

Electronic Supplementary Information

Table 1. Interatomic distances in FeSb₂ (Pnn2) structure derived from the ICSD file 15003.

Fe-X (X=Sb,Fe)

	Label	Elmt	Fractional Coordinates			Orthogonal Coordinates			Bond Distance		
			x	y	z	xor[Å]	yor[Å]	zor[Å]	d [Å]	error	d/(rA+rB)
TARG.	Fe1	Fe	0.0000	0.0000	0.0000	0.000	0.000	0.000			
1.	Sb1	Sb	-0.1881	-0.3565	0.0097	1.374	0.580	-2.101	2.5763 ± 0.0007		1.43
2.	Sb1	Sb	0.1881	0.3565	0.0097	-1.339	-0.540	2.133	2.5763 ± 0.0007		1.43
3.	Sb1	Sb	0.3119	-0.1435	-0.4903	-2.147	0.538	-1.323	2.5783 ± 0.0011		1.43
4.	Sb1	Sb	-0.3119	0.1435	-0.4903	0.380	-2.528	-0.335	2.5783 ± 0.0011		1.43
5.	Sb1	Sb	-0.3119	0.1435	0.5097	2.181	-0.499	1.356	2.6165 ± 0.0011		1.45
6.	Sb1	Sb	0.3119	-0.1435	0.5097	-0.345	2.567	0.368	2.6165 ± 0.0011		1.45
7.	Fe1	Fe	0.0000	0.0000	-1.0000	-1.802	-2.029	-1.691	3.1974 ± 0.0003		2.32
8.	Fe1	Fe	0.0000	0.0000	1.0000	1.802	2.029	1.691	3.1974 ± 0.0003		2.32
9.	Sb1	Sb	-0.1881	-0.3565	-0.9903	-0.427	-1.449	-3.792	4.0820 ± 0.0013		2.27
10.	Sb1	Sb	0.1881	0.3565	-0.9903	-3.141	-2.570	0.442	4.0820 ± 0.0013		2.27
11.	Sb1	Sb	0.1881	0.3565	1.0097	0.462	1.489	3.825	4.1303 ± 0.0013		2.29
12.	Sb1	Sb	-0.1881	-0.3565	1.0097	3.176	2.609	-0.409	4.1303 ± 0.0013		2.29

Sb-X (X=Fe,Sb)

	Label	Elmt	Fractional Coordinates			Orthogonal Coordinates			Bond Distance		
			x	y	z	xor[Å]	yor[Å]	zor[Å]	d [Å]	error	d/(rA+rB)
TARG.	Sb1	Sb	0.1881	0.3565	0.0097	-2.024	-1.520	-0.481			
1.	Fe1	Fe	0.0000	0.0000	0.0000	0.000	0.000	-0.000	2.5763 ± 0.0007		1.87
2.	Fe1	Fe	0.5000	0.5000	0.5000	-2.484	-3.050	-2.505	2.5784 ± 0.0011		1.87
3.	Fe1	Fe	0.5000	0.5000	-0.5000	-2.577	-3.841	0.591	2.6166 ± 0.0011		1.90
4.	Sb1	Sb	-0.1881	0.6435	0.0097	-4.343	0.161	-0.122	2.8873 ± 0.0009		1.60
5.	Sb1	Sb	0.1881	0.3565	-0.9903	-2.117	-2.311	2.615	3.1975 ± 0.0023		1.78
6.	Sb1	Sb	0.1881	0.3565	1.0097	-1.930	-0.729	-3.578	3.1975 ± 0.0023		1.78
7.	Sb1	Sb	0.6881	0.1435	-0.4903	-0.060	-4.381	0.497	3.6058 ± 0.0013		2.00
8.	Sb1	Sb	-0.3119	0.1435	-0.4903	-1.367	1.136	1.868	3.6058 ± 0.0013		2.00
9.	Sb1	Sb	0.6881	0.1435	0.5097	0.033	-3.590	-2.599	3.6058 ± 0.0013		2.00
10.	Sb1	Sb	-0.3119	0.1435	0.5097	-1.274	1.927	-1.229	3.6058 ± 0.0013		2.00
11.	Sb1	Sb	0.3119	-0.1435	-0.4903	1.276	-1.912	1.169	3.7100 ± 0.0013		2.06
12.	Sb1	Sb	0.3119	0.8565	0.5097	-5.000	-2.494	-2.471	3.7100 ± 0.0013		2.06
13.	Sb1	Sb	0.3119	-0.1435	0.5097	1.369	-1.120	-1.928	3.7100 ± 0.0013		2.06
14.	Sb1	Sb	0.3119	0.8565	-0.4903	-5.093	-3.286	0.626	3.7100 ± 0.0013		2.06

Figure S1. Schematic representations of the FeSb_2 (Pnn2) crystal structure. Green and black balls represent Fe and Sb atoms, respectively.

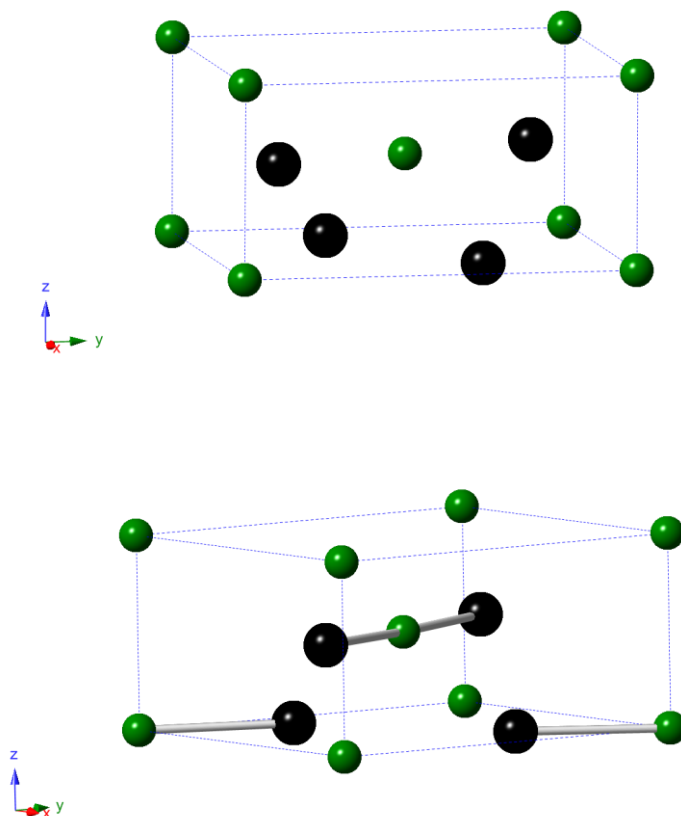


Figure S2. Ex situ X-ray diffraction patterns of electrodes prepared during the first discharge at 160, 260, 400 and 530 mAh g⁻¹ between 2 θ =14-19°. The data is the same as in Figure 4.

The growing broad peaks around 2 θ =14-14.5° and 17-18° are attributed to the growth of Na₃Sb nanocrystalline domains (*c.f.* Figure 4 and 5). The 2 θ angles measured with Cu K α are converted to Mo K α for comparison with Figure 4 and 5.

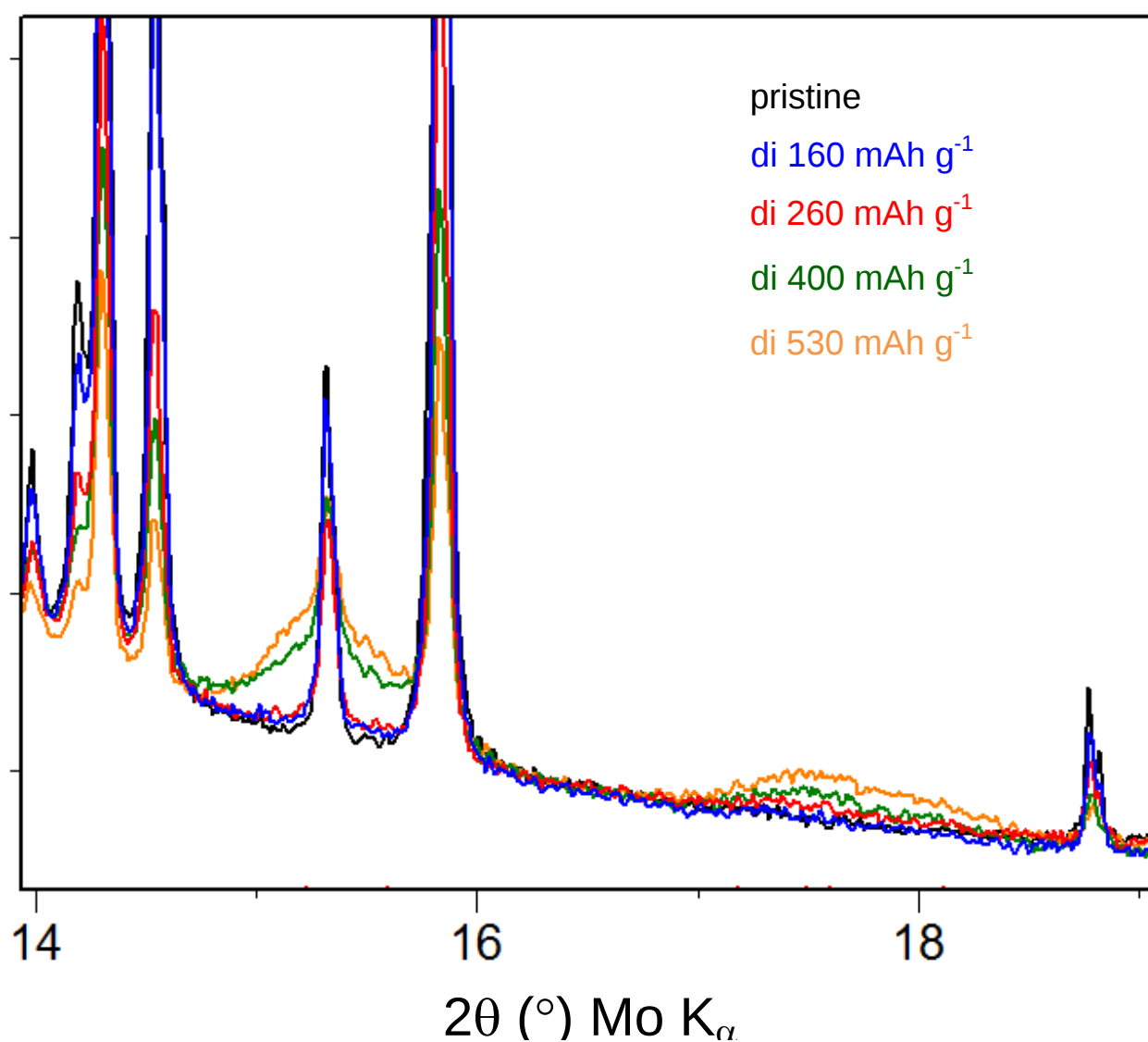


Figure S3. *Ex situ* ^{57}Fe Mössbauer spectra of electrodes prepared during the first electrochemical cycle. Alternative fits to those presented in Figure 6 are shown.

