Electronic Supplementary Information

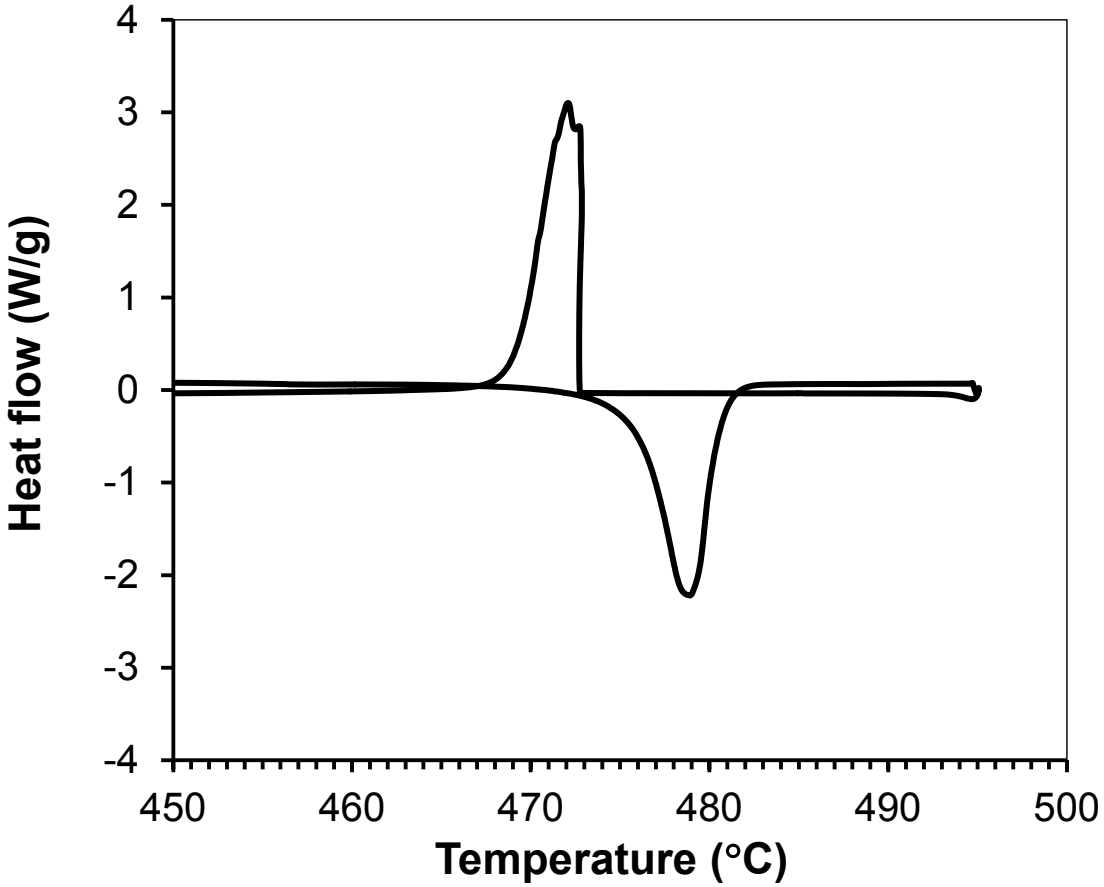

Figure S1. DSC curve for the alloy compound of composition x = 2.35 assigned to Na_7Sn_3, from 0 to 500 °C (shown here from 450 to 500 °C). Melting and crystallization are measured at 478 and 472 °C, respectively, giving an estimated melting/solidification equilibrium point of 475 °C.

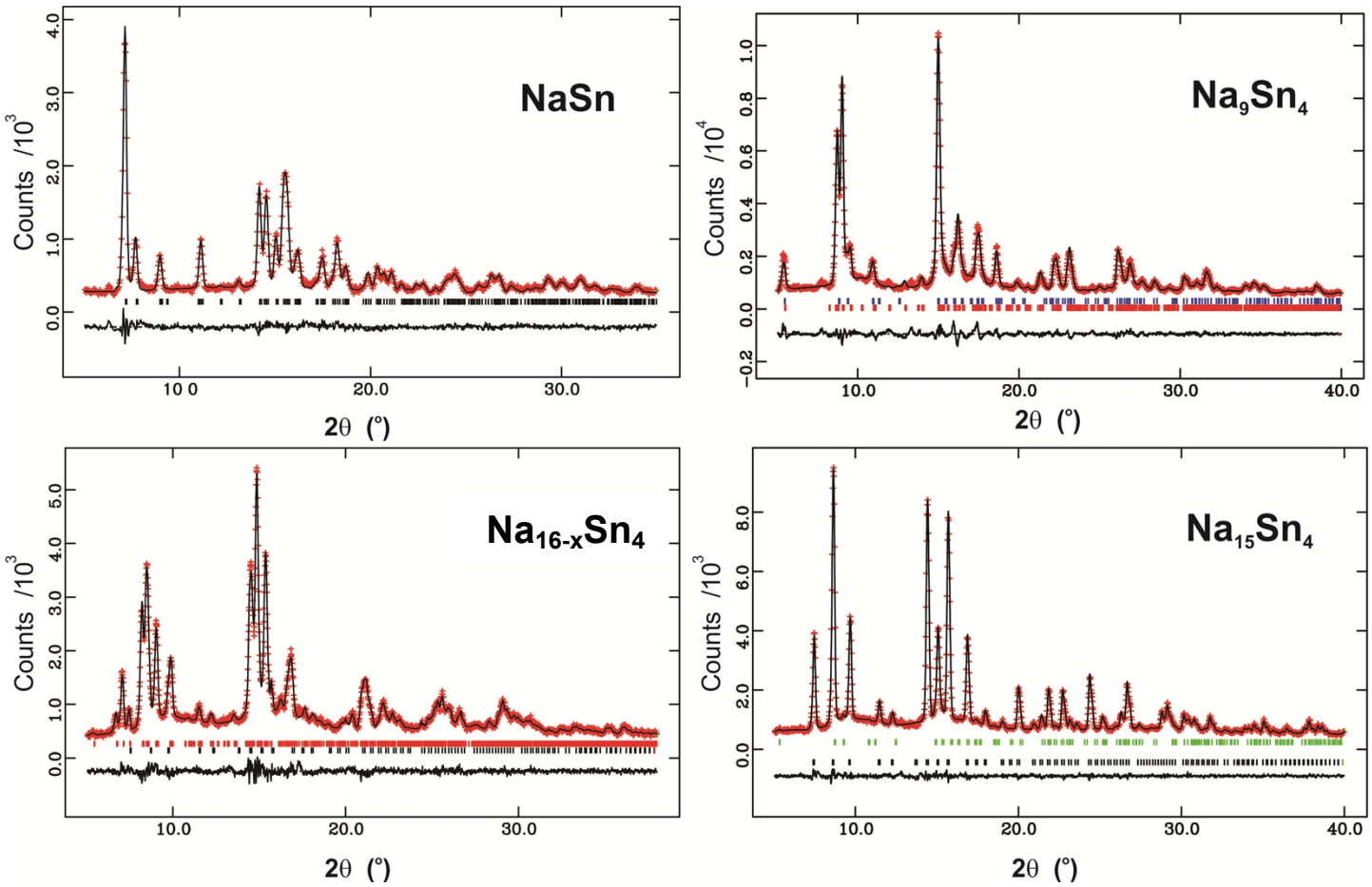

Figure S2. Powder XRD patterns of model compounds NaSn, Na_9Sn_4, $Na_{15}Sn_4$ and $Na_{16-x}Sn_4$ measured inside sealed glass capillaries, and corresponding Rietveld refinements. Weak peaks from Mo K_β radiation are typically present at a level of ~2% of K_α peak intensity.

Sn $M_{5,4}$-edge and Na K-edge XANES characterization of Sn anodes

The Sn M-edge TEY and TFY XANES spectra (Figure S3) correspond to the transitions from Sn 3d core level into unoccupied electronic states above the Fermi level. Unfortunately, these transitions are weak and provide little information about how the electronic structure of Sn evolves during cycling. Na K-edge XANES corresponds to the transitions from the Na 1s core level into the unoccupied electronic states above the Fermi level. Two prominent peaks *a* and *b* are present in both the TEY and TFY spectra (Figure S4a and S4b). An additional low energy feature *m*, which is most notably for the Na metal reference sample, can be observed for some of the Na-Sn electrodes in the TFY. Due to the surface oxidation of the Na metal surface and SEI formation on the Na-Sn electrodes [10], surface sensitive (<10 nm) TEY XAS spectra (Figure S3a) only show two prominent peaks *a* and *b* representing ionic Na compounds related to the SEI layer.

TFY XANES (Figure S3b) provides information for the deeper layer of electrodes (~100 nm), which is representative of the sodiation/desodiation process during discharge/charge respectively. As the electrode is sodiated (discharged from 0.45 V to 0 V), there is a systematic increase in the relative intensity of the low energy feature, *m* that represents the onset of Na alloying with Sn. The TFY ionic Na species (*a* and *b*) are very similar to the TEY spectra, supporting the contribution is primarily from the surface SEI compounds observed in the TEY. Upon charging, varying ionic contributions from the SEI layer are observed within the TEY and TFY across all charging potentials, while the metallic Na, *m*, broadens at 0.2 V before significantly attenuating at 0.4 V and is not visible at 0.6 V and higher.

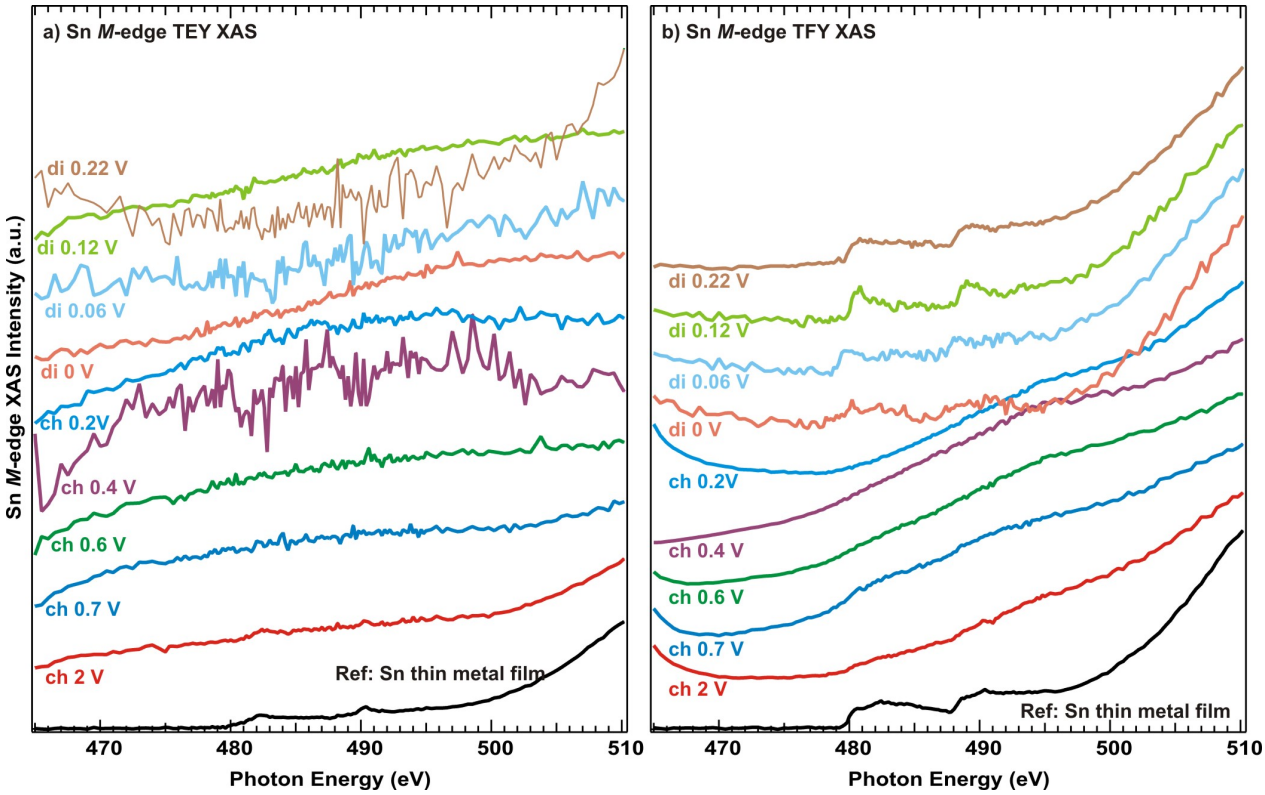

Figure S3. (a) TEY and (b) TFY of Sn $M_{5,4}$-edge XAS of Sn-Na anode during (de)sodiation and Sn metal reference (black). (di = discharge, ch = charge).

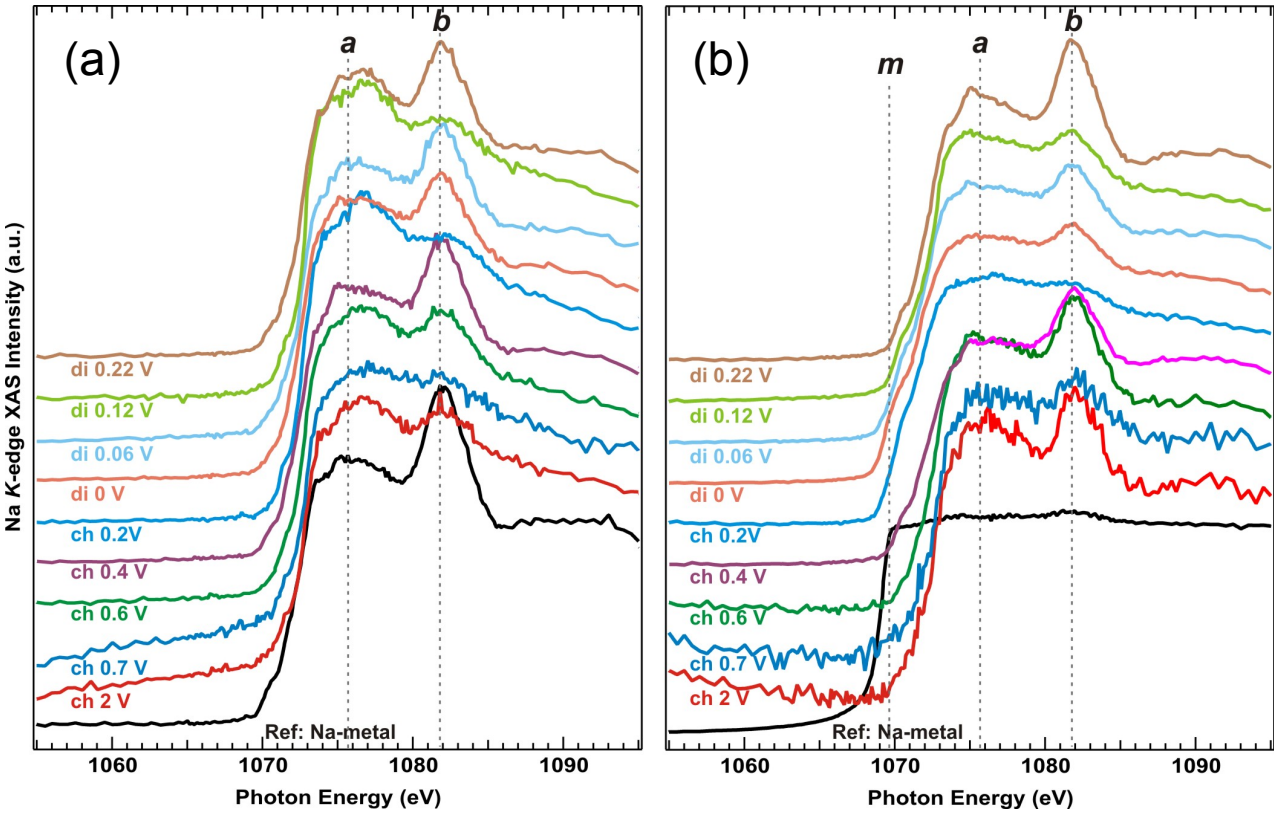

Figure S4. (a) Na K-edge total electron yield and (b) total fluorescence yield XANES of Sn thin film electrodes during (de)sodiation along with Na metal reference (black). Peaks *a* and *b* represent Na ionic species, while *m* pre-edge is for metallic Na. *di* = discharge, *ch* = charge.

Table S1. Interatomic distances from Sn atoms in NaSn (I41/acd).

		Fractional Coordinates			Orthogonal Coordinates			Bond Distance
Label	Elmt	x	y	z	xor[Å]	yor[Å]	zor[Å]	d [Å] error
TARG. Sn1	Sn	0.0695	0.1261	0.9352	16.338	-0.552	-0.474	
1. Sn1	Sn	0.1239	0.3195	0.8148	14.393	-2.609	0.428	2.9717 ± 0.0026
2. Sn1	Sn	-0.1239	0.1805	0.8148	14.122	-1.384	-2.271	2.9717 ± 0.0026
3. Sn1	Sn	-0.0695	0.3739	0.9352	16.356	-3.261	-1.705	2.9762 ± 0.0030
4. Na2	Na	0.1252	0.1248	1.1250	19.672	-0.346	-0.160	3.3551 ± 0.0026
5. Na2	Na	0.3748	0.1248	0.8750	15.537	-0.307	2.786	3.3657 ± 0.0111
6. Na1	Na	0.2500	0.3750	1.0000	17.734	-2.935	1.530	3.4123 ± 0.0118
7. Na1	Na	0.2500	-0.1250	1.0000	17.475	2.278	1.097	3.4299 ± 0.0117
8. Na2	Na	-0.1252	-0.1248	0.8750	15.007	1.843	-2.633	3.4882 ± 0.0112
9. Na1	Na	-0.2500	0.1250	1.0000	17.205	-0.781	-3.890	3.5316 ± 0.0200
10. Na1	Na	0.1250	0.0000	0.7500	13.105	0.674	0.253	3.5337 ± 0.0038
11. Sn1	Sn	-0.0695	-0.1261	1.0647	18.341	2.049	-2.319	3.7661 ± 0.0027
12. Sn1	Sn	0.4305	0.1261	1.0647	18.872	-0.129	3.102	4.4027 ± 0.0028
13. Na2	Na	-0.1252	0.3752	1.1250	19.602	-3.183	-2.549	4.6780 ± 0.0084
14. Sn1	Sn	0.3761	-0.1805	0.8148	14.334	2.832	2.619	5.0031 ± 0.0029
15. Na2	Na	0.1252	0.6248	0.8750	15.597	-5.746	0.622	5.3600 ± 0.0115
16. Na2	Na	0.1252	-0.3752	0.8750	15.077	4.680	-0.244	5.3866 ± 0.0115
17. Na2	Na	-0.3748	0.3752	0.8750	15.068	-3.596	-4.797	5.4378 ± 0.0115
18. Sn1	Sn	0.3761	0.1805	0.6852	12.276	-1.029	3.113	5.4395 ± 0.0025
19. Sn1	Sn	0.1239	-0.1805	1.1853	20.557	2.881	-0.522	5.4395 ± 0.0025
20. Na1	Na	-0.1250	0.5000	0.7500	13.165	-4.765	-1.915	5.4676 ± 0.0080
21. Sn1	Sn	0.0695	0.6261	1.0647	18.844	-5.668	-0.222	5.7023 ± 0.0029
22. Sn1	Sn	0.0695	-0.3739	1.0647	18.324	4.758	-1.088	5.7023 ± 0.0029
23. Na2	Na	-0.1252	0.1248	0.6250	10.802	-0.947	-2.067	5.7743 ± 0.0044
24. Sn1	Sn	-0.1239	-0.1805	0.6852	11.689	2.283	-2.402	5.7765 ± 0.0026
25. Sn1	Sn	0.3761	0.3195	1.1853	21.019	-2.104	2.535	5.7765 ± 0.0026
26. Na1	Na	-0.3750	0.0000	0.7500	12.705	0.222	-4.949	5.8163 ± 0.0169
27. Sn1	Sn	-0.4305	-0.1261	0.9352	15.808	1.626	-5.895	5.8661 ± 0.0030
28. Sn1	Sn	0.5695	-0.1261	0.9352	16.606	2.530	4.511	5.8661 ± 0.0030
29. Na1	Na	-0.1250	0.0000	1.2500	21.575	0.823	-3.046	5.9942 ± 0.0073
30. Na1	Na	0.3750	0.5000	0.7500	13.564	-4.313	3.288	5.9987 ± 0.0114

Table S2. Interatomic distances from Sn atoms in Na_9Sn_4 (Cmcm).

Sn1 site

	Label	Elmt	Fractional Coordinates x	y	z	Orthogonal Coordinates xor[Å]	yor[Å]	zor[Å]	Bond Distance d [Å]	error
TARG.	Sn1	Sn	0.0000	0.1658	0.2022	1.524	5.986	0.371		
1.	Sn1	Sn	0.0000	0.1658	0.2978	1.512	8.816	0.477	2.8317	± 0.0057
2.	Na3	Na	0.0000	0.4930	0.1560	4.589	4.621	0.611	3.3634	± 0.0061
3.	Na1	Na	0.5000	0.3160	0.2500	2.666	7.300	3.254	3.3672	± 0.0044
4.	Na1	Na	-0.5000	0.3160	0.2500	3.178	7.504	-2.138	3.3672	± 0.0044
5.	Na4	Na	0.0000	-0.1300	0.1350	-1.233	3.995	0.034	3.4171	± 0.0054
6.	Na3	Na	-0.5000	-0.0070	0.1560	0.171	4.719	-2.529	3.4423	± 0.0044
7.	Na3	Na	0.5000	-0.0070	0.1560	-0.342	4.515	2.863	3.4423	± 0.0044
8.	Na2	Na	0.0000	0.1490	0.0820	1.382	2.428	0.223	3.5638	± 0.0072
9.	Na1	Na	0.0000	-0.1840	0.2500	-1.752	7.398	0.114	3.5768	± 0.0065
10.	Na4	Na	0.5000	0.3700	0.1350	3.185	3.896	3.174	3.8707	± 0.0045
11.	Na4	Na	-0.5000	0.3700	0.1350	3.698	4.101	-2.218	3.8707	± 0.0045
12.	Na3	Na	0.0000	0.4930	0.3440	4.564	10.186	0.819	5.2039	± 0.0079
13.	Na3	Na	-0.5000	-0.0070	0.3440	0.147	10.284	-2.321	5.2553	± 0.0074
14.	Na3	Na	0.5000	-0.0070	0.3440	-0.366	10.080	3.071	5.2553	± 0.0074
15.	Sn1	Sn	-1.0000	0.1658	0.2022	2.036	6.190	-5.021	5.4200	± 0.0100
16.	Sn1	Sn	1.0000	0.1658	0.2022	1.012	5.782	5.763	5.4200	± 0.0100
17.	Sn1	Sn	0.5000	0.6658	0.2022	5.942	5.888	3.511	5.4210	± 0.0090
18.	Sn1	Sn	-0.5000	-0.3342	0.2022	-2.894	6.085	-2.769	5.4210	± 0.0090
19.	Sn1	Sn	-0.5000	0.6658	0.2022	6.454	6.092	-1.880	5.4210	± 0.0090
20.	Sn1	Sn	0.5000	-0.3342	0.2022	-3.406	5.880	2.623	5.4210	± 0.0090
21.	Sn2	Sn	-0.5000	0.0000	0.0482	0.250	1.529	-2.643	5.5295	± 0.0081
22.	Sn2	Sn	0.5000	0.0000	0.0482	-0.262	1.325	2.749	5.5295	± 0.0081
23.	Sn2	Sn	0.0000	0.5000	0.0482	4.668	1.430	0.498	5.5367	± 0.0085
24.	Na4	Na	0.0000	-0.1300	0.3650	-1.262	10.803	0.289	5.5649	± 0.0090
25.	Na4	Na	0.5000	0.3700	0.3650	3.156	10.704	3.429	5.8544	± 0.0085
26.	Na4	Na	-0.5000	0.3700	0.3650	3.668	10.908	-1.963	5.8544	± 0.0085

Sn2 site

	Label	Elmt	Fractional Coordinates x	y	z	Orthogonal Coordinates xor[Å]	yor[Å]	zor[Å]	Bond Distance d [Å]	error
TARG.	Sn2	Sn	0.0000	0.5000	0.0482	4.668	1.430	0.498		
1.	Sn2	Sn	0.0000	0.5000	-0.0482	4.680	-1.423	0.391	2.8554	± 0.0058
2.	Na5	Na	0.0000	0.8290	0.0230	7.746	0.687	0.762	3.1782	± 0.0064
3.	Na3	Na	0.0000	0.4930	0.1560	4.589	4.621	0.611	3.1937	± 0.0065
4.	Na2	Na	0.5000	0.6490	0.0820	5.800	2.330	3.363	3.2100	± 0.0045
5.	Na2	Na	-0.5000	0.6490	0.0820	6.312	2.534	-2.029	3.2100	± 0.0045
6.	Na5	Na	-0.5000	0.3290	0.0230	3.329	0.785	-2.378	3.2372	± 0.0045
7.	Na5	Na	0.5000	0.3290	0.0230	2.816	0.581	3.014	3.2372	± 0.0045
8.	Na2	Na	0.0000	0.1490	0.0820	1.382	2.428	0.223	3.4446	± 0.0067
9.	Na5	Na	0.0000	0.1710	-0.0230	1.601	-0.680	0.126	3.7405	± 0.0059
10.	Na5	Na	-0.5000	0.6710	-0.0230	6.531	-0.574	-2.125	3.7908	± 0.0045
11.	Na5	Na	0.5000	0.6710	-0.0230	6.019	-0.778	3.267	3.7908	± 0.0045
12.	Na4	Na	-0.5000	0.3700	0.1350	3.698	4.101	-2.218	3.9299	± 0.0049
13.	Na4	Na	0.5000	0.3700	0.1350	3.185	3.896	3.174	3.9299	± 0.0049
14.	Na4	Na	0.0000	0.8700	0.1350	8.115	4.002	0.922	4.3221	± 0.0067
15.	Na2	Na	-0.5000	0.3510	-0.0820	3.548	-2.323	-2.475	4.9167	± 0.0068
16.	Na2	Na	0.5000	0.3510	-0.0820	3.035	-2.527	2.917	4.9167	± 0.0068
17.	Na2	Na	0.0000	0.8510	-0.0820	7.966	-2.421	0.665	5.0730	± 0.0075
18.	Sn2	Sn	-1.0000	0.5000	0.0482	5.180	1.634	-4.894	5.4200	± 0.0100
19.	Sn2	Sn	1.0000	0.5000	0.0482	4.156	1.226	5.889	5.4200	± 0.0100
20.	Sn2	Sn	-0.5000	0.0000	0.0482	0.250	1.529	-2.643	5.4210	± 0.0090
21.	Sn2	Sn	0.5000	1.0000	0.0482	9.086	1.332	3.638	5.4210	± 0.0090
22.	Sn2	Sn	-0.5000	1.0000	0.0482	9.598	1.536	-1.754	5.4210	± 0.0090
23.	Sn2	Sn	0.5000	0.0000	0.0482	-0.262	1.325	2.749	5.4210	± 0.0090
24.	Sn1	Sn	0.5000	0.6658	0.2022	5.942	5.888	3.511	5.5295	± 0.0081
25.	Sn1	Sn	-0.5000	0.6658	0.2022	6.454	6.092	-1.880	5.5295	± 0.0081
26.	Sn1	Sn	0.0000	0.1658	0.2022	1.524	5.986	0.371	5.5367	± 0.0085

Table S3. Interatomic distances from Sn atoms in Na_7Sn_3 (R-3m).

	Label	Elmt	Fractional Coordinates x	y	z	Orthogonal Coordinates xor[Å]	yor[Å]	zor[Å]	Bond Distance d [Å]	error
TARG.	Sn1	Sn	0.0000	0.0000	0.4331	0.000	0.000	-9.701		
1.	Sn1	Sn	0.0000	0.0000	0.5669	0.000	0.000	-12.699	2.9971	± 0.0000
2.	Na3	Na	0.0000	0.0000	0.2866	0.000	0.000	-6.420	3.2816	± 0.0000
3.	Na2	Na	-0.3333	-0.6667	0.4772	-1.568	2.715	-10.690	3.2872	± 0.0000
4.	Na2	Na	-0.3333	0.3333	0.4772	-1.568	-2.715	-10.690	3.2872	± 0.0000
5.	Na2	Na	0.6667	0.3333	0.4772	3.135	0.000	-10.690	3.2872	± 0.0000
6.	Na3	Na	-0.6667	-0.3333	0.3801	-3.135	-0.000	-8.513	3.3525	± 0.0000
7.	Na3	Na	0.3333	-0.3333	0.3801	1.568	2.715	-8.513	3.3525	± 0.0000
8.	Na3	Na	0.3333	0.6667	0.3801	1.568	-2.715	-8.513	3.3525	± 0.0000
9.	Na2	Na	-0.6667	-0.3333	0.5228	-3.135	-0.000	-11.710	3.7232	± 0.0000
10.	Na2	Na	0.3333	-0.3333	0.5228	1.568	2.715	-11.710	3.7232	± 0.0000
11.	Na2	Na	0.3333	0.6667	0.5228	1.568	-2.715	-11.710	3.7232	± 0.0000
12.	Na1	Na	-0.3333	-0.6667	0.3333	-1.568	2.715	-7.467	3.8500	± 0.0000
13.	Na1	Na	0.6667	0.3333	0.3333	3.135	0.000	-7.467	3.8500	± 0.0000
14.	Na1	Na	-0.3333	0.3333	0.3333	-1.568	-2.715	-7.467	3.8500	± 0.0000
15.	Na3	Na	-0.3333	-0.6667	0.6199	-1.568	2.715	-13.887	5.2291	± 0.0000
16.	Na3	Na	0.6667	0.3333	0.6199	3.135	0.000	-13.887	5.2291	± 0.0000
17.	Na3	Na	-0.3333	0.3333	0.6199	-1.568	-2.715	-13.887	5.2291	± 0.0000
18.	Sn1	Sn	-1.0000	-1.0000	0.4331	-4.703	2.715	-9.701	5.4300	± 0.0000
19.	Sn1	Sn	1.0000	1.0000	0.4331	4.703	-2.715	-9.701	5.4300	± 0.0000
20.	Sn1	Sn	-1.0000	0.0000	0.4331	-4.703	-2.715	-9.701	5.4300	± 0.0000
21.	Sn1	Sn	1.0000	0.0000	0.4331	4.703	2.715	-9.701	5.4300	± 0.0000
22.	Sn1	Sn	0.0000	-1.0000	0.4331	0.000	5.430	-9.701	5.4300	± 0.0000
23.	Sn1	Sn	0.0000	1.0000	0.4331	0.000	-5.430	-9.701	5.4300	± 0.0000
24.	Sn1	Sn	-0.6667	-0.3333	0.2336	-3.135	-0.000	-5.232	5.4594	± 0.0000
25.	Sn1	Sn	0.3333	-0.3333	0.2336	1.568	2.715	-5.232	5.4594	± 0.0000
26.	Sn1	Sn	0.3333	0.6667	0.2336	1.568	-2.715	-5.232	5.4594	± 0.0000

Table S4. Interatomic distances from Sn atoms in $Na_{15}Sn_4$ (I-43d).

	Label	Elmt	Fractional Coordinates x	y	z	Orthogonal Coordinates xor[Å]	yor[Å]	zor[Å]	Bond Distance d [Å]
TARG.	Sn1	Sn	0.7083	0.7083	0.7083	-0.000	0.000	-16.120	
1.	Na2	Na	0.8730	0.6548	0.5330	2.026	-2.478	-15.634	3.2378 ± 0.0137
2.	Na2	Na	0.6548	0.5330	0.8730	1.133	2.994	-15.634	3.2378 ± 0.0125
3.	Na2	Na	0.5330	0.8730	0.6548	-3.159	-0.516	-15.634	3.2378 ± 0.0133
4.	Na2	Na	0.9048	0.8770	0.7170	0.257	-1.866	-18.957	3.4050 ± 0.0135
5.	Na2	Na	0.7170	0.9048	0.8770	-1.745	0.710	-18.957	3.4050 ± 0.0124
6.	Na2	Na	0.8770	0.7170	0.9048	1.487	1.156	-18.957	3.4050 ± 0.0138
7.	Na2	Na	0.4670	0.6270	0.6548	-1.486	1.157	-13.267	3.4189 ± 0.0146
8.	Na2	Na	0.6270	0.6548	0.4670	-0.259	-1.866	-13.267	3.4189 ± 0.0132
9.	Na2	Na	0.6548	0.4670	0.6270	1.745	0.708	-13.267	3.4189 ± 0.0121
10.	Na1	Na	0.5000	0.7500	0.8750	-2.322	2.683	-16.121	3.5482 ± 0.0052
11.	Na1	Na	0.7500	0.8750	0.5000	-1.163	-3.352	-16.121	3.5482 ± 0.0008
12.	Na1	Na	0.8750	0.5000	0.7500	3.485	0.669	-16.121	3.5482 ± 0.0038
13.	Na2	Na	1.0952	0.6230	0.7170	4.387	-1.527	-18.474	5.2072 ± 0.0160
14.	Na2	Na	0.6230	0.7170	1.0952	-0.871	4.562	-18.474	5.2072 ± 0.0132
15.	Na2	Na	0.7170	1.0952	0.6230	-3.515	-3.036	-18.474	5.2072 ± 0.0119
16.	Sn1	Sn	0.7917	0.7083	0.2917	0.773	-4.917	-13.593	5.5827 ± 0.0015
17.	Sn1	Sn	0.2917	0.7917	0.7083	-4.645	1.790	-13.593	5.5827 ± 0.0109
18.	Sn1	Sn	0.7083	0.2917	0.7917	3.872	3.128	-13.593	5.5827 ± 0.0000
19.	Sn1	Sn	0.9583	0.9583	0.9583	-0.000	0.000	-21.810	5.6898 ± 0.0052
20.	Sn1	Sn	0.4583	0.4583	0.4583	-0.000	0.000	-10.431	5.6898 ± 0.0052
21.	Na2	Na	0.8452	0.4670	0.3730	3.513	-3.039	-12.785	5.7184 ± 0.0129
22.	Na2	Na	0.3730	0.8452	0.4670	-4.388	-1.523	-12.785	5.7184 ± 0.0146
23.	Na2	Na	0.4670	0.3730	0.8452	0.875	4.561	-12.785	5.7184 ± 0.0130
24.	Sn1	Sn	0.4583	0.5417	1.0417	-0.772	5.812	-15.489	5.8971 ± 0.0050
25.	Sn1	Sn	0.5417	0.9583	1.0417	-3.869	3.131	-19.282	5.8971 ± 0.0030
26.	Sn1	Sn	0.9583	1.0417	0.5417	-0.777	-4.917	-19.282	5.8971 ± 0.0050
27.	Sn1	Sn	1.0417	0.5417	0.9583	4.647	1.785	-19.282	5.8971 ± 0.0074
28.	Sn1	Sn	1.0417	0.4583	0.5417	5.420	-2.237	-15.489	5.8971 ± 0.0074
29.	Sn1	Sn	0.5417	1.0417	0.4583	-4.647	-3.575	-15.489	5.8971 ± 0.0030

Table S5. Interatomic distances from Sn atoms in $Na_{16-x}Sn_4$ '$Na_{14.78}Sn_4$' (Pnma).

Sn1 site

	Label	Elmt	Fractional Coordinates x	y	z	Orthogonal Coordinates xor[Å]	yor[Å]	zor[Å]	Bond Distance d [Å]	error
TARG.	Sn1	Sn	0.1660	0.2500	0.0956	-2.170	1.676	-1.350		
1.	Na8	Na	0.3067	0.2500	-0.0320	0.744	3.043	-1.315	3.2196	± 0.0048
2.	Na3	Na	0.1491	0.2500	0.2397	-5.455	1.527	-1.354	3.2882	± 0.0058
3.	Na2	Na	0.4919	0.2500	0.1291	-2.918	4.879	-1.268	3.2901	± 0.0063
4.	Na5	Na	0.3425	-0.2500	0.0808	-1.825	3.336	1.479	3.2976	± 0.0046
5.	Na5	Na	0.3425	0.7500	0.0808	-1.824	3.479	-4.090	3.2976	± 0.0046
6.	Na4	Na	-0.0501	0.2500	-0.0172	0.390	-0.458	-1.405	3.3334	± 0.0044
7.	Na1	Na	-0.1647	0.2500	0.1341	-3.064	-1.566	-1.434	3.3639	± 0.0064
8.	Na6	Na	0.0221	-0.2500	0.1546	-3.522	0.199	1.398	3.4002	± 0.0044
9.	Na6	Na	0.0221	0.7500	0.1546	-3.522	0.342	-4.171	3.4002	± 0.0044
10.	Na4	Na	0.0501	-0.2500	0.0172	-0.390	0.458	1.405	3.4991	± 0.0044
11.	Na4	Na	0.0501	0.7500	0.0172	-0.389	0.601	-4.163	3.4991	± 0.0044
12.	Na7	Na	0.3559	-0.2500	0.2200	-4.997	3.483	1.482	4.3899	± 0.0048
13.	Na7	Na	0.3559	0.7500	0.2200	-4.996	3.626	-4.086	4.3899	± 0.0048
14.	Sn1	Sn	0.1660	-0.7500	0.0956	-2.171	1.533	4.218	5.5700	± 0.0100
15.	Sn1	Sn	0.1660	1.2500	0.0956	-2.170	1.819	-6.918	5.5700	± 0.0100
16.	Na8	Na	-0.3067	-0.2500	0.0320	-0.744	-3.043	1.315	5.6040	± 0.0082
17.	Na8	Na	-0.3067	0.7500	0.0320	-0.744	-2.900	-4.254	5.6040	± 0.0082
18.	Sn2	Sn	0.6593	0.7500	0.1699	-3.839	6.599	-4.010	5.8386	± 0.0086
19.	Sn2	Sn	0.6593	-0.2500	0.1699	-3.840	6.455	1.559	5.8386	± 0.0086
20.	Na7	Na	-0.1441	-0.2500	0.2800	-6.388	-1.419	1.356	5.8898	± 0.0066
21.	Na7	Na	-0.1441	0.7500	0.2800	-6.388	-1.275	-4.213	5.8898	± 0.0066
22.	Na1	Na	0.1647	-0.2500	-0.1341	3.064	1.566	1.434	5.9296	± 0.0084
23.	Na1	Na	0.1647	0.7500	-0.1341	3.065	1.709	-4.134	5.9296	± 0.0084
24.	Sn2	Sn	-0.3407	-0.2500	0.1699	-3.889	-3.361	1.306	5.9483	± 0.0088
25.	Sn2	Sn	-0.3407	0.7500	0.1699	-3.888	-3.218	-4.262	5.9483	± 0.0088
26.	Na6	Na	-0.0221	0.2500	-0.1546	3.522	-0.199	-1.398	5.9938	± 0.0096

Sn2 site

	Label	Elmt	Fractional Coordinates x	y	z	Orthogonal Coordinates xor[Å]	yor[Å]	zor[Å]	Bond Distance d [Å]	error
TARG.	Sn2	Sn	0.3407	0.2500	0.8301	-18.901	3.474	-1.306		
1.	Na8	Na	0.3067	0.2500	0.9680	-22.045	3.156	-1.315	3.1604	± 0.0055
2.	Na7	Na	0.1441	0.2500	0.7200	-16.401	1.532	-1.356	3.1660	± 0.0042
3.	Na7	Na	0.6441	0.2500	0.7800	-17.744	6.447	-1.230	3.1907	± 0.0057
4.	Na2	Na	0.5081	-0.2500	0.8709	-19.823	5.050	1.520	3.3650	± 0.0045
5.	Na2	Na	0.5081	0.7500	0.8709	-19.822	5.194	-4.048	3.3650	± 0.0045
6.	Na1	Na	0.1647	-0.2500	0.8659	-19.726	1.679	1.433	3.3777	± 0.0045
7.	Na1	Na	0.1647	0.7500	0.8659	-19.725	1.822	-4.135	3.3777	± 0.0045
8.	Na3	Na	0.3509	-0.2500	0.7397	-16.841	3.492	1.480	3.4657	± 0.0046
9.	Na3	Na	0.3509	0.7500	0.7397	-16.840	3.636	-4.088	3.4657	± 0.0046
10.	Na6	Na	-0.0221	0.2500	0.8454	-19.267	-0.086	-1.398	3.5797	± 0.0072
11.	Na5	Na	0.6575	0.2500	0.9192	-20.916	6.594	-1.226	3.7150	± 0.0057
12.	Na6	Na	0.4779	0.2500	0.6546	-14.895	4.801	-1.272	4.2205	± 0.0067
13.	Na4	Na	-0.0501	0.2500	0.9828	-22.400	-0.345	-1.405	5.1806	± 0.0071
14.	Sn2	Sn	0.3407	-0.7500	0.8301	-18.902	3.331	4.262	5.5700	± 0.0100
15.	Sn2	Sn	0.3407	1.2500	0.8301	-18.900	3.618	-6.874	5.5700	± 0.0100
16.	Na3	Na	-0.1491	-0.2500	0.7603	-17.334	-1.414	1.354	5.7811	± 0.0085
17.	Na3	Na	-0.1491	0.7500	0.7603	-17.334	-1.270	-4.214	5.7811	± 0.0085
18.	Na4	Na	0.0501	0.7500	1.0172	-23.179	0.714	-4.164	5.8379	± 0.0066
19.	Na4	Na	0.0501	-0.2500	1.0172	-23.179	0.571	1.404	5.8379	± 0.0066
20.	Sn1	Sn	0.8340	-0.2500	0.9044	-20.571	8.254	1.602	5.8386	± 0.0086
21.	Sn1	Sn	0.8340	0.7500	0.9044	-20.570	8.397	-3.966	5.8386	± 0.0086
22.	Sn1	Sn	-0.1660	-0.2500	0.9044	-20.619	-1.563	1.350	5.9483	± 0.0088
23.	Sn1	Sn	-0.1660	0.7500	0.9044	-20.619	-1.420	-4.218	5.9483	± 0.0088
24.	Na3	Na	0.8509	-0.2500	0.7603	-17.286	8.403	1.607	5.9488	± 0.0089
25.	Na3	Na	0.8509	0.7500	0.7603	-17.285	8.546	-3.961	5.9488	± 0.0089
26.	Na5	Na	0.1575	0.2500	0.5808	-13.228	1.648	-1.352	5.9596	± 0.0096

Table S6. Structural parameters derived from Rietveld refinement for NaSn (I41/acd) (ICSD 409434).

Site	*x*	*y*	*z*	$U_i/U_e \times 100$ (Å^2)
Na1	0.6264(11)	0.8764(11)	0.125	1.7(5)
Na2	0.8855(22)	0	0.25	1.7(5)
Sn1	0.06809(29)	0.12634(27)	0.93575(18)	3.54(17)

Table S7. Structural parameters derived from Rietveld refinement for Na_9Sn_4 (Cmcm) with positions taken from the literature (ICSD 105166).

Site	*x*	*y*	*z*	$U_i/U_e \times 100$ (Å^2)
Na1	0	0.816	0.25	8.5(4)
Na2	0	0.149	0.418	8.5(4)
Na3	0	0.493	0.156	8.5(4)
Na4	0	0.130	0.635	8.5(4)
Na5	0	0.171	0.523	8.5(4)
Sn1	0	0.1658	0.2022	2.62(14)
Sn2	0	0.5	0.0482	2.62(14)

Table S8. Structural parameters derived from Rietveld refinement for Na_9Sn_4 (Cmcm) (ICSD 105166) with positions and fractional occupancy refined.

Site	*x*	*y*	*z*	*occupancy*	$U_i/U_e \times 100$ (Å^2)
Na1	0	0.7847(50)	0.25	1.00	2.3(4)
Na2	0	0.1694(38)	0.4067(10)	1.00	2.3(4)
Na3	0	0.5180(45)	0.1683(8)	1.00	2.3(4)
Na4	0	0.0404(29)	0.6422(11)	1.00	2.3(4)
Na5	0	0.1592(36)	0.5284(9)	1.00	2.3(4)
Sn1	0	0.1605(8)	0.20543(22)	1.00	3.65(15)
Sn2	0	0.5071(12)	0.04632(27)	0.785(12)	3.65(15)

Table S9. Structural parameters derived from Rietveld refinement for $Na_{15}Sn_4$ (I-43d) (ICSD 105167) with occupancy of Na fixed at fully occupied.

Site	*x*	*y*	*z*	$U_i/U_e \times 100$ (Å^2)	*Frac*
Na1	0.375	0	0.25	4.48(15)	1.00
Na2	0.6260(4)	0.6519(5)	0.4596(6)	4.48(15)	1.00
Sn	0.45863(10)	0.45863(10)	0.45863(10)	3.06(6)	1.00

Table S10. Structural parameters derived from Rietveld refinement for $Na_{16-x}Sn_4$ (Pnma) (ICSD 105168).

Site	*x*	*y*	*Z*	$U_i/U_e \times 100$ (Å^2)
Na1	0.3353	0.25	0.3659	3.59(32)
Na2	0.4919	0.25	0.1291	3.59(32)
Na3	0.1491	0.25	0.2397	3.59(32)
Na4	0.9499	0.25	0.9828	3.59(32)
Na5	0.6575	0.25	0.9192	3.59(32)
Na6	0.9779	0.25	0.8454	3.59(32)
Na7	0.6441	0.25	0.78	3.59(32)
Na8	0.8067	0.25	0.532	3.59(32)
Sn1	0.1649(7)	0.25	0.0964(3)	3.87(15)
Sn2	0.3426(8)	0.25	0.8303(3)	3.87(15)

Table S11. Structural parameters derived from Rietveld refinement for Na_7Sn_3 XRD data in R-3m.

Site	Position	*x*	*y*	*z*	*Occupancy*	$U_i/U_e \times 100$ (Å^2)
Na1	3b	0	0	0.5	0.8	11.04(26)
Na2	6c	0	0	0.3514(5)	1.0	11.04(26)
Na3	6c	0	0	0.2136(5)	0.95	11.04(26)
Sn1	6c	0	0	0.06337(9)	1.0	3.23(7)

Table S12. Structural parameters derived from Rietveld refinement for Na_7Sn_3 neutron diffraction data in R-3m.

Site	Position	*x*	*y*	*z*	*Occupancy*	$U_i/U_e \times 100$ (Å^2)
Na1	3b	0	0	0.5	0.8	7.36(12)
Na2	6c	0	0	0.3490(3)	1.0	7.36(12)
Na3	6c	0	0	0.2131(3)	0.95	7.36(12)
Sn1	6c	0	0	0.06428(11)	1.0	2.06(7)

Table S13. Structural parameters derived from Rietveld refinement for Na_7Sn_3 neutron diffraction data in R3m.

Site	Position	*x*	*y*	*z*	Occupancy	$U_i/U_e \times 100$ (Å^2)
Na1	3a	0	0	0.4939(6)	0.8	6.15(13)
Na2a	3a	0	0	0.3505(6)	1.0	6.15(13)
Na2b	3a	0	0	0.6476(6)	1.0	6.15(13)
Na3a	3a	0	0	0.2192(15)	0.95	6.15(13)
Na3b	3a	0	0	0.7945(15)	0.95	6.15(13)
Sn1a	3a	0	0	0.07267(22)	1.0	2.18(7)
Sn2b	3a	0	0	0.945987	1.0	2.18(7)

Table S14. Results obtained from fitting the Sn K-edge EXAFS of Sn electrode films. N, R, σ^2, ΔE_0 and R factor represent the coordination number, the interatomic distance (Å), the Debye-Waller factor, the shift in the edge energy and the quality of fit.

Sample	R (Å)	N (± 0.5)	σ^2 (Å^2)	ΔE_0 (eV)	R-factor
β-Sn	2.98 3.10	4 (fixed) 2 (fixed)	0.008	-0.009	0.010
NaSn powder Sn - Sn Sn - Na Sn - Na	 2.97 3.36 3.60	 3 (fixed) 2.0 (fixed) 2.0 (fixed)	0.006	-1.69	0.002
0.22 V Film Sn - Sn Sn - Na Sn - Na	 3.09 (.02) 3.09 (.09) 3.38 (.21)	 2.2 0.5 0.5	0.010	1.87	0.013
0.12 V Film Sn - Sn Sn - Na	 2.94 (.005) 3.18 (.03)	 2.0 1.1	0.007	-1.52	0.008
0.4 V Film Sn - Sn Sn - Na Sn - Na	 2.98 (.006) 3.17 (.009) 3.37 (.008)	 2.0 2.7 2.7	0.008	7.34	0.005
0.6 V Film Sn - Sn Sn - Na Sn - Na	 2.89 (.004) 3.26 (.08) 3.48 (.06)	 2.9 0.8 0.8	0.007	-2.10	0.006