MnSn₂ negative electrode for Na-ion batteries: a conversion-based reaction dissected

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Abstract:

To date, the most common negative electrodes used in Na-ion batteries are based on hard carbons, offering around ca. 250 mAh/g gravimetric capacity but only 400 mAh/cm³ volumetric capacity due to their low density. Negative electrode materials based on intermetallics could outperform this with both a higher gravimetric capacity (400+ mAh/g) and a higher volumetric capacity (1000+ mAh/cm³) but often struggle with cycling stability. Here MnSn₂ is investigated as an electrode material for Na-ion batteries for the first time and delivers 400 mAh/g for over 50 cycles, by far outperforming its parent (Sn) in terms of cycling stability. The 1st cycle and the 10th cycle of the Na/MnSn₂ reaction is probed using electrochemical methods and operando XRD to reveal the formation and ageing reaction mechanisms. It is shown that MnSn₂ benefits from a robust reaction mechanism where all features seen in the 1st cycle (insertion into MnSn₂, formation of Na₁₅Sn₄, Na_{15-x}Sn₄, Na₇Sn₃ and MnSn₂ reformation) are still visible in the 10th cycle, explaining the cycling stability.

Introduction

Sodium-ion batteries are expected to offer cheaper large scale electrochemical energy storage in the near future, however, currently many challenges still remain in different areas (materials and electrolyte) before this goal is achievable.¹⁻⁶ In particular a novel negative electrode material must be found as the most commonly used negative electrode in Li-ion batteries, graphite, does not intercalate Na-ions.^{7, 8} Hard carbons and intermetallic materials are the most promising candidates currently under investigation.⁶ The former has the problem of low volumetric energy density while the latter struggles with large volume expansion during cycling, leading to poor cycling stability. To mitigate the large volume expansion of intermetallic materials such as Sn which take up 3.75 Na per formula unit upon sodiation,⁹⁻¹¹ one can use inactive-active intermetallics instead.¹²⁻¹⁶ We implement this strategy here using the “inactive” transition metal Mn (which doesn’t alloy with Na) and investigate MnSn₂ as a negative electrode material for Na-ion batteries.

MnSn₂ has been successfully used as a negative electrode material in Li-ion batteries, providing a specific charge of above 500 mAh/g for more than 20 cycles.¹⁷ Out of the three isostructural MSn₂ materials (M = Co, Fe, Mn), MnSn₂ is the least studied. It was first suggested as an anode material for Li-ion batteries already in 2000 by Beaulieu *et al.* who investigated a range of C-Mn-Sn compositions,¹⁸ yet electrochemical tests on MnSn₂ were not performed until 2013. Mahmoud *et al.* cycled MnSn₂ and investigated the discharge mechanism in detail, finding the formation of Li₇Sn₂ alloy and the extrusion of Mn nanoparticles.¹⁷ On charge they suggest that back reaction of Mn with Li_xSn could occur but encouraged further investigations. The following year Philippe *et al.* provided a more detailed investigation into the charge reaction mechanism of MnSn₂ using XRD, ¹¹⁹Sn Mössbauer, X-ray photoelectron and Auger spectroscopies.¹⁹ At full lithiation they observed that some unreacted MnSn₂ was still present. On delithiation the ¹¹⁹Sn Mössbauer spectra could not be fitted simply using the characteristic doublet of Li₇Sn₂ and that of MnSn₂ but needed an additional doublet with flexible parameters. This changing doublet could arise either from a lower lithium content tin phase Li_xSn or from a ternary Mn-Li-Sn phase. The Mössbauer parameters of these two intermediates would be expected to be similar and the additional phase could therefore not be identified unambiguously. At higher potentials back reaction of Mn with Sn to form magnetic MnSn₂ particles was also observed. Recently Mahmoud *et al.* investigated the solid electrolyte interphase (SEI) formed on MnSn₂ using impedance spectroscopy, concluding that the capacity fade of the material arose mainly from the continuous growth of the SEI layer along cycling.²⁰

So far, MnSn_2 has not been investigated in Na-ion batteries. Theoretically, it offers a promising specific charge of 688 mAh/g upon full conversion from MnSn_2 to $\text{Na}_{15}\text{Sn}_4$ and extruded Mn metal. We therefore investigated MnSn_2 as a negative electrode material for Na-ion batteries, probing it electrochemically first and then using operando XRD to identify the reaction mechanism in the 1st cycle as well as after ageing in the 10th cycle with our custom made XRD cell.

Experimental Methods

The MnSn_2 alloy was prepared by mechano-synthesis in a Pulverisette 7 premium line (Fritsch). In an Ar-filled glovebox, two grams of stoichiometric mixture of Mn (Aldrich, > 99.5%) and Sn (ABCR, 325 mesh) were placed in a 45 mL stainless steel ball-milling vessel containing 30 stainless steel balls of 5 mm diameter each. The powder was milled at 800 rpm in cycles of 15 min active/10 min passive for 99 cycles.

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 NaClO_4 (AlfaAesar) in PC (BASF) + 5 vol.% FEC (BASF).

Galvanostatic cycling was performed by applying a current of 18.35 mA/g, which corresponds to 1 Na^+ /5 hrs reacting per formula unit. If the full specific charge of the material (688 mAh/g) is achieved this corresponds to a cycling rate of C/37.5 (full charge or discharge in 37.5 hours). A potentiostatic step to 1/5th of the calculated current was applied at the end of every galvanostatic step. Along this paper all the potentials will be given using Na^+/Na as reference.

The structure of the intermetallic was analysed using a Panalytical Empyrean diffractometer equipped with a Cu $K\alpha$ radiation source (XRD). Measurement of the pristine sample was performed on a flat rotating zero background plate. The diffractogram was then analysed using the FullProf Suite Program.²¹ Operando XRD measurements were performed in a homemade cell with a beryllium window in the Bragg-Brentano geometry described elsewhere.²² 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 μL of electrolyte

were used in the XRD cell to soak the glass fiber separator. One in situ diffractogram was recorded at 50°C by pausing the cell at the appropriate potential for 24 h to enable pattern collection.

A Carl Zeiss UltraTM 55 electron microscope at 3 kV in secondary electron detection mode was used for morphology analysis (SEM).

Results and Discussion

Figure 1 shows the XRD diffractogram with the Le Bail refinement and an SEM picture of the synthesised MnSn_2 powder. All peaks could be indexed in the tetragonal space group $I4/mcm$ and no impurities were detected. The lattice parameters obtained are slightly smaller than the ones reported in literature (Table 1), which could arise from the mechanosynthesis method which puts the material under tremendous strain during synthesis. The SEM image and the broad peaks in the diffractogram reveal the small particle size (nanometers to a few micrometers) and the small crystallite size of the powder, respectively. The particles show a ragged morphology typical of the mechanosynthesis method.

Figure 1: Le Bail refinement and SEM image of MnSn_2 powder synthesised via mechanosynthesis.

Table 1: Lattice parameters extracted from the Le Bail refinement and reference of MnSn_2 .

	a	c	Unit cell volume ($\text{\AA}^3$)	χ^2

MnSn₂ refinement	6.606(7)	5.406(9)	236.01	2.12
MnSn₂ reference (JCPDS n° 01-074-4896, 23)	6.659	5.447	241.53	-

The cycling performance of MnSn₂ cells is shown in Figure 2. MnSn₂ achieved 525 mAh/g on the 1st sodiation of which 400 mAh/g were reversible. Thereafter, the cell generally achieves around 400 mAh/g, slowly declining with only 2.5% of the specific charge lost between the 2nd and the 10th cycle. Of this specific charge about 17 mAh/g can be attributed to the Super C65 conductive additive used. Between the 2nd and 50th cycle 10.2% of the specific charge were lost. The cell shows no abrupt cell failure in the first 50 cycles. The feature at around 40 cycles arose from a problem with the cycling device. In terms of long-term performance MnSn₂ thus clearly outperforms Sn electrodes cycled in equivalent conditions where cell failure is dramatic from about 800 mAh/g down to 120 mAh/g within the first 50 cycles. The coulombic efficiency of the MnSn₂ cell is 75% in the 1st cycle and lies between 90-94% in subsequent cycles.

Figure 2: Cycling performance of MnSn₂ electrode compared to Sn electrode.

The galvanostatic curves and corresponding derivative curves for MnSn₂ cycled in a Na-ion cell are shown in Figure 3. The galvanostatic curves show that some charge is consumed between the OCV state at ca. 2.2 V and ca. 0.3 V. This phenomenon is attributed to the formation of the

solid electrolyte interphase (SEI), which we investigated in detail in previous work²⁴ using a Sn model electrode. After the SEI formation in the 1st cycle, the derivative curve shows a shoulder at 0.18 V followed by the only peak in the 1st sodiation at the very low potential of 0.02 V. Here we expect the conversion of MnSn_2 to $\text{Na}_{15}\text{Sn}_4$ and Mn nanoparticles as was observed for Sn⁹ and for the related isostructural materials CoSn_2 and FeSn_2 .²⁵ On the 1st desodiation, two potential plateaus are observed, one at 0.18 V and one at 0.53 V. The extra potential plateau on desodiation indicates that a transformation to a phase distinct from the MnSn_2 pristine occurs. In the 2nd cycle, two sodiation potential plateaus are visible, one at 0.2 V and one at 0.04 V. While the lower potential plateau does not shift in potential, a significant shift is visible for the higher sodiation potential plateau which moves to 0.21 V in the 5th cycle and 0.24 V in the 20th cycle. This shift could be indicative of either i) the decrease of a local overpotential hindering the reaction or ii) a compositional change in the Mn-Sn-Na material formed at the end of the previous desodiation. Further evidence for a compositional change can be found when looking at the desodiation. In the derivative curves, only two significant desodiation peaks are visible in the 1st cycle (0.18 V and 0.53 V) yet by the 20th cycle the desodiation reaction has four clear features (0.18 V, 0.26 V, 0.53 V and 0.63 V). This is clear evidence that the material and its reaction pathway have significantly changed with cycling. The appearance of these new potential plateaus seems analogous to the mechanism observed in the cyclic voltammogram of FeSn_2 , where new peaks appeared at 0.29 V and 0.64 V.²⁵ Interestingly, no potential shifts in the lowest sodiation peak and the desodiation peaks are observed, indicating that no general overpotential increase in the cell is occurring.

Figure 3: Galvanostatic curves and their derivatives for MnSn_2 electrodes for 1st, 2nd, 5th and 20th cycle.

To investigate the reaction mechanism occurring in the cell during cycling we used operando XRD. The operando XRD measured during the sodiation reaction of MnSn_2 is presented as a contour plot with the corresponding electrochemistry in Figure 4. At OCV (time 0 h) only peaks ascribable to the MnSn_2 pristine phase are observed, as expected. In the first four hours of cycling, a slight shift to lower angles is visible for the MnSn_2 peaks at 35.5° (211) and at 38.5° (112 and 220). This shift indicates a small expansion of the lattice parameters of the MnSn_2 structure in the a and b lattice direction. The peak at 33.1° (002) does not shift indicating that no expansion in the c lattice direction is occurring. This expansion pattern is consistent with the tetragonal structure of MnSn_2 . The gradual shift suggests a solid solution where a small amount of Na^+ ions has been inserted into the MnSn_2 structure. Thereafter, the conversion reaction to $\text{Na}_{15}\text{Sn}_4$ is observed, with peaks starting to appear after 21 h. The formation of $\text{Na}_{15}\text{Sn}_4$ is analogous to the ex situ samples at full sodiation observed for the CoSn_2 and FeSn_2 systems.²⁵ The potentiostatic step at 5 mV starts after 34 h of cycling and shows a slow decay in the current yet no stabilisation, indicating that the conversion reaction is not yet complete. The electrochemistry is thus in agreement with the XRD data where peak intensities continue to change (decrease for MnSn_2 phase and increase for $\text{Na}_{15}\text{Sn}_4$ phase) along the potentiostatic step at 5 mV.

Figure 4: 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 MnSn₂. JCPDS n° 01-074-4896²³ (MnSn₂) and n° 03-065-2166²⁶ (Na₁₅Sn₄).

At full sodiation (48 h) about 20% of the original MnSn₂ pristine signal is still present as given by peak analysis (Figure 5). Interestingly, when comparing the sodiation to the lithiation of MnSn₂, the lithiation was a simple one step conversion reaction where no insertion into MnSn₂ had been observed in contrast to the sodiation.¹⁷ This difference in mechanism is rather surprising given the smaller size of the Li⁺-ion compared to the Na⁺-ion. There is, however, an analogy between the sodium and lithium system as well, unreacted MnSn₂ was also observed to remain at full lithiation for the Li/MnSn₂ cell exactly as seen here.¹⁹

Figure 5: MnSn₂ signal at 38.45° at OCP (black) and at full sodiation (red). This peak was chosen as it experiences no overlap with other phases during sodiation.

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 desodiation of MnSn₂. The z intensity scale is the same as in Figure 4. JCPDS n° 03-065-2166²⁶ (Na₁₅Sn₄) and n° 01-074-4896²³ (MnSn₂). Na₇Sn₃ is not yet indexed in any crystallographic database.

On desodiation (Figure 6), the $\text{Na}_{15}\text{Sn}_4$ peaks are seen to shift to higher angles, forming a solid solution sodium-deficient phase with the suggested chemical formula $\text{Na}_{15-x}\text{Sn}_4$ phase. Unfortunately, the patterns of this intermediate 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 (mainly electrolyte decomposition). 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 from any amorphous sodium containing phases or surface reactions. After 62 h of cycling the $\text{Na}_{15-x}\text{Sn}_4$ phase shows the biggest shift just before disappearing. At this point 4 Na^+ ions were extracted from what we assume to be fully sodiated $\text{Na}_{15}\text{Sn}_4$, yielding the maximum sodium-deficient composition of $\text{Na}_{11.0}\text{Sn}_4$. This approximation is based on the assumption that the tin content of the structure is unchanged and that no reactions other than sodium extraction from $\text{Na}_{15}\text{Sn}_4$ occur concurrently.

Just before the $\text{Na}_{15-x}\text{Sn}_4$ peaks disappear a new set of peaks is formed at 59 h and 185 mV. It is an intermediate phase which disappears after 68 h at 300 mV. This intermediate phase is analogous to an intermediate phase observed in the Na-Sn system by different groups.^{9-11, 27} It belongs to the space group R-3m in the trigonal crystal class but there is still debate whether the exact composition is Na_5Sn_2 ²⁷ or Na_7Sn_3 .²⁸ For this paper the composition Na_7Sn_3 will be used to refer to the phase subsequently. The signal of the Na_7Sn_3 phase at room temperature was unfortunately very weak and the intermediate could not be isolated in an ex situ sample to offer a better structural analysis. However, by using an in situ measurement at 50°C, a better quality pattern of this intermediate phase was obtained.

The Le Bail refinement of the supposed Na_7Sn_3 at 50°C isolated during the cycling of the MnSn_2 cell is shown in Figure 7 with the lattice and peak shape parameters given in

Table 2. The lattice parameters obtained are slightly smaller than the ones found in the literature, indicating that most probably the chemical composition deviates from the Na_7Sn_3 structure. The cell parameters are very elongated and even though they were published as a unit cell,²⁸ the possibility that the refinement has led to a supercell rather than a unit cell is still plausible.

Table 2: Data from the Le Bail refinement and from literature.

	Le Bail Refinement (Figure 8)	Literature ²⁸
Lattice parameter a (Å)	5.42(7)	5.442
Lattice parameter c (Å)	22.39(2)	22.438
Cell Volume (Å ³)	571.1(4)	575.6
Halfwidth parameters (u, v, w)	0.8934, -0.0742, 0.0508	-

Figure 7: Le Bail refinement of the intermediate phase “Na₇Sn₃” during MnSn₂ desodiation recorded over 24 h at 50°C. The + marks the peak of a cell part, which was excluded in the refinement (shaded dashed area).

Above 0.3 V the intermediate phase disappears to the benefit of an amorphous phase. Though another potential plateau follows at 530 mV (roughly 70th – 75th h), the reactions taking place are not visible in the contour plot indicating an amorphous phase at this point. The last minor potential plateau before the potentiostatic step is seen after 76 h at about 670 mV where the onset of a partial reformation of the MnSn₂ starting phase is observed with corresponding peaks

growing rapidly. The potentiostatic step at 1 V shows a rapidly decaying current, indicating that the reformation reaction as well as other desodiation processes have reached completion. The recombination observed here is similar to the recombination observed in the lithium system where back reaction of Sn with Mn to form magnetic MnSn_2 grains was detected during the second half of delithiation.¹⁹

To find out whether the reaction mechanism is stable, we investigated how the cycling mechanism changes after multiple cycles. In our custom made XRD cell (described elsewhere²²) we cycled an MnSn_2 electrode for 9 cycles and then measured the 10th cycle operando using an in-house diffractometer. The results for this 10th cycle of sodiation and desodiation of MnSn_2 are shown as a contour plot in Figure 8 along with the electrochemistry on the right hand side.

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 10th cycle of MnSn_2 . 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.

The electrochemistry shows two distinct potential plateaus on sodiation (250 mV and 40 mV) and four potential plateaus on desodiation (170 mV, 250 mV, 530 mV and 640 mV). The current decay in the potentiostatic step at 5 mV is much more rapid at this point than it was in the 1st cycle, indicating a less hindered reaction. This difference can be attributed to decreased active material particle size, resulting from the large mechanical strains that are typical for conversion reactions during cycling.

After 10 cycles, the insertion of Na^+ into MnSn_2 before the conversion reaction is even more apparent with a small but clear shift of the MnSn_2 peaks to lower angles in the first five hours of cycling. Since no ternary phase of Na-Mn-Sn has been reported previously in the literature, this equilibrium can potentially only be reached electrochemically. After ageing the intermediate phase Na_7Sn_3 not only appears during desodiation but can also be accessed during sodiation. The Na_7Sn_3 intermediate in the 10th cycle shows a distinct intense peak at around 33° , a diffuse peak at around 33.8° and another peak at 38.4° . The peak at 34.5° is difficult to distinguish from the underlying MnSn_2 peak and $\text{Na}_{15}\text{Sn}_4$ peak at this same angle. Comparing the two Na_7Sn_3 intermediate states formed during sodiation (below 47 mV, 21-33 h) and during desodiation (above 174 mV, 51-64 h) more closely with each other makes some differences apparent. To see these subtle differences better, we isolated the peak at 33° and show how it changes whether formed on the 10th sodiation, the 10th desodiation or in our Le Bail refined in situ pattern at 50°C (Figure 9).

Figure 9: Na_7Sn_3 peak at 33° when formed on the 10th sodiation, the 10th desodiation and in situ at 50°C .

The intensity of the peak when formed during sodiation is stronger than when formed during desodiation. Furthermore a slight shift in the peak position is visible (Figure 9) which is why we termed the Na_7Sn_3 formed upon sodiation “modified”. The shift to a lower angle during sodiation of the most intense peak of Na_7Sn_3 at 33° by about 0.3° can also be clearly seen in the magnified and scale re-adjusted contour plot in Figure 10. We hypothesize that this shift in the peak position comes from a slight change in the Na-content.

Figure 10: Magnification of 10th cycle MnSn_2 contour plot to the region around 33° with many overlapping features. The current is given in mA as an absolute value. 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.

Figure 11: Scan taken during the 10th desodiation at 750 mV. The stars (*) mark peaks which abruptly appeared at 710 mV but could not be identified

The formation of $\text{Na}_{15}\text{Sn}_4$ on sodiation and its desodiation via the intermediate solid solution $\text{Na}_{15-x}\text{Sn}_4$ are still dominant features in the reaction mechanism. Likewise the recombination of Mn and Sn to form MnSn_2 at the end of desodiation is still a functioning mechanism for this reaction. The onset of reformation is slightly higher in potential at 705 mV rather than the 670 mV as was the case in the 1st cycle. Additionally, a novel phase is observed to form rapidly towards the end of desodiation when the cell reaches exactly 710 mV. A diffractogram after this point showing the peaks that appeared is presented in Figure 11. The unknown phase has

peaks at 28.7°, 30.5°, 32° and 32.6° and 42.4°. It could not be indexed with any of the known binary phases possible from combining the elements Na, Sn and Mn. We thus hypothesise that the novel phase observed has the ternary nature $\text{Na}_x\text{Sn}_y\text{Mn}_z$.

Conclusion:

MnSn_2 shows promising cycling performance (400 mAh/g for 50 cycles) as a negative electrode material for Na-ion cells. Its reaction mechanism was probed using operando X-ray diffraction in both the 1st and the 10th cycle to uncover a fairly robust reaction mechanism summarized in Table 3. In the first cycle, we observe a small insertion into the MnSn_2 structure before the conversion reaction to $\text{Na}_{15}\text{Sn}_4$ and transition metal nanoparticles. On desodiation a solid solution of the form $\text{Na}_{15-x}\text{Sn}_4$ is observed before being replaced by the intermediate phase Na_7Sn_3 . The final step on the 1st desodiation is the partial reformation of MnSn_2 . Comparing the operando XRDs of the 1st and 10th cycles of MnSn_2 , in fact no features were lost with cycling. This robust reaction mechanism is presumably part of the reason why MnSn_2 performs so well electrochemically. Upon ageing MnSn_2 does develop two additional features, however, the formation of Na_7Sn_3 on sodiation and a new unknown phase above 0.71 V with peaks at 28.7°, 30.5°, 32° and 32.6° and 42.4°. We thus show that MnSn_2 is a promising intermetallic negative electrode material for Na-ion batteries and encourage further work in this area.

Table 3: Summary of features in the cycling of MnSn_2 during the 1st cycle and the 10th cycle.

	1st cycle	10th cycle
Na insertion into MnSn_2 structure	✓	✓
Na_7Sn_3 intermediate during sodiation	-	✓
$\text{Na}_{15}\text{Sn}_4$ formed	✓	✓
$\text{Na}_{15-x}\text{Sn}_4$ solid solution	✓	✓
Na_7Sn_3 intermediate during desodiation	✓	✓
Reformation of MnSn_2	✓	✓
New phase above 0.7 V	-	✓

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