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FeSn₂ and CoSn₂ electrode materials for Na-ion batteries

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Abstract:

Alloys have the potential to fill the void for a reliable, high-performing anode material for sodium ion batteries. Here we investigate for the first time CoSn₂ and FeSn₂ and their reaction with sodium. These tin alloys can achieve capacities of up to 680 mAh/g if fully exploited, almost double of the standard anode material used today. We elucidate the reaction mechanism of these two isostructural alloys by analogy to the well understood Sn-Na system, and demonstrate that the transition metal believed to be inactive by the community in fact strongly influences the reaction mechanism.

Introduction

Sodium ion batteries are expected to offer cheap electrochemical energy storage in the near future, however their viability and commercialization are still under debate as some scientific challenges remain [1-6]. Contrary to lithium ion batteries, graphite cannot be used as a reliable anode, since it achieves almost no reversible specific charge when reacting with sodium. [7, 8] Recently, hard carbons were found to intercalate sodium and give a reversible specific charge of around 250 mAh/g, but unfortunately these disordered carbons have very low volumetric energy density.[9-11] Sn, Sb and their alloys offer high energy density both gravimetrically and volumetrically making them anodes of choice despite their high volume changes occurring during cycling.[12, 13]

One method to mitigate this problem is by alloying an active metal with an inactive metal.[14] This methodology has been successfully applied for both the lithium and the sodium ion system.[4, 15] We decided to investigate the MSn_2 ($M = \text{Co or Fe}$) family as anodes in sodium ion batteries, crystallising in the $I4/mcm$ space group. These materials have been investigated in lithium ion batteries using impedance spectroscopy,[16] Mössbauer spectroscopy [17, 18] and X-ray diffraction.[19] Micro- as well as nano-sized particles demonstrated a reversible reaction with lithium achieving a high specific charge (400-600 mAh/g for 50 cycles).[20, 21] In the sodium system, electrodeposited $CoSn_2$ on nickel foam was investigated by Gonzalez *et al.* and a powder mixture of Sn, CoSn and Co_3Sn_2 was studied by Yui *et al* yielding a capacity of 300 mAh/g for 30 cycles.[22, 23] Since $CoSn_2$ and $FeSn_2$ crystallize in the same space group the impact of the inactive transition metal Co and Fe can be evaluated. The synthesis, structure and electrochemical properties of this family in sodium ion batteries are presented here.

Experimental

The CoSn_2 and FeSn_2 alloys were prepared by mechano-synthesis in a Pulverisette 7 premium line (Fritsch). In the glovebox two grams stoichiometric mixtures of Fe (Aldrich, >99.5%) or Co (Alfa Aesar, 99.8%) and Sn (ABCR, 325mesh) were placed in a 45 mL stainless steel ball-milling vessel containing 30 stainless steel balls of 5 mm diameter each. For the synthesis of CoSn_2 0.3978 g of Co and 1.6022 g of Sn were mixed, for FeSn_2 0.3808 g of Fe and 1.6192 g of Sn were mixed. The powders were milled at 800 rpm in cycles of 10min active/10min passive. 60 and 99 cycles were performed to obtain FeSn_2 and CoSn_2 , respectively.

The electrodes were cast onto aluminium foil via doctor blading from a suspension of 70% active material (608 mg), 18% SuperC65 (154 mg, IMERYS) and 12% Sodium carboxymethyl cellulose (104 mg, CMC, AlfaAesar) in water (2.4g). 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).

Cyclic voltammetry was performed between 5 mV and 1.5 V vs. Na^+/Na and using a scan rate of 20 $\mu\text{V/s}$. Galvanostatic cycling was performed by applying a current of 18.1 mA/g and 18.3 mA/g for CoSn_2 and FeSn_2 , respectively. This current corresponds to 1 $\text{Na}^+/\text{5 hrs}$ reacting per formula unit, which if the full specific charge of the material (680mAh/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. Along the manuscript all the potentials will be given using Na^+/Na as reference.

The *ex situ* samples were cycled at the same galvanostatic rate of 1 $\text{Na}^+/\text{5 hrs}$ to 5 mV and held in a potentiostatic step until the current had fallen to 1/5th of the original current applied. The cells were disassembled in the glovebox and the electrodes washed in DMC. Capillaries of the material were then prepared for XRD measurement to avoid exposure to air and moisture.

The structure of the intermetallics was analysed using a Panalytical Empyrean diffractometer equipped with a Cu K α radiation source (XRD). Measurement was performed on a flat rotating plate for the

pristine samples and in capillaries for *ex situ* samples. For the capillaries a step size of 0.033° with a time per step of 200s was used and the measurement was repeated 6 times to increase the quality of the data. The diffractograms were then analysed using the FullProf Suite Program.[24]

A Carl Zeiss UltraTM 55 electron microscope at 3 kV in secondary electron detection mode was used to take scanning electron microscope images (SEM).

Results and Discussion

Figure 1a and 1b shows the XRD diffractograms and Le Bail refinement performed on the synthesized CoSn_2 and FeSn_2 . All peaks are indexed using the space group $I4/mcm$. No impurities were detected for both materials. The Bragg peaks for both samples are broad, indicating small average crystallite size. Figure 1c and 1d show the SEM images of the synthesised powders. A very broad particle size distribution can be observed with sub-micron particles up to particles tens of microns large, typical of the mechanosynthesis method.

The cyclic voltammogram (CV) of CoSn_2 together with the first cycle CV from the Sn reference system is shown in Figure 2a. On the first cathodic sweep a slight shoulder is observed at 0.5 V, characteristic of solid electrolyte interphase (SEI).[4] The largest feature is only observed at low potential close to 5 mV. The current is still growing when the cut-off potential is reached, indicating that the reaction has not yet reached completion. The CV of Sn shows the strongest reductive activity at this potential and XRD studies have shown that $\text{Na}_{15}\text{Sn}_4$ forms here;[12, 25, 26] we hypothesized that CoSn_2 turns into $\text{Na}_{15}\text{Sn}_4$ and Co° at this point. Indeed, *ex situ* samples at full sodiation verify this hypothesis and are presented in Figure 4. On the first anodic sweep five contributions can be found, a small peak at 0.08 V, a shoulder at 0.16 V, an intense peak at 0.21 V, plus two minor oxidative peaks at 0.27 V and 0.52 V. With three known alloys in the Co-Sn phase diagram and eight known alloys in the Na-Sn phase diagram a range of mechanisms are possible to explain the multitude of contributions to the desodiation of CoSn_2 [27, 28]. By comparison with Sn, the shoulder at 0.16 V can be attributed to the desodiation of $\text{Na}_{15}\text{Sn}_4$, however, surprisingly beyond that none of the oxidative peaks seen for Sn match those of CoSn_2 indicating that the presence of the cobalt significantly changes the reaction pathway.

In subsequent cycles, a new reductive peak appears at ca. 0.19 V in the cathodic sweep. This peak is the reaction of a new product that was stabilized at the end of the first cycle which is not CoSn_2 , as this peak didn't appear during the first cycle. The peak at ca. 0.19 V is visible in all subsequent cycles,

however i) it shifts to higher potential along cycling, and ii) it grows with each cycle. These phenomenon can be explained as follows i) the shift indicates that the material is not the same at the end of each cycle and that its chemical composition is changing, ii) the peak growing with each cycle, confirms that the material is most probably not reacting fully initially (Also see Figure 4). The same phenomenon is also observed for the peak at 5 mV which grows with cycle number, indicating that more material is converted to $\text{Na}_{15}\text{Sn}_4$. We believe an activation mechanism as depicted in Figure 2c is occurring, leading to new material becoming accessible from the core of particles. The fact that this activation occurs over multiple cycles despite the slow sweep rate leads us to conclude that the Na reacts slowly with CoSn_2 . Such slow reactions are in agreement with what Ellis *et al.* reported for the reaction of sodium with their tin-cobalt-carbon nanocomposite.[29]

In the anodic sweeps the lowest peak at 0.08 V and the highest one at 0.5 V are shifting to higher potentials and growing slightly. However, the main peaks (shoulder at 0.16 V and peak at 0.21 V) defy this trend and remain at the same potential. This evidences that there is no general overpotential increase in the whole cell but instead the potential shifts observed for some of the features arise from localized overpotentials or mechanism changes. The peak at 0.21 V grows significantly with cycling from 35% in the 1st cycle to 53% by the 10th cycle.

Its growth also contributes to increasing the overall reversibility of the reaction (specific charge during oxidation / specific charge during reduction) from just 62% in the 1st cycle, to 89% in the 2nd cycle, and finally up to 96% by the 10th cycle.

Figure 2b shows the cyclic voltammogram of FeSn_2 together with the first cycle for the Sn reference system. On the first cathodic sweep a large peak is observed at 0.72 V. Most likely this peak is SEI formation even if the potential is a bit high compared to the theoretical value.[30] The largest current is only observed at 5 mV, similar to the CV of CoSn_2 . Analogous to the CoSn_2 system, this peak is the formation of $\text{Na}_{15}\text{Sn}_4$ [12, 25, 26] and Fe° , as verified by *ex situ* XRD (Figure 4). Such a single step conversion without intermediate phases would be analogous to the single step reaction of FeSn_2 to

Li₇Sn₂ in the Li-ion system.[17] On the first anodic sweep a small peak is seen at 0.08 V, a shoulder at 0.16 V and the most intense peak appears at 0.2 V. These three features are analogous to what was seen for CoSn₂ (Figure 2a). A second set of oxidative peaks is seen at 0.53 V (peak) and 0.68 V (shoulder). In subsequent cycles the cathodic sweeps show two shoulders at 0.42 V and 0.2 V followed by the highest intensity peak at low potential. The two shoulders were not observed in the first cycle, where FeSn₂ was the starting material. This indicates that a new material was stabilized after the first desodiation. The reactions of this stabilized phase give rise to the two shoulders seen in all subsequent cycles. The peak at low potential close to 5 mV grows with every cycle, supporting the theory of an activation mechanism (Figure 2c) analogous to the CoSn₂ system.

Comparing the different anodic sweeps one can see that i) the current increases for almost all phenomena and ii) the peaks at potentials below 0.25 V do not shift. The shoulder at 0.16 V and peak at 0.2 V grow the most and their contribution rises from 37% to 45% of the total specific charge achieved during oxidation from the 1st to the 10th cycle.

Additionally, two new peaks appear by the 10th cycle, one at 0.29 V and one at 0.64 V (Figure 2b). The peak at 0.29 V is a feature attributable to the cycling of Sn (Figure 3). The exact overlap of the most intense oxidative peak in the Sn system with the new oxidative peak in the FeSn₂ system, verifies our hypothesis of transition metal extrusion and subsequent cycling of Sn.[31-33] At higher potentials the FeSn₂ system and the Sn system show no analogy indicating that the transition metal likely plays a role here and a partial recombination of Sn with Fe is likely.

Figure 4a and b present the X-ray diffractograms of ex situ samples taken at the first full sodiation of CoSn₂ and FeSn₂, respectively. All peaks could be indexed by the combination of the I4/mcm space group (MSn₂ phase) and the I-43d space group (Na₁₅Sn₄ phase). The χ^2 value for the refinement is 5.74 for CoSn₂ at full sodiation and 7.76 for FeSn₂ at full sodiation. This dual phase at full sodiation verifies the incomplete reaction of the MSn₂ (M = Co, Fe) phases and the formation of Na₁₅Sn₄ as the fully sodiated phase for this Sn alloy family hypothesised from the CV data. As a consequence of the

formation of $\text{Na}_{15}\text{Sn}_4$ the transition metal Co or Fe must have been extruded, however, no peaks attributable to the Co^0 nor Fe^0 phases could be identified. This indicates that the transition metals were most likely extruded as nanoparticles and are therefore not identifiable with XRD, as reported in similar mechanisms in literature.[33, 34]

The galvanostatic cycling stability of CoSn_2 and FeSn_2 is shown in Figure 5. A potentiostatic step was applied after each galvanostatic sweep to ensure equilibrium was reached. FeSn_2 always outperforms CoSn_2 in terms of specific charge achieved; however, it also fails sooner than CoSn_2 . Both materials show an increase in specific charge with cycle number initially, in agreement with our suggested activation mechanism. Further evidence for this theory is the significant discrepancy between the theoretical specific charge ($>600\text{mAh/g}$) and the experimental specific charge (Figure 5). Upon sodiation the material undergoes a volume expansion of more than 400%, which leads to cracking of the particle and allows more of the “unreacted” core to be accessed with every cycle (Figure 2c), leading to a rise in specific charge with cycle number. Of course this cracking eventually leads to fading, most likely as a result of the pulverization of the electrode and electrical isolation of particles. The decreased coulombic efficiency shortly before the specific charge fades supports this explanation. At this stage, sodium reacts with the host material which expands and breaks into smaller particles to accommodate the strain (good sodiation specific charge). Some of these smaller particles are then no longer integrated in the conductive matrix and thus become electrically disconnected (poor desodiation specific charge).

The galvanostatic profiles are shown in Figure 6a and b. Overall this system has far fewer potential plateaus than the Na-Sn system,[12, 26, 35] indicating that some intermediate states are suppressed by the presence of the inactive metal. The first charge is very distinct from the other charges (also seen in Figure 2a and b), a characteristic that has been reported in other materials reacting via a conversion reaction.[32, 36] In the first sodiation the conversion from the MSn_2 material to $\text{Na}_{15}\text{Sn}_4$ occurs for both systems in one dominant low potential plateau. Generally a complete recovery to MSn_2 on desodiation doesn't occur but rather a new intermediate with a different stoichiometry is formed on

desodiation which cycles subsequently. The reaction of this intermediate gives rise to the upper sodiation potential plateau seen from the second cycle onwards at 0.23 V and 0.27 V for CoSn₂ and FeSn₂, respectively. These potentials are in agreement with the number of electrons involved in the system (fewer electrons involved leads to reactions at higher potential).[37]

In the 10th cycle increased polarisation is observed on desodiation for the second potential plateau of FeSn₂, indicating that the energy barrier to extract sodium from the system has risen for this individual reaction. These new conditions even change the reaction pathway as evidenced by the appearance of a new potential plateau at 0.64 V in the 10th cycle. This new feature is in good agreement with the CV presented in Figure 2b, where a new peak in current is observed to grow at 0.64 V. No such mechanism is observed for the CoSn₂ system. For both CoSn₂ and FeSn₂ the overall polarisation increases after the 20th cycle on desodiation, which we attribute to the SEI building up on the particles and thus decreasing the accessibility of the material (kinetic effect).

Conclusion

FeSn₂ and CoSn₂ react electrochemically with sodium through a conversion based reaction at low potentials ($\approx$ 5mV) leading to the formation of Na₁₅Sn₄ and the extrusion of the transition metals into nanoparticles. However, distinct differences between the two alloys remain since FeSn₂ always outperforms CoSn₂ in terms of specific charge. Additionally the failure mechanisms of the two materials are different. While FeSn₂ develops a new potential plateau on desodiation after repeated cycling, indicating a chemical (composition) change in the active material, CoSn₂ shows no such feature. The electrochemistry presented here demonstrates that the “inactive metal” in alloy based battery materials has an influence on the reaction mechanisms (different intermediate phases and Na pathways) and thus affects the electrochemical performance.

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Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure Caption

Figure 1 X-ray diffractograms of (a) CoSn₂ and (b) FeSn₂ and SEMs of (c) CoSn₂ and (d) FeSn₂ at two different magnifications.

Figure 2 Cyclic voltammetry of (a) CoSn₂ and (b) FeSn₂ with a first cycle Sn reference CV. (c) Schematic of activation mechanism which occurs with cycling.

Figure 3 Cyclic voltammetry of aged FeSn₂ and Sn, showing the emerging peak in FeSn₂ appearing exactly at the same potential as the most intense peak of the Sn CV.

Figure 4 X-ray diffractograms of *ex situ* samples at full sodiation for (a) CoSn₂ and (b) FeSn₂. The χ^2 value for the refinement was 5.74 and 7.76 for (a) and (b) respectively.

Figure 5 Capacity retention of CoSn₂ and FeSn₂ during galvanostatic cycling followed by a potentiostatic step in 1M NaClO₄ in PC.

Figure 6 Normalized galvanostatic curves for selected cycles from Figure 4 for (a) CoSn₂ and (b) FeSn₂. The black curve corresponds to the cycle where the maximum sodiation specific charge was achieved.