dissolved. To rule out the possibility of larger particles remaining undissolved during the drop periods, the measurements were promptly terminated after the final drop and the resulting ingot from the solidified Sn-bath containing approx. 3 at. % S was subsequently cut, embedded and polished. Detailed investigations employing SEM/EDX revealed the presence of pure Sn along with SnS, which obviously precipitated upon cooling. This observation aligns with the expectation from the equilibrium phase diagram presented in Lindwal et al. [40], indicating the formation of a two phase region between Sn and SnS at lower temperatures, when the liquid phase with up to 3 at% S (maximum concentration of the bath) is cooled. No visible traces of undissolved SnS or SnS₂ were detected. Respective backscattered electron (BSE) images and EDX results can be found in Supplementary information (Figure S1 and Table S1).

Table 3. Enthalpy of solution in tin, formation enthalpy and electrochemical work released on GCPL lithiation. All values refer to one mole of substance.

Material	Calorimetry		Full Lithiation	
	$\Delta_{\text{Sol}} \bar{H}_{\text{in Sn}}^{\infty}$ in kJ mol ⁻¹	$\Delta_{\text{f}} H^{\circ}$ in kJ mol ⁻¹	ω_{el} in kJ mol ⁻¹ (experimental)	$\Delta_{\text{r}} G^{\circ}$ in kJ mol ⁻¹ (calculated)
PR-SnS	58.9 ± 0.9	-48.8 ± 2.2	-222.5	-258.0
HM-SnS	54.8 ± 0.9	-52.8 ± 2.0	-212.5	-258.0
PR-SnS ₂	48.8 ± 1.4	-51.1 ± 2.8	-245.3	-304.4

HM-SnS ₂	48.4 ± 0.9	-50.1 ± 2.2	-248.0	-304.4
MKN-SnS ₂	45.8 ± 0.4	-47.6 ± 1.8	-232.7	-304.4
MKN-SnS ₂ -BM	53.0 ± 0.5	-54.7 ± 1.4	-200.8	-304.4

4.3. Electrochemical determination of the Gibbs free energy

Each of the six aforementioned compounds underwent electrochemical lithiation using the galvanostatic discharge at slow specific currents of 5.5 mA g⁻¹ for SnS and 6.045 mA g⁻¹ for SnS₂. These specific discharge currents correspond to a C/200 rate (discharge in 200 hours), assuming a theoretical specific capacity of 1209 mAh g⁻¹ for SnS₂ and 1111 mAh g⁻¹ for SnS. The discharge curves for all compounds investigated in this work are shown in Figure 11. The individual curves for each compound are given in Supplementary information (Figures S2-S4). The electric work of the lithiation process can be derived by plotting the change of cell potential, E , as a function of the molar amount of Li (n_{Li}) in phase B. By integrating the area under the E vs. n_{Li} curve and multiplying the value with the Faraday constant, F , the electric work, ω_{el} , of the process can be calculated. Consequently, the total energy that is released during discharge is proportional to the total area under the curve. Under standard equilibrium conditions at constant pressure (1 atm) and temperature (298.15 K), it should correspond to the standard Gibbs energy of the reaction according to the following equation:

$$-\Delta_f G^\circ (\text{Li}_x\text{B}) = -F \int_0^{x=y} E(x) dx \quad (8)$$

The values for the electric work determined by galvanostatic discharge for all compounds are listed in Table 3, together with the calculated Gibbs energies of the reactions. The Gibbs energy of the reactions were calculated using the thermodynamic data tabulated in Table 4 which all refer to one mole of atoms. It should be noted that all values in Table 3 correspond to the reaction of one mole of atoms of the respective tin sulfide.

Table 4. Enthalpy, entropy, and Gibbs energy of formation of SnS, SnS₂, Li₂S and Li₁₇Sn₄. All values refer to one mole of substance under standard conditions.

Compound	$\Delta_f H^\circ$ in kJ mol ⁻¹	$\Delta_f S^\circ$ in J mol ⁻¹ K ⁻¹	$\Delta_f G^\circ$ in kJ mol ⁻¹	Reference
SnS	-54.8	-0.96	-53.85	[34]
SnS ₂	-50.5	-2.78	-47.70	[34]
Li ₂ S	-147.1	-9.90	-144.2	calc. from [Bin_1999]
Li ₁₇ Sn ₄	-40.2	-12.9	-36.4	[42]

The complete lithiation reaction for SnS can be expressed as $\text{SnS} + 6.25 \text{Li} \rightarrow \text{Li}_2\text{S} + \text{Li}_{4.25}\text{Sn}$. According to the discharge experiments at C/200, the electric work for HM-SnS is -212.5 kJ mol⁻¹. Using values from literature listed in Table 4, the standard Gibbs energy of formation is calculated to be -258.0 kJ mol⁻¹.

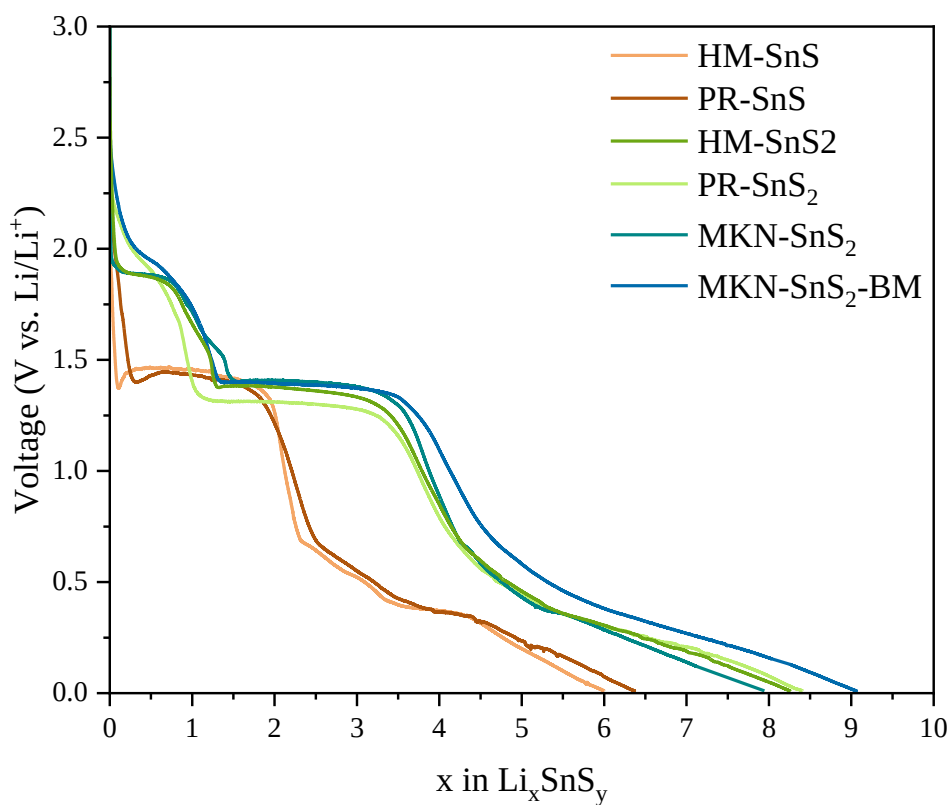


Figure 11. Cell potential as a function of the molar amount of Li of HM-SnS₂. The cell was discharged with constant current of C/200.

Similarly, the experimentally determined electric work of SnS_2 relates to the full lithiation reaction: $\text{SnS}_2 + 8.25 \text{ Li} \rightarrow 2 \text{ Li}_2\text{S} + \text{Li}_{4.25}\text{Sn}$. According to the experiments at slow discharge rate, a value of $-248.0 \text{ kJ mol}^{-1}$ was obtained. However, when using values from literature listed in Table 4, the standard Gibbs energy of formation is calculated to be $-304.4 \text{ kJ mol}^{-1}$.

There are several reasons for the mismatches between the calculated and experimental values. However, the main reason is that at room temperature even at low specific currents, the spontaneous diffusion of Li within the solid phases is insufficient to establish bulk electrochemical equilibrium. Additionally, other factors such as the presence of amorphous products, parasitic reactions, or mechanical stress due to the formation of Li_2S via the conversion reaction can contribute to this disparity. Even techniques like galvanostatic intermittent titration (GITT), which incorporate relaxation time between small current steps, fail to reproduce equilibrium conditions at room temperature [30].

Despite the differences between the experimentally measured and theoretical values for the electric work, a clear correlation can be observed between the enthalpy of formation of reactants and the electric work of the lithiation reaction. Specifically, compounds with more negative enthalpies of formation exhibit lower amounts of electric work released. For instance, PR-SnS had an enthalpy of formation of $-48.8 \pm 2.2 \text{ kJ mol}^{-1}$ and a measured electric work of $-222.5 \text{ kJ mol}^{-1}$ whereas, HM-SnS, which had a more negative enthalpy of formation of $-52.8 \pm 2.0 \text{ kJ mol}^{-1}$, showed a less negative electric work of $-212.5 \text{ kJ mol}^{-1}$. On the other hand, as the enthalpy of formation of PR-SnS₂ and HM-SnS₂ are similar to each other within the experimental error ($-51.1 \pm 2.8 \text{ kJ mol}^{-1}$ for PR-SnS₂ and $-50.1 \pm 2.2 \text{ kJ mol}^{-1}$ for HM-SnS₂) the experimentally determined electric work values for the self-synthesized SnS₂ compounds are also similar ($-245.3 \text{ kJ mol}^{-1}$ for PR-SnS₂ and $-248.0 \text{ kJ mol}^{-1}$ for HM-SnS₂). It was shown that the commercially available MKN-SnS₂ sample had a less negative enthalpy of formation of $-47.6 \pm 1.8 \text{ kJ mol}^{-1}$, corresponding to a more negative electric work of $-232.7 \pm 1.4 \text{ kJ mol}^{-1}$. After ball-milling, the enthalpy of formation of the MKN-SnS₂-BM sample acquires a more negative value of $-54.7 \pm 1.4 \text{ kJ mol}^{-1}$, whereas the electric work during lithiation becomes less negative at $-200.8 \text{ kJ mol}^{-1}$.

These results show that the greater the stability of the educts, the more energy is required to break the compounds apart during the lithiation reaction, resulting in a less exergonic process at the end of discharge. However, it should be noted that the electric work released is influenced by many thermodynamic and kinetic

parameters which can also vary. Thus, although the thermodynamic equilibrium values of the electric work could not be attained in the electrochemical experiments, the observed trends, however, agree qualitatively with thermodynamic considerations.

5. Conclusion

SnS and SnS₂ materials exhibiting various morphologies and particle sizes were synthesized via the precipitation reaction and hydrothermal methods. These tin sulfides, particularly SnS₂, are under consideration as active anode materials in Li-ion batteries. Generally, the materials synthesized via the hydrothermal reaction exhibit larger crystallite sizes compared to those synthesized via the precipitation reaction. The results of this study revealed that the enthalpies of formation of as-prepared SnS become less exothermic as the crystallite size decreased. However, no similar effect could be observed for the as-synthesized SnS₂ samples. Interestingly, when as-synthesized SnS₂ was compared to commercially purchased SnS₂, the latter exhibited an even smaller, less negative enthalpy of formation. This finding is surprising, considering that the nano-crystalline state is generally assumed to be less stable than the macro-crystalline state. However, it was observed that the commercially available, macro-crystalline SnS₂ consisted of quite large platelets, which may reflect a non-equilibrium morphological growth of the powder particles. When this sample was subjected to ball-milling, a nano-crystalline material with smaller, spherical particles was obtained. The measured enthalpy of formation of the ball-milled material was significantly more negative compared to the pristine material. Therefore, the high energy state associated with the presence of large flat particles (spherical particles are usually considered lowest energy) may have been released during ball-milling. Furthermore, a correlation between the stability of starting materials and electric work released during electrochemical lithiation at low specific currents (C/200) was drawn. It was found that the lithiation reactions involving starting materials with more negative enthalpies of formation release less electric work during the discharge reaction. This observation aligns well with the notion that more energy is required to decompose the more stable educts.

6. Acknowledgements

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6. Appendix 2

Kurzfassung

In den letzten Jahren haben Zinnsulfide, insbesondere SnS und SnS₂, in der Energiespeicherforschung große Aufmerksamkeit erregt. Ihre hohen theoretischen spezifischen Kapazitäten (1111 mAh g⁻¹ für SnS und 1209 mAh g⁻¹ für SnS₂) machen diese Gruppe von Materialien zu vielversprechenden Kandidaten für anodenaktive Materialien für Li-Ionen-Batterien. Außerdem haben sie den Vorteil, dass sie kostengünstig und umweltfreundlich sind. Während des Lithiierungsprozesses gehen Sn-S-basierte Materialien eine Umwandlungsreaktion mit Li ein und bilden Li₂S und Sn. Eine weitere Lithiierung löst die Legierungsreaktion zwischen Sn und Li aus, wodurch verschiedene intermetallische Sn-Li-Phasen entstehen. Diese neu gebildeten Sn-Li-Phasen haben ein wesentlich größeres Einheitszellenvolumen als ihre Ausgangsphasen, sodass die Partikel bei wiederholtem Legieren und Entlegieren von Zinn Risse bekommen. Letztlich führt die kontinuierliche Rissbildung in den Partikeln meist zu einer Pulverisierung des Anodenmaterials, zu Kontaktverlust zwischen den Partikeln und zu Kapazitätsabfall. Bei kleinen Zinnpartikeln, die sich bei der Umwandlung von Sn-S-basierten Materialien in einer Li₂S-Matrix abgeschieden haben, kann das Problem der Partikelrissbildung und des Kapazitätsabfalls jedoch gemildert werden.

Im Mittelpunkt dieser Arbeit steht das Verständnis und die Bewertung der Beziehung der Struktur und des Verarbeitungsprozesses von Sn-S-Materialien und Sn-S-basierten Elektroden. Solche Untersuchungen können zu messbaren Verbesserungen der elektrochemischen Leistung dieser Materialklasse führen.

Für die Synthese von SnS- und SnS₂-Materialien wurden die Fällungsmethode und hydrothermale Reaktionen verwendet. In allen Fällen wurde SnCl_x · yH₂O (x = 2; y = 2 für SnS und x = 4; y = 5 für SnS₂) als Sn-Quelle und Thioacetamid als S-Quelle verwendet. Die physikalisch-chemischen Eigenschaften der synthetisierten Materialien wurden mittels Pulverröntgendiffraktometrie (PXRD) untersucht. Die Strukturparameter wurden durch Rietveld-Analyse der gemessenen Muster ermittelt. Darüber hinaus wurde die Morphologie der Proben mit Hilfe der Rasterelektronenmikroskopie (REM) charakterisiert und die Kristallinität der Proben mit Hilfe der Transmissionselektronenmikroskopie (TEM) untersucht. Das Vorhandensein von Oberflächenverunreinigungen, die sich während der Materialsynthese bilden können, wurde mittels Röntgen-

Photoemissionsspektroskopie (XPS) untersucht. Außerdem wurden die so hergestellten Materialien der Tropfenlösungskalorimetrie unterzogen, um die Bildungsenthalpie zu bestimmen. Die Ergebnisse zeigten keinen signifikanten Unterschied in der Bildungsenthalpie pro Mol Atome zwischen SnS und SnS₂, ebenso wie zwischen denselben Verbindungen mit unterschiedlichen Kristallitgrößen.

Weiters wurde die elektrochemische Leistungsfähigkeit der so hergestellten Materialien verglichen. Es wurden entsprechende Knopfzellen mit den SnS_x-Aktivmaterialien gegen Li/Li⁺ gefertigt. Auf diese Weise wurden Materialien mit gleicher chemischer Zusammensetzung, aber unterschiedlicher Partikelgröße und Morphologie mit Materialien mit unterschiedlicher chemischer Zusammensetzung und sehr ähnlicher Morphologie verglichen.

Mit der *in-situ*-Dilatometrie-Technik wurden die Veränderungen der Dicke von SnS- und SnS₂-Elektroden während des Zyklus untersucht. *Ex-situ*-XRD und *ex-situ*-SEM wurden eingesetzt, um die Rolle der Kristallchemie und der Partikelmorphologie für die elektrochemische Leistung *post-mortem* zu untersuchen. Die Ergebnisse zeigten, dass sich die Elektrode aus teilweise amorphem SnS₂, das durch Präzipitation synthetisiert wurde, bei der Legierungsbildung am wenigsten ausdehnt. Außerdem zeigen die Zyklierungsdaten, dass teilmorphes SnS₂ leistungstärker als SnS und gut kristallisiertes SnS₂ ist. Zwei Effekte könnten für diese Ergebnisse verantwortlich sein. Erstens bilden sich allgemein dickere Li₂S-Schichten auf Partikeln mit geringerer spezifischer Oberfläche, wodurch die Volumenänderungen von Sn während des Zyklierens besser zurückgehalten werden. Zweitens wird angenommen, dass Li₂S und Sn aufgrund des Interkalationsschritts vor der Umwandlungsreaktion in SnS₂ auf atomarer Ebene homogen verteilt sind, was wiederum dazu beiträgt, die Volumenausdehnung während des Zyklus zu minimieren.