

## Elucidation of the reaction mechanisms of isostructural $\text{FeSn}_2$ and $\text{CoSn}_2$ negative electrode for Na-ion batteries

Leonie O. Vogt, Claire Villevieille

### Additional information about the GITT measurement:

The graph presented in Figure S1 shows one relaxation for the phase formed in Section II and one for the phase formed in Section IV, each plotted on a potential scale spanning 0.4 V. After the cell enters OCP both relaxation profiles show a jump to higher potentials which can be assigned to the instant disappearance of the ohmic overpotential as well as the rapid disappearance ( $< 1$  s) of the overpotentials from the double layer capacitance. The overpotential due to liquid diffusion limits is expected to reach equilibrium within the first hour of relaxation. Diffusion in the solid can take much more time to relax and can therefore be tracked without interference from other overpotentials beyond the 2<sup>nd</sup> hour of relaxation. The phase formed in Section II shows 140 mV of relaxation here, which indicates a much slower solid diffusion than that of the phase in section IV (only 35 mV relaxation).

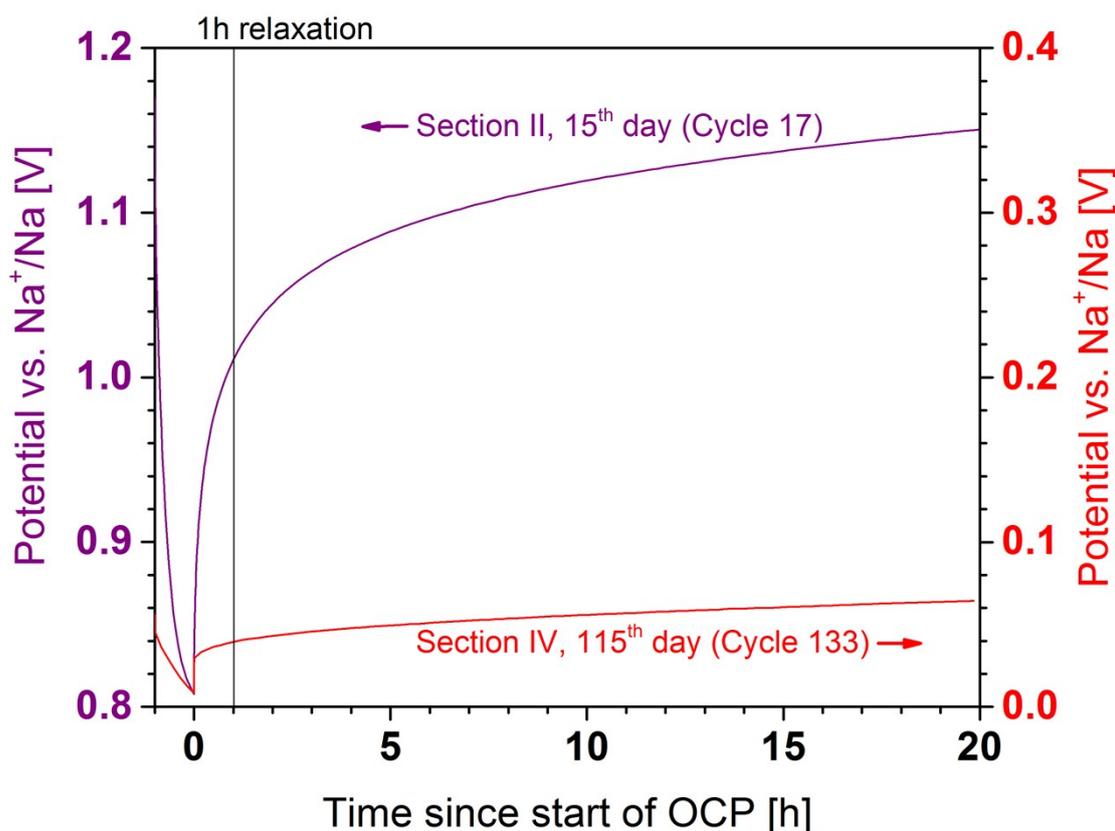


Figure S1: feature of the GITT of  $\text{FeSn}_2$  performed at a rate of  $C/30$  followed by 20 hours of OCP. The purple rectangle in Region II and the red one in Region IV, mark cycles enlarged in the bottom graph.

## Operando XRD of FeSn<sub>2</sub> along the first cycle

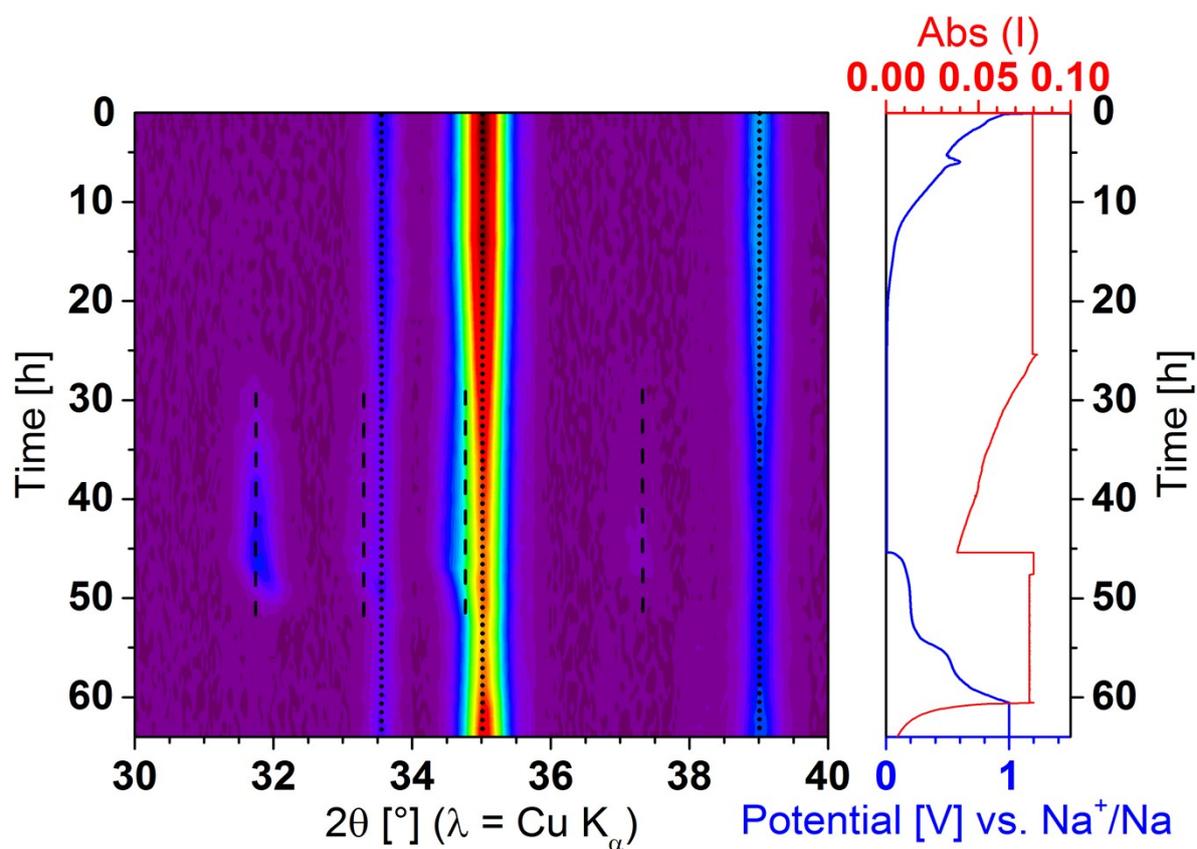


Figure S2: Operando XRD contour plot and corresponding electrochemistry of a Na-FeSn<sub>2</sub> cell during the 1st cycle. The current is given in mA as an absolute value.

## <sup>119</sup>Sn Mössbauer spectroscopy

Unfortunately, the materials are highly metastable once in contact with Na as seen with the GITT measurement. <sup>119</sup>Sn Mössbauer spectroscopy was performed on CoSn<sub>2</sub> samples and unfortunately, when sending samples to be analyzed by spectroscopy, the samples strongly relaxed as can be seen in the Figure S3.

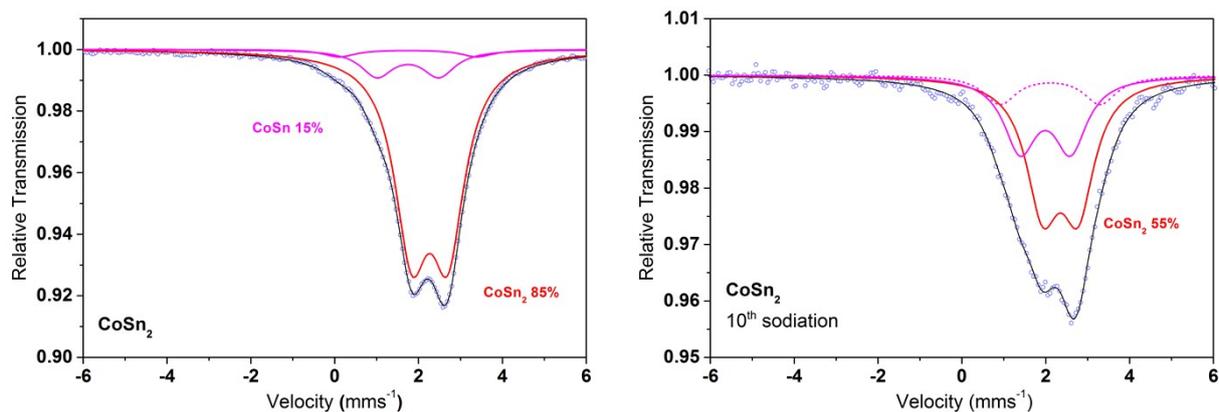


Figure S3: Mössbauer spectra for  $\text{CoSn}_2$  in pristine state and at the end of the 10<sup>th</sup> sodiation.

Figure S3 and Table S1 show the Mössbauer data for the pristine sample of  $\text{CoSn}_2$  and one at the end of the 10<sup>th</sup> sodiation. The pristine sample shows no relaxation, since it was not electrochemically activated. However, at the end of the 10<sup>th</sup> full sodiation, surprisingly there is still 55% of  $\text{CoSn}_2$  present in the cell which may reflect the amount of material which never cycled electrochemically (higher value than the one seen in the paper due to the larger electrode used (thicker electrode leading to slower kinetics)). Surprisingly, it was not possible to identify any Na-Sn alloys despite the fact that  $\text{Na}_{15}\text{Sn}_4$  had been clearly detected by operando XRD (Figure 6, 7 and 11). Instead two new additional contributions which could not be identified in the Mössbauer database were observed (contributing 32% and 13% to the spectra). Even though  $\text{CoSn}_2$  had been partly sodiated, with time the Na-Sn phases disappeared to the benefit of more stable phases closer to the thermodynamic equilibrium (see GITT measurement). This measurement makes then Mössbauer spectroscopy a non-suitable technique for the ex situ analyses of the reaction mechanisms.

Table S1:  $^{119}\text{Sn}$  Mössbauer data for  $\text{CoSn}_2$  pristine and at the end of the 10<sup>th</sup> sodiation.  $\delta$  = isomer shift relative to  $\text{BaSnO}_3$ ,  $\Delta$  = quadrupole splitting,  $\Gamma$  = line width, C = contribution, A = absorption.

Samples	$\delta$ (mm/s)	$\Delta$ (mm/s)	$\Gamma$ (mm/s)	C (%)	Attribution	A (%)
<b>CoSn<sub>2</sub> pristine</b>	2.14 (1)	0.82 (1)	0.97 (3)	85	CoSn <sub>2</sub>	8.37
	1.85 (4)	1.68 (5)	0.97 (3)	10	CoSn	
	1.78 (3)	2.80 (4)	0.97 (3)	5	CoSn	
<b>CoSn<sub>2</sub> 10<sup>th</sup> sodiation</b>	2.26 (3)	0.84 (3)	0.96 (5)	55	CoSn <sub>2</sub>	4.57
	1.90 (4)	1.20 (5)	0.96 (5)	32	?	
	2.01 (6)	2.39 (11)	0.96 (5)	13	?	

### X-ray diffraction: new phase detected after 10<sup>th</sup> cycle

Taking a closer look at the new peaks which appeared in the desodiated state of the electrode after ageing we noticed that all the new peaks appeared abruptly at exactly 710 mV during desodiation regardless of whether the electrode material was CoSn<sub>2</sub> or FeSn<sub>2</sub>. Scans at 750 mV are shown for all three systems in Figure S3.

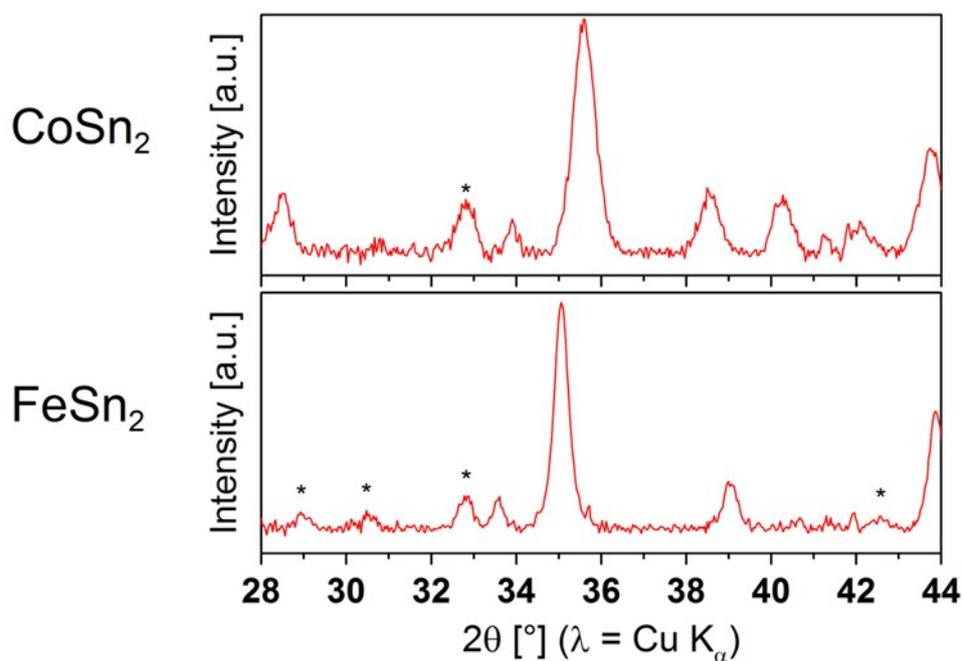


Figure S4: Scans taken during the 10<sup>th</sup> desodiation at 750 mV. The stars (\*) mark peaks which abruptly appeared at 710 mV.

## X-ray absorption measurement

### XANES

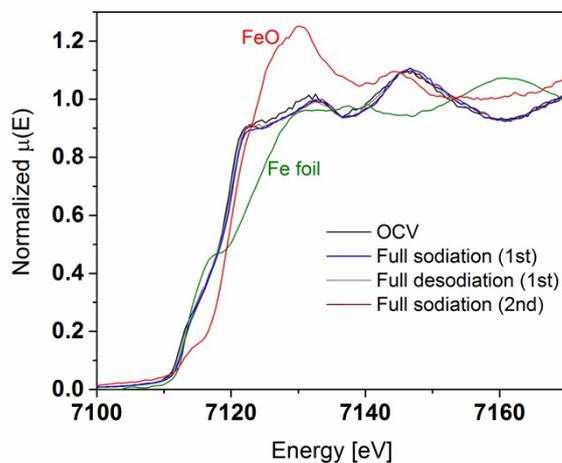


Figure S5: XANES spectra at the Fe K-edge for the reference Fe foil and FeSn<sub>2</sub> at three different stages of cycling.

### EXAFS part

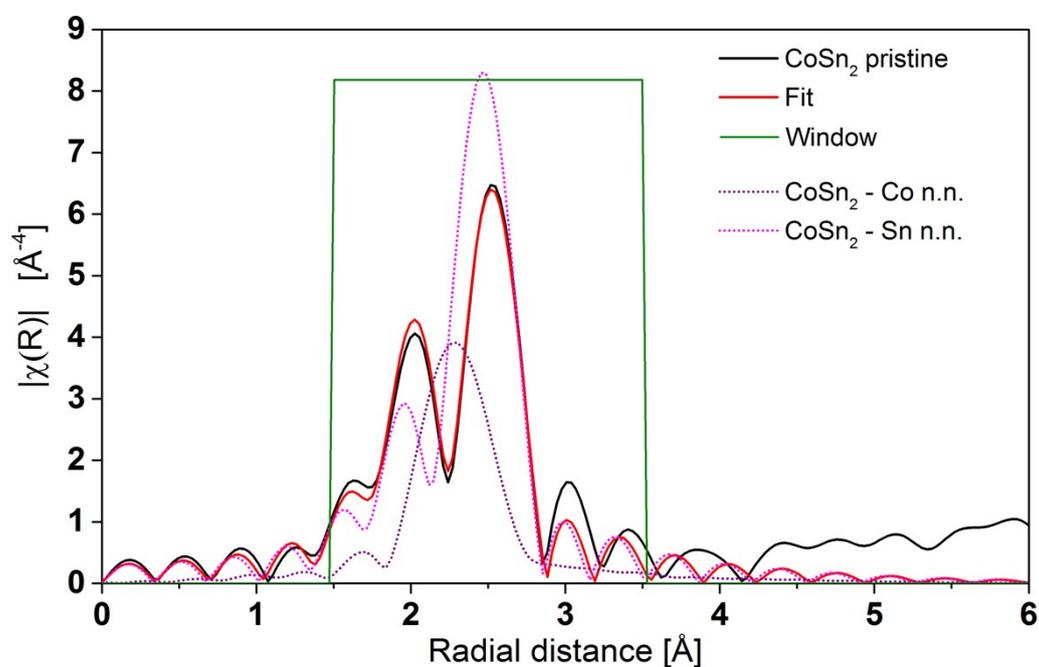


Figure S6: Fit (red) of the Fourier transform of the EXAFS-spectrum of pristine CoSn<sub>2</sub> (black) along with the fitting window (green) and the two contributions used to compose the fit (dotted lines).

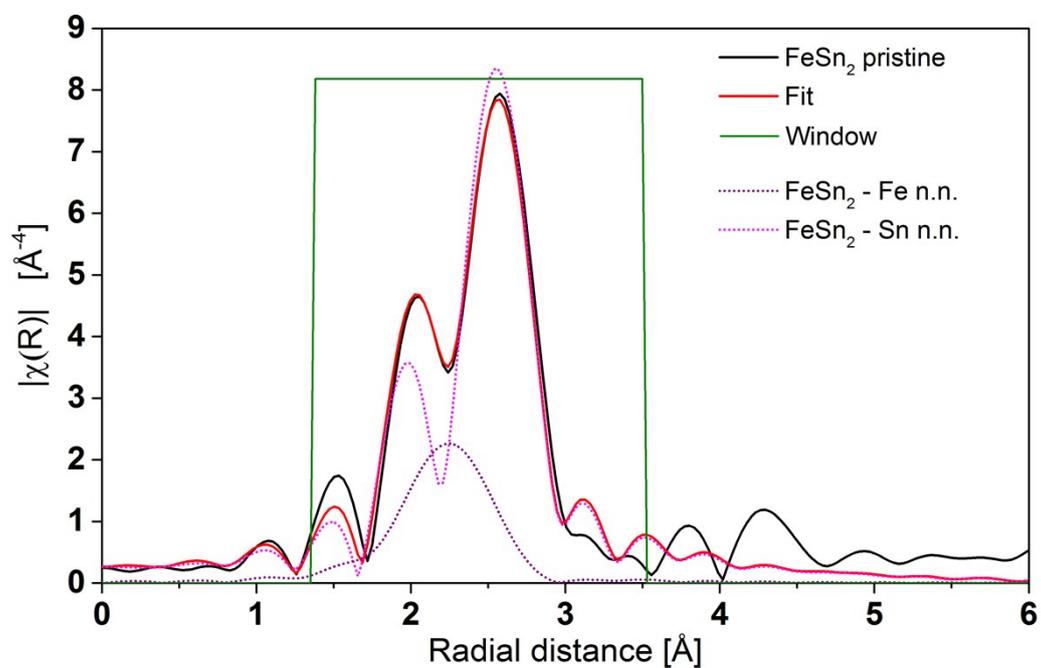


Figure S7: Fit (red) of the Fourier transform of the recorded EXAFS-spectrum of pristine FeSn<sub>2</sub> (black) along with the fitting window (green) and the two paths used to compose the fit (dotted lines).