Elucidation of the reaction mechanisms of isostructural FeSn₂ and CoSn₂ negative electrode for Na-ion batteries

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Abstract

Alternatives to hard carbons need to be identified to improve the energy density of Na-ion batteries. Negative electrode materials based on intermetallics generally outperform the different carbon-based electrode. They have the advantages to present a high gravimetric capacity (> 500 mAh/g) and a very high volumetric capacity, due to their density. However those advantages are counter balanced by their lack of stability due to the large volume changes they experience along cycling. FeSn₂ and CoSn₂ are investigated as negative electrode materials for Na-ion batteries. The 1st cycle and the 10th cycle of the Na/MSn₂ reaction is probed using operando XRD coupled to XAS to reveal the formation and ageing reaction mechanisms occurring along cycling. The role of the transition metal and the number of electron involved in both materials reveal different reaction pathways leading to the recombination of FeSn₂ at the end of the desodiation, whereas CoSn₂ is unable to recombine and thus its electrochemical performance fades faster.

Introduction

Stationary energy storage is gaining importance, as the world moves towards relying on renewable but intermittent energy sources. Cost is the most prevalent factor for such stationary energy storage applications and in light of this, research on Na-ion batteries has been growing. Unlike lithium, sodium is extremely abundant all across the world and its production is consequently cheap.¹ However, no suitable anode materials have yet been found for sodium ion batteries since graphite cannot be used. Thus, research into this area is imperative to allow commercialisation of Na-based system.²

Active materials based on P, Sb and Sn have been shown to react reversibly with sodium; however their reactions are accompanied by large volume changes which lead to fast fading of the performance.³⁻⁶ By alloying these active elements to transition metals that do not react directly with sodium, this effect can be mitigated. Following this approach, we decided to explore the family MSn_2 (with $M = Co$ and Fe) as promising sodium-ion battery anode materials. The two alloys have the same structure and space group, yet they show different electrochemical performances with $FeSn_2$ always outperforming $CoSn_2$.⁷ To date, the reaction mechanisms of both alloys were not explored in Na-ion batteries but only in Li-ion batteries. The crystalline alloy $CoSn_2$ was first investigated as an anode material for Li-ion batteries by Bousquet *et al.* using ex situ XRD and in situ ^{119}Sn Mössbauer spectroscopy.⁸ They noticed a reaction mechanism in two steps i) a slight lattice parameter increase initially, indicating that a small Li insertion in the $CoSn_2$ structure, followed by ii) a conversion reaction giving a Li_xSn phase with the extrusion of the Co nanoparticles. A later study by Naille *et al.* found that the fully discharged state was in fact Li_7Sn_2 yet with around 20% of unreacted $CoSn_2$.⁹ Reports on the exact delithiation mechanism are scarce; no crystalline phases seem to be present making analysis difficult. ^{119}Sn Mössbauer spectroscopy possibly reveals a ternary Li-Co-Sn phase during delithiation yet unfortunately no more detail on this structure is given.⁸

In a similar manner, $FeSn_2$ was intensively investigated as an anode material for Li-ion batteries¹⁰⁻¹⁵ During lithiation $FeSn_2$ reacts directly in a one-step reaction to a lithiated tin phase, however disagreement on whether this phase is $Li_{4.4}Sn$ ¹¹ or Li_7Sn_2 ¹³ remains. Either way the use of ^{57}Fe Mössbauer spectroscopy revealed that Fe was extruded as nanoparticles located at the interface of the Li-Sn alloy grains.^{12, 13} On delithiation, some back reaction of Sn with Fe to form $FeSn_2$ was detected yet some Fe nanoparticles remains even at full delithiation.^{12, 13}

In 2013, an electrodeposited amorphous $CoSn_2$ film on nickel foam was explored as an anode material for both Li-ion and Na-ion batteries by Gonzalez *et al.*,¹⁶ however, the Na-ion battery performance was very poor with the irreversible specific charge being greater than 70%. In the same year Ellis *et al.* explored the reaction of a tin cobalt carbon nanocomposite.¹⁷ At 60°C the composite delivered around 180 mAh/g for 16 cycles. 130 mAh/g of this could be attributed to the carbon matrix while the remaining 50 mAh/g are delivered by the conversion reaction of 38% of the Sn content in the nanocomposite to $Na_{15}Sn_4$. The remaining tin is

hypothesized to be inaccessible at the centre of large CoSn grains. In 2015 Yui *et al.* tested a Sn-Co powder from Mitsubishi (9:1 ratio) in a Na-ion battery cell.¹⁸ The powder was found to be a mixture of Sn, CoSn and Co₃Sn₂. It demonstrates good cyclability delivering 300 mAh/g for 30 cycles when PAA binder was used. The coulombic efficiency could be increased to 99.9% by pre-doping the electrode with Na. A follow-up paper by the same group demonstrated an even better cyclability of 400 mAh/g for 20 cycles. Recently, we investigated the reaction mechanisms of MnSn₂ used as negative electrodes of Na-ion batteries and identify an interesting reaction mechanisms evolving during cycling and we discover an intermediate phase Na-Mn-Sn helping to maintain the good electrochemical performance.¹⁹

To date, the reaction mechanism of FeSn₂ and CoSn₂ has not been investigated in Na-ion batteries and especially the role of the transition metal in isostructural family. Theoretically, both offer a promising specific charge larger than 650 mAh/g (two to three times larger in term of gravimetric capacity than hard carbon materials) once converted to Na₁₅Sn₄. We therefore explore FeSn₂ and CoSn₂ as negative electrode materials for Na-ion batteries, probing it electrochemically mechanisms by combining operando X-ray diffraction coupled to ex situ X-ray absorption in the 1st cycle as well as after ageing in the 10th cycle.

Experimental part

The synthesis of CoSn₂ and FeSn₂ was reported elsewhere⁷.

The electrodes were cast onto aluminium foil via doctor blading from a suspension of 70 wt.% active material, 18 wt.% SuperC65 (IMERYS) and 12% sodium carboxymethyl cellulose (CMC, AlfaAesar) in water. After drying in air the electrodes were punched and dried further at 80°C under vacuum for two hours. Typical electrode loading was between 3-4 mg/cm². The electrochemical cells were assembled in an argon filled glovebox using sodium metal (Sigma-Aldrich) as counter electrode and glass fibers as separator soaked with 1 M NaClO₄ (AlfaAesar) in PC (BASF) + 5 vol.% FEC (BASF).

Galvanostatic cycling was performed by applying a current of 18.1 mA/g and 18.3 mA/g for CoSn₂ and FeSn₂, respectively. This current corresponds to 1 Na⁺/5 hrs reacting per formula unit, which if the full specific charge of the material (680 mAh/g) is achieved is a cycling rate of C/37.5. A potentiostatic step to 1/5th of the current was applied at the end of every galvanostatic step. The GITT measurements were performed by applying a C/30 rate for one hour, followed by a 20 hour relaxation period. Along this paper all the potentials will be given using Na⁺/Na as reference.

The XRD analyses were performed on a Panalytical Empyrean diffractometer equipped with a Cu K α radiation source (XRD). Operando XRD measurements were performed in a homemade cell with a beryllium window in the Bragg-Brentano geometry described elsewhere.²⁰ A self-standing electrode was used for these experiments, composed of 70 wt% Sn, 18 wt% SuperC65 and 12 wt% CMC binder. The electrode was cast from a water-based

suspension onto copper foil and delaminated from the copper foil upon drying at 100°C for 1 h. 250 μ L of electrolyte were used in the XRD cell to soak the glass fiber separator.

Ex situ XAS samples: The electrodes were extracted from the cell and then washed in dimethyl carbonate (DMC) and then dried. The washing process serves to remove any remaining salt residue and the solid electrolyte interphase (SEI) on the surface of the electrode. XAS ex situ samples were measured in capillaries (1mm diameter) at X05LA beamline at the Swiss Light Source, Paul Scherrer Institute. The mass of active material to be filled homogeneously into the capillary was determined using the program XAFSmass. The parameters used were: $\mu_{\text{r}}d = 2$, $S = 0.45 \text{ cm}^2$ and the data table applied was Henke. Extended X-ray Absorption Fine Structure (EXAFS) was measured at the transition metal edge for the two MSn_2 structures ($M = \text{Co}, \text{Fe}$) by sweeping the energy from about 50 eV below the edge jump to about 1000 eV above the edge jump. All data was treated using Demeter with Strawberry Perl suite getting path lengths for modelling from references in the ICSD database.

Results

Electrochemical properties of CoSn_2 and FeSn_2

The first cycle of the two alloys are plotted in Figure 1. In the first sodiation (solid lines), both alloys first show quite a steep slope downwards from 1.3V starting potential. At 0.65 V CoSn_2 shows a first bump whereas FeSn_2 only shows this at 0.55 V. The plateau is slightly longer for FeSn_2 than for CoSn_2 leading to a higher specific charge for the former. At around 0.08 V both alloys show another sloping plateau, bringing them to 5 mV at around 160 mAh/g. A 20-hour potentiostatic step was applied at this voltage leading to a specific charge of 420 mAh/g for FeSn_2 and 320 mAh/g for CoSn_2 . Upon desodiation two plateaus are seen for both alloys. The first plateau is at the same voltage for both alloys while the second starts ever so slightly lower for CoSn_2 than for FeSn_2 . The length of the first plateau is much longer for FeSn_2 which ultimately also results in a higher specific charge achieved. At the end of the desodiation, FeSn_2 gives back 240 mAh/g whereas CoSn_2 gives only 190 mAh/g resulting on the irreversible charge loss of 43% and 41% for FeSn_2 and CoSn_2 respectively. Such a large irreversible charge loss is common to conversion/alloy-based materials with large particle size. Most of the charges are consumed by the solid electrolyte interphase (SEI) formation coupled to the large volume change occurring during cycling, generating cracks and thus, particles disconnection.

Figure 1: First cycle of FeSn_2 and CoSn_2 .

The galvanostatic curves after the 1st formation cycle of CoSn_2 (Figure 2) show two main sodiation potential plateaus, a short potential plateau at 0.25 V and a long sodiation potential plateau at 0.04 V. Both potential plateaus show a dip, where a lower potential is accessed briefly before reaching a higher value again as sodiation progresses. Interestingly on desodiation no such features are present, indicating that the desodiation occurs along a simpler, less hindered reaction pathway compared to the sodiation. On desodiation, there is one long potential plateau at around 0.2 V and a short potential plateau at around 0.51 V.

Figure 2: Galvanostatic curves and their derivatives for CoSn_2 for the 2nd, 5th and 20th cycle.

It is interesting to note that the polarisation seems to be reduced significantly over 20 cycles in sodiation whereas almost no difference can be observed in desodiation. This feature is more visible in the derivative curves. Such a reduced overpotential would be expected for an activation mechanism as the reaction of small particles is expected to be easier than for the large micron-sized particles present initially (mechanism caused by the large volume changes occurring in the materials along sodiation/desodiation as described elsewhere [ref]). The growth in intensity of all the peaks in the derivative curve along cycling also supports the hypothesis of more material becoming involved in the sodiation process with cycling.

Furthermore, the derivative curve gives insight into the number of reaction steps involved on sodiation and desodiation. The lower desodiation potential plateau actually consists of two processes as indicated by the shoulder at 0.15 V before the intense peak at 0.2 V.

FeSn₂ (Figure 3) reacts slightly differently than CoSn₂. On sodiation only one dominant lower potential plateau is visible in the 2nd cycle at 0.04 V. Only in the course of cycling does an upper sodiation potential plateau at around 0.25 V develop, growing in intensity from the 5th to the 20th cycle. The growth in specific charge achieved thus comes from the development of a new reaction pathway. As with CoSn₂ a decrease in the overpotential of the cell is observed with cycling, shifting the sodiation potential plateaus to higher potentials. Interestingly, on desodiation a small additional potential plateau is visible at 0.63 V for FeSn₂ from the beginning, in addition to the two desodiation potential plateaus at 0.18 V and 0.54 V, which were also present for CoSn₂.

Figure 3: Galvanostatic curves and their derivatives for FeSn₂ for the 2nd, 5th and 20th cycle.

When looking at the derivative curve the development of the peak at 0.25 V on sodiation can be clearly tracked. On desodiation no shoulder is observed for the lower potential plateau, unlike CoSn₂. This may be because the process responsible for the shoulder in CoSn₂ i) is either not present in the FeSn₂ system or ii) is present but occurs at exactly the same potential as the dominant process at 0.18 V.

Relaxation measurements: Galvanostatic intermittent titration technique (GITT)

The GITT of the first sodiation of CoSn₂ is shown in Figure 4. The top of the curve marked with a black line gives an approximation of the “thermodynamic potential” after 20 hours of relaxation. For the first eight days of the GITT measurement (Region I), the large potential change under current flow and during relaxation of over 750 mV indicates that predominantly surface reactions are occurring at this potential, which easily relaxes back to the “bulk” potential during OCP. Thereafter, the bulk sodiation starts to occur and the potential relaxation reduces to around 200 mV, drawing out a sloping thermodynamic potential curve (Region II). Finally, the slope flattens and the uptake of Na⁺ leads to the formation of a stable

bulk phase as indicated by the potential relaxation during OCP reducing further to only 60 mV (Region III). From the last 25 days of the measurement, it becomes apparent that the reaction which is usually seen very close to the cut-off potential of 5 mV, in fact has a “thermodynamic potential” of around 70 mV.

Figure 4: GITT of CoSn_2 . 1 hour sodiation at a rate of $C/30$ was followed by 20 hours of OCP.

The GITT confirms that the first sodiation of CoSn_2 occurs without bypassing a stable intermediate state but rather via a direct conversion of CoSn_2 into one final phase. A total of 4.8 Na^+ is transferred per formula unit of which the first 0.8 Na^+ could be attributed to SEI formation. Thus 3.8 Na^+ are expected to have been transferred to each CoSn_2 unit, which is only half of the theoretical prediction of 7.5 Na^+ .

Figure 5 (top) shows the GITT of the sodiation of FeSn_2 . As with CoSn_2 initially surface reactions dominate the cell, which can be seen by the large relaxation potential of around 750 mV in the first eight days of measurement (Region I). Interestingly, then a phase with a large overpotential seems to be formed between the 8th and the 21st day of cycling (Region II). This occurs between a “thermodynamic potential” of 1.3 to 1.1 V. Here the relaxation reduces to around 350 mV indicating that a more stable phase is formed than the easily reversible surface reactions. As the relaxation is still quite large, it seems that the phase formed here most probably has slow sodiation. This intermediate phase seems to be unique to the reaction of FeSn_2 and nothing analogous was seen in the GITT of CoSn_2 . This feature could arise from the Fe_2O_3 oxide impurity detected using ^{57}Fe Mössbauer spectroscopy (not shown), which has been shown to react at these high potentials.^{21, 22}

Thereafter, from the 24th to the 40th cycling day the potential relaxation rapidly decreases to be only 100 mV. The thermodynamic potential slopes down before evening out at 70 mV. Around 6 Na^+ were transferred per formula unit of FeSn_2 . Again roughly 1 Na^+ is most probably

consumed by irreversible reactions. Thus, we estimate that around 5 Na⁺ reacted with the bulk of every FeSn₂ formula unit, which is far below the predicted 7.5 Na⁺ upon full conversion to Na₁₅Sn₄. Additional information on the relaxation observed in the region II and region IV can be found in Supplementary Materials (Figure S1).

Figure 5: GITT of FeSn₂. 1 hour sodiation at a rate of C/30 was followed by 20 hours of OCP.

As can be seen, the two materials do not perform the same in terms of amount of Na reacted since FeSn₂ always outperforms CoSn₂. Thus, as one moves across the periodic table to use transition metals with more electrons, the specific charge achieved by the material deteriorates. This can be explained by looking at the metallic bonding. The strength of bonds in metals directly correlates with the number of electrons and nuclei involved in the bonding, the number of 4s and 3d delocalised electrons.²³ FeSn₂ has the least amount of electrons involved in its bonding and therefore has the weakest bonds which favour its conversion to form Na₁₅Sn₄. The opposite is true for CoSn₂ with the most electrons in its metallic bonds and the poorest electrochemistry.

To better understand why the electrochemistry of CoSn₂ and FeSn₂ is different, their reaction mechanisms were investigated using a combination of ex situ samples and operando analysis techniques like powder X-ray diffraction (XRD). In addition, we not only study the first cycle but we also investigate the ageing mechanism by comparing the first cycle with later cycles.

Operando XRD of the 1st cycle

The XRD patterns obtained during the first sodiation of CoSn_2 are displayed in the form of a XRD contour plot in Figure 6 and Figure 7 with the corresponding electrochemistry on the right hand side. CoSn_2 (tetragonal, $I4/mcm$, JCPDS n° 01-077-4978²⁴) is the only phase present at OCV as expected. When cycling commences the potential drops rapidly in the first hour before a potential plateau is reached at around 0.5 V. From literature, we know that the so called solid electrolyte interphase (SEI) is built up at this potential.³ This is a surface modification rather than a bulk reaction and it is thus unsurprising that no changes are seen in the XRD contour plot at this stage. After ca. 20 h, the potential drops again and reaches a low potential plateau at < 0.1 V, the most dominant reaction in the sodiation procedure. At this low potential the CoSn_2 peaks start to diminish in intensity. After ca. 50 h, four new peaks start to appear and grow in intensity as the CoSn_2 peaks continue to diminish. The four new peaks belong to $\text{Na}_{15}\text{Sn}_4$ (cubic, $I-43d$, n° 03-065-2166²⁵). The formation of $\text{Na}_{15}\text{Sn}_4$ must result in the extrusion of cobalt, yet the XRD signature of cobalt was not observed, indicating that the cobalt has no long range order and is most probably in the form of nanoparticles²⁶⁻²⁸. The reaction mechanism on sodiation is thus analogous to the lithiation in $\text{CoSn}_2\text{-Li}$ cells, where CoSn_2 was found to convert to Li_7Sn_2 ^{8,9} or $\text{Li}_{4.4}\text{Sn}$ ²⁹ and extruded Co nanoparticles.

Figure 6: XRD contour plot on the left and the corresponding current (absolute value in mA) and potential of the cell on the right during the 1st sodiation of CoSn_2 .

After 64 h of cycling the cell reaches 5 mV, however since the specific charge achieved at this point is far from the theoretical specific charge, a potentiostatic step was applied to complete sodiation. However, despite the long potentiostatic step applied (ca.20 h), the CoSn_2 phase is still visible at the end of full sodiation, indicating that a part of the electrode did not react at all, or that only the surface of particles reacted, leaving an unreacted core. From peak analysis about 60% of the original CoSn_2 phase is still present at the end of full sodiation. For the reaction between CoSn_2 and lithium, unreacted CoSn_2 at full lithiation was also observed, however it was only about 20%, indicating a more complete reaction in the lithium system.⁹

The first desodiation of CoSn_2 is shown in Figure 7. The $\text{Na}_{15}\text{Sn}_4$ peaks are shifting to higher angles immediately as desodiation begins, a feature only reported by our group in the case of MnSn_2 [ref]. A shift to higher angles indicates a solid solution in the $\text{Na}_{15}\text{Sn}_4$ system, maintaining the same cubic crystal system but with shrinking lattice parameters. Interestingly, for the desodiation of $\text{Na}_{15}\text{Sn}_4$ in Na-Sn cells no such lattice shrinking had been observed either^{4, 30}. Thus, the presence of the transition metal seems to play a role in this new reaction pathway.

Figure 7: XRD contour plot on the left and the corresponding current (absolute value in mA) and potential of the cell on the right during the 1st desodiation of CoSn_2 .

Unfortunately, the patterns of this intermediate $\text{Na}_{15-x}\text{Sn}_4$ phase are too low in quality to perform a structural analysis to quantify the “exact” sodium content. Instead, we use an approximate method based on the electrochemical data to estimate how much sodium was extracted from the system in the process of forming $\text{Na}_{15-x}\text{Sn}_4$ without taking into account possible and probable other reactions. To do this, we assume that going from full sodiation to the shifted spectra of $\text{Na}_{15-x}\text{Sn}_4$ all the sodium extracted from the system via electrochemistry is extracted from the $\text{Na}_{15}\text{Sn}_4$ phase rather than any amorphous sodium containing phases or surface reactions that might be present at full sodiation. After 93 h of cycling the $\text{Na}_{15-x}\text{Sn}_4$ phase shows the biggest shift just before disappearing. At this point 2.4 Na^+ have been extracted from what we assume to be fully sodiated $\text{Na}_{15}\text{Sn}_4$, yielding the maximum sodium-deficient composition of $\text{Na}_{12.6}\text{Sn}_4$ before another conversion reaction takes place and this phase vanishes.

Upon further desodiation no more changes are observed in the XRD patterns. We do not see any increase in the intensity of the peaks belonging to the CoSn_2 phase. Here, we can formulate some hypotheses i) Co and Sn do not recombine to form CoSn_2 after the first cycle, ii) CoSn_2 is recombined in a highly disordered manner with nanosized particles or in amorphous solid, thus not detectable by XRD and, iii) a new phase totally amorphous is involved. From our previous paper⁷, we know that the signature of CoSn_2 is not visible after the first cycle and that a new peak in cathodic sweep appears which evolves constantly after each subsequent cycles. Thus, we believe that hypothesis 1 is more favourable than hypothesis 2, even if we cannot exclude it. For the hypothesis 3, more investigations are described in the XRD analysis after 10 cycles, presented below in Figure 11. The potentiostatic step at the end of desodiation shows a current which falls off very rapidly, indicating that the reaction is complete after reaching 1 V. This amorphous nature of the reactions on charge was also seen for CoSn_2 cells cycled against lithium, where no back reaction of Co and Sn to form CoSn_2 was observed either.⁹

Similar approach was applied to FeSn_2 . Unfortunately, with standard cycling protocol we were unable to obtain any valuable results for FeSn_2 (Supplementary Materials Figure S2). Thus, we opted for a modified cycling protocol including six potentiostatic steps on sodiation (500, 400, 300, 200, 100, and 50 mV, Figure 8). Allowing reactions to reach completion at each of these potentials should reveal any metastable phases with slow kinetics that might not have a chance to form during galvanostatic cycling. However, despite this additional time granted to the system no intermediate phases were found as seen by the unchanged contour plot in the first 55 h of sodiation (Figure 8).

Initially only FeSn_2 peaks (tetragonal, $I4/mcm$, n° 01-077-4977²⁴) are present, as expected. At very low potentials (< 0.1 V and ca. 60 h of cycling) the FeSn_2 peaks slowly diminish in intensity and shortly after (ca. 70 h) a new set of peaks belonging to $\text{Na}_{15}\text{Sn}_4$ appears. This conversion reaction is analogous to the lithium ion system where FeSn_2 was observed to convert to $\text{Li}_{4.4}\text{Sn}$ ^{11, 31} or Li_7Sn_2 ^{13, 15} in a one-step reaction. Above 100 h a potentiostatic step is applied at

5 mV. The current during this potentiostatic step falls off very slowly, hinting that the conversion reaction is still ongoing. This is confirmed by further growth in the $\text{Na}_{15}\text{Sn}_4$ peaks and further fading of the FeSn_2 peaks in the XRD contour plot. At full sodiation (190 h) about 15% of FeSn_2 is still present, which is far less than was the case at the full sodiation of CoSn_2 . Incomplete reaction of the MSn_2 active material on discharge seems to be a common trend; it was also observed for the Li-FeSn_2 cells tested by Mao *et al.*¹¹

Figure 8: XRD contour plot on the left and the corresponding current (absolute value in mA) and potential of the cell on the right during the 1st sodiation of FeSn_2 .

On desodiation (Figure 9), the $\text{Na}_{15}\text{Sn}_4$ peaks are seen to shift to higher angles as was the case for the CoSn_2 system, forming the sodium-deficient cubic phase $\text{Na}_{15-x}\text{Sn}_4$. Using the same approximation as used for CoSn_2 , we calculated by means of electrochemistry that roughly 3.6 Na^+ have been extracted from the system for every $\text{Na}_{15}\text{Sn}_4$ formula unit yielding a composition of $\text{Na}_{11.4}\text{Sn}_4$ just before the conversion reaction.

Figure 9: XRD contour plot on the left and the corresponding current (absolute value in mA) and potential of the cell on the right during the 1st desodiation of FeSn₂.

Figure 10 shows the evolution of the peak position of the most intense peak of the Na₁₅Sn₄ phase (220). As the electrode is desodiated a shift to higher angles is observed. This shift is roughly linear for the first 21 h of desodiation (i.e. from the 195th to the 226th h of cycling) with a rate of change of 0.0052°/h. During this time, the differential capacity plot shows two main features, a shoulder at 204 h (indicated by a black arrow) and a dominant peak at 221 h. Right after this dominant reaction, the rate of the shift in the 2θ position triples (0.0163°/hr) leading to an additional shift to higher angles of 0.22° in the following 13 h. The differential capacity shows another minor shoulder at 231 h (indicated by a red arrow). The total shift in peak position of the sodium-deficient phase observed between the 195th and the 239th hour of cycling is 0.36° and the differential capacity indicates that three separate processes occur during this time. The lattice parameter is thus found to shrink from 13.36 Å to 13.16 Å. This is a decrease of 0.2 Å in nominal terms or a relative shrinkage of 1.5% compare to the original structure Na₁₅Sn₄.

Figure 10: Shift in the 2θ position of the most intense peak of cubic $\text{Na}_{15}\text{Sn}_4$ just above 19° (220) plotted over time together with the corresponding differential capacity dQ/dE . Error in position of peak maxima is $\pm 0.03^\circ$.

As desodiation continues, after the disappearance of the $\text{Na}_{15-x}\text{Sn}_4$ phase, it seems that no other phase appears at first. However, during the second desodiation potential plateau at above 0.5 V the peaks attributed to FeSn_2 increase in intensity. It thus seems that a part of the extruded Fe recombines with Sn to reform FeSn_2 , a process which was not observed for the CoSn_2 system. As the intensity scales of Figure 8 and Figure 9 are the same the intensity of the FeSn_2 peaks at OCV in Figure 8 can be directly compared to the FeSn_2 peaks at the end of desodiation in Figure 9. This comparison shows that despite some recombination occurring, the amount of crystalline FeSn_2 at the end of the 1st desodiation is far less than the amount of crystalline FeSn_2 present at OCV showing that the recombination to FeSn_2 is not complete. Comparing this reaction to its lithium counterpart, back reaction of Sn with Fe to form FeSn_2 was detected on delithiation in FeSn_2/Li cells but some Fe remained at full delithiation, indicating that recombination was not complete in the lithium system as well.^{12, 13}

Ageing mechanisms studied by operando XRD

A typical characteristic of conversion-based anode materials is that their reaction mechanisms evolve during cycling due to the large structural changes the materials undergo and the

difficult recombination occurring. Generally the 10th cycle reaction mechanism looks very different from that of the 1st cycle. We thus decided to study and analyse the 10th cycle reaction mechanism by means of operando XRD and ¹¹⁹Sn Mössbauer spectroscopy to investigate how the material ages with cycling. Unfortunately, as can be seen in Supplementary Information Figure S3 and Table S1, Mössbauer spectroscopy was not a suitable technique with ex situ samples because of the relaxation of the samples.

Figure 11 shows the 10th sodiation and desodiation of a CoSn₂ electrode. The electrochemistry displays two potential plateaus on sodiation (230 mV and 40 mV) followed by a potentiostatic step at 5 mV and on desodiation there are also two potential plateaus (180 mV and 530 mV) followed by a potentiostatic step at 1.5 V. During the potentiostatic steps the current stabilized at different rates compared to what was observed during the 1st cycle. After sodiation the fall-off current is faster than was the case in the 1st cycle, indicating that the reaction is less kinetically hindered (most probably due to the reduction of the particle size caused by mechanical stress from large volume changes). However, the drop-off of current at the end of sodiation is still slow when compared to the potentiostatic step at 1.5 V after desodiation where the current is nearly zero in just over an hour.

Figure 11: XRD contour plot on the left and the corresponding current (absolute value in mA) and potential of the cell on the right during the 10th cycle of CoSn₂. Due to the weak intensity caused by the amorphisation of the materials along cycling, the intensity scale had to be adjusted for the 10th cycle and cannot be compared directly to the intensities in the 1st cycle.

At first glance we can see analogous features and new features when compared to the 1st cycle. The residual presence of some CoSn₂ at full sodiation is still seen even after ten cycles. On sodiation along the first potential plateau at 230 mV no changes are visible, however, along the second potential plateau at around 40 mV we can again see the formation of Na₁₅Sn₄ occurring. As the intensity of the CoSn₂ phase does not change between the desodiation and sodiation extremes, Na₁₅Sn₄ must be formed from an amorphous tin-containing phase. Along desodiation, the solid solution of Na_{15-x}Sn₄ is formed again as evidenced by the shift of the Na₁₅Sn₄ peaks to higher angles.

A new peak (32.8°, marked in grey in Figure 11, see Supplementary Materials, Figure S4) was observed during cycling at potentials between ca. 1.5 V to 0.7 V. This peak is visible during the first two hours of sodiation (0-2 h) and the last five hours of desodiation (55-60 h). The complete disappearance and reappearance of this peak at roughly the same intensity indicates that this phase is electrochemically active. The appearance of the peak was very abrupt indicating a comparatively fast reaction.

In a similar manner, the 10th cycle of FeSn₂ was investigated and the operando XRD contour plot along with the corresponding electrochemistry on the right is shown in Figure 12. The electrochemistry shows three potential plateaus on sodiation (500 mV, 255 mV and 45 mV, the upper most of which can be attributed to SEI formation because new electrolyte was added to the cell) and three potential plateaus on desodiation (185 mV, 540 mV and 630 mV). The potentiostatic step after sodiation shows rapid current decay but seems to asymptote to roughly a quarter of the original current, which could indicate Na plating. This current decay is faster during the 5 mV potentiostatic step in the 10th cycle than in the 1st cycle. In the potentiostatic step after desodiation the current decays close to zero within an hour as was the case previously (1st cycle).

Figure 12: XRD contour plot on the left and the corresponding current (absolute value in mA) and potential of the cell on the right during the 10th cycle of FeSn₂. Due to the weak intensity caused by the amorphisation of the materials along cycling, the intensity scale had to be adjusted for the 10th cycle and cannot be compared directly to the intensities in the 1st cycle.

Like for CoSn₂ some novel and some familiar features are visible in the 10th cycle of the FeSn₂-Na cell compared to the 1st cycle. Once again, the formation of Na₁₅Sn₄ is seen at the end of sodiation with no intermediate states observed prior to that. On desodiation, the formation of the solid solution Na_{15-x}Sn₄ still offers a functioning pathway by which sodium is extracted from the electrode. During the lower potential plateau at 185 mV the Na_{15-x}Sn₄ phase disappears to the benefit of an amorphous phase. However, while reformation of FeSn₂ was observed on desodiation above 0.5 V during the 1st cycle, no such recombination of Fe with Sn was observed during the 10th cycle. This loss of the recombination pathway with ageing was also observed for the reaction of FeSn₂ with lithium.³¹ During the potential plateau at 540 mV no changes were seen, such that the majority of the electrode remains amorphous. Finally on the last desodiation potential plateau at 630 mV after 73 h two new peaks are seen to appear abruptly at 30.6° and 32.8° (see Supplementary Materials, Figure S4). This abrupt transition at potentials > 0.6 V is analogous to the new peak seen in the 10th cycle of the CoSn₂ system.

X-ray absorption spectroscopy (XAS)

In analysing the oxidation state using the X-ray absorption near edge structure (XANES) method we expected to first see the transition metal with a non-zero oxidation state and during cycling see it shift to a zero oxidation state at full sodiation, indicating the extrusion of metallic transition metal upon the formation of $\text{Na}_{15}\text{Sn}_4$. However, when analysing the X-ray absorption near-edge structure (XANES) of the MSn_2 materials the transition metal already showed an oxidation state of zero, most probably due to the metal bonding delocalizing the charge between M and Sn. To see this, the XANES of FeSn_2 is shown in Figure S5 as an example along with the spectra of the Fe reference foil. The onset of the edge jump for the reference foil and the FeSn_2 pristine sample is at the same energy with no difference in pre-edge features, indicating that the oxidation state of the Fe in FeSn_2 and in Fe foil is the same.³² XANES could thus not be used to distinguish a change in oxidation state by energy shifts in the edge jump and pre-edge features of the Fe K-edge absorption. Thus, we focused on the EXAFS part.

The Fourier transform of the EXAFS spectra of pristine CoSn_2 is shown in Supplementary Materials, Figure S6). The fit is in fairly good agreement with the experimental data at low radial distances ($< 2.9 \text{ \AA}$), however divergence in both the intensity and the periodicity of the oscillations is seen between $2.9 \text{ \AA}$ and $3.5 \text{ \AA}$. This could arise in parts due to longer paths not being considered in the fitting process; as such paths generally display more contribution at higher radial distances. Furthermore as the pristine CoSn_2 was synthesised via mechanosynthesis, a method known to cause structural defects,³³ the mismatch between the Fourier transform and the fit could come from the synthesis. Figure 13 shows the Fourier transform of the EXAFS spectra of CoSn_2 at the 28th sodiation. The fit shows that CoSn_2 is still present after 28th cycle, however we noticed also the contribution of Co^0 nanoparticles confirming the conversion reaction mechanism. However, at high radial distances $> 2.9 \text{ \AA}$ the fit diverges from the structure observed. This can be explained by the data at these higher radial distances being less reliable and/or the model used for the fit is incomplete. Lee *et al.*³⁴ studying the lithiation of a Sn-Co-C composite anode material observed a similar behaviour in their EXAFS data and indicated that lithiation did not break the Co-Sn bonds, suggesting a ternary phase of Li-Sn-Co. Such a ternary phase had also been proposed by Bousquet *et al.*⁸ on the basis of their Mössbauer data.

Comparing the Fourier transforms of the pristine and the cycled materials, we noticed that, the biggest changes are observed in the decrease of the peak at $2.5 \text{ \AA}$ and the growth in the features above $2.9 \text{ \AA}$. While the fit used takes the former into account well, the latter is totally neglected and cannot be reproduced by the model used. A longer bond length between Co and another species must then be also present. This could be an indication of a ternary phase containing Co, Sn and Na. Co and Na do not react with each other, however, a ternary phase may be a possibility, despite never having been reported previously. With Na having a larger van-der-Waals radius than Sn ³⁵ and fewer protons and electrons than Sn, a Co-Na environment would be expected to show a longer metallic bond length in theory than the Co-Sn bond length, which could potentially lead to the features observed at high radial distances.

Taking into account the unknown phase discover by operando XRD after ageing (10th cycle), we can reasonably think that along cycling a new ternary Na-Co-Sn phase appears.

Figure 13: (left) Fit of the Fourier transform of the recorded EXAFS-spectrum of CoSn₂ at the 28th sodiation; (right) Fit of the Fourier transform of the recorded EXAFS-spectrum of FeSn₂ at the 48th sodiation (black)

The Fourier transform of the pristine Fe K-edge EXAFS of FeSn₂ is shown in Supplementary Materials, Figure S7. As for CoSn₂, the fit is in agreement with the experimental data with a dominant contribution arising from FeSn₂ and a bit of iron oxide. The Fourier transform of an ex situ sample at the 48th sodiation (aged) is shown in Figure 12 along with its fit. The aged FeSn₂ sample shows a completely different spectrum and fit compared to the aged CoSn₂ sample. Aged FeSn₂ could be fitted very well using only the first two shells of FeSn₂ and Fe metal. The iron environment dominated the fit indicating that the majority of the iron is in metallic form at this stage, confirming the extrusion of Fe nanoparticles along cycling. These EXAFS analyses have strong parallels with what was observed for Li/FeSn₂ cells where a reduction in the signal of the Fe-Sn bonds was reported in conjunction with an increase in the signal for Fe-Fe metal bonds.³¹

Role of the transition metal

From the novel phase identified by operando XRD after 10 cycles (also identified in our recent study on MnSn₂¹⁹), we can see that the angles at which the peaks are observed are close yet not identical. The simultaneous appearance of these new phases, at 710 mV, point toward a similar mechanism between the different MSn₂ cells. We hypothesise that the novel peaks belong to a crystalline Na_xM_ySn_z phase (M = Co, Fe, Mn¹⁹) formed at this potential. By comparing the peaks of this new phase in FeSn₂ and MnSn₂, we immediately notice that the MnSn₂ peaks at 28.6°, 32.6° and 42.3° all lie about 0.2° below the peaks seen for aged FeSn₂. From the pristine materials, we know that MnSn₂ Bragg reflexions were simply shifted to lower angles compared to the Bragg peaks of pristine FeSn₂. This shift to lower angles is the hallmark of an analogous but larger unit cell, which can be attributed to the larger size of the transition metal element Mn than Fe. For the Na_xM_ySn_z hypothesis, the novel peaks appearing

upon ageing involve the transition metal which would change between the different aged MSn_2 cells. Assuming the novel phases are identical except for the change in transition metal, the transition metal size ($\text{Mn} > \text{Fe} > \text{Co}$) would be expected to influence the lattice parameters, leading to slightly larger parameters for the system containing Mn compared to the other two systems. The data shows exactly these tendencies and would thus be in agreement with the strong impact of the transition metal upon cycling.

Thus, the differences in the reaction mechanisms of the MSn_2 family members lie in the degree of recombination to the original phase on desodiation and in the formation of an additional Na-Sn intermediate phase different from the ternary $\text{Na}_x\text{M}_y\text{Sn}_z$. MnSn_2 ¹⁹ shows both of these features in the first as well as the 10th cycle. FeSn_2 shows partial recombination but no Na-Sn intermediate phase and CoSn_2 has none of these two features. MnSn_2 is thus the only material allowing the intermediate phase Na_7Sn_3 to be accessed¹⁹. We hypothesise that the weaker bonding interactions between Mn and Sn due to the lower proton and electron numbers of Mn allow Sn to remain independent such that the Na_7Sn_3 intermediate can be formed.

Conclusions

FeSn_2 and CoSn_2 show relatively good electrochemical performance (better than hard-carbons) as a negative electrode material for Na-ion batteries. Their reaction mechanisms were investigated using operando X-ray diffraction in both the 1st and the 10th cycle and couple with the x-ray absorption spectroscopy performed on the pristine sample and on aged samples. In the first cycle, we observe a direct conversion of the intermetallic into $\text{Na}_{15}\text{Sn}_4$ and extruded transition metal nanoparticles (evidence by XAS). On desodiation, both of them reacted through a solid solution of $\text{Na}_{15-x}\text{Sn}_4$ type. At the end of the full desodiation, CoSn_2 is not recombined whereas FeSn_2 is recombined to a certain extent showing the importance of the transition metal in such reaction. After 10 cycles, operando XRD measurements reveal that the mechanisms presented in the first cycle is roughly kept in both cases where a new ternary phase is identified so far not reported yet in the ICSD database.

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