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Supplementary Information

Sn-Bi-Sb Alloys as Anode Materials for Sodium Ion Batteries

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Supporting Figures

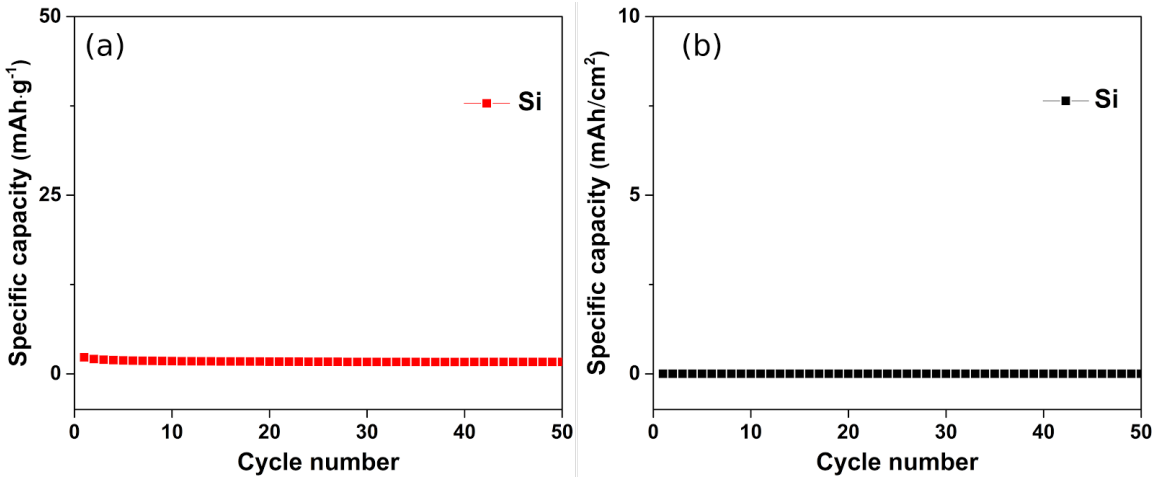

Fig. S1 Specific Na storage capacity versus cycle number of the Si substrate used in this study. (a) Normalized to the average weight of a 100 nm thin film used in this study. (b) Normalized to the surface area of the substrate.

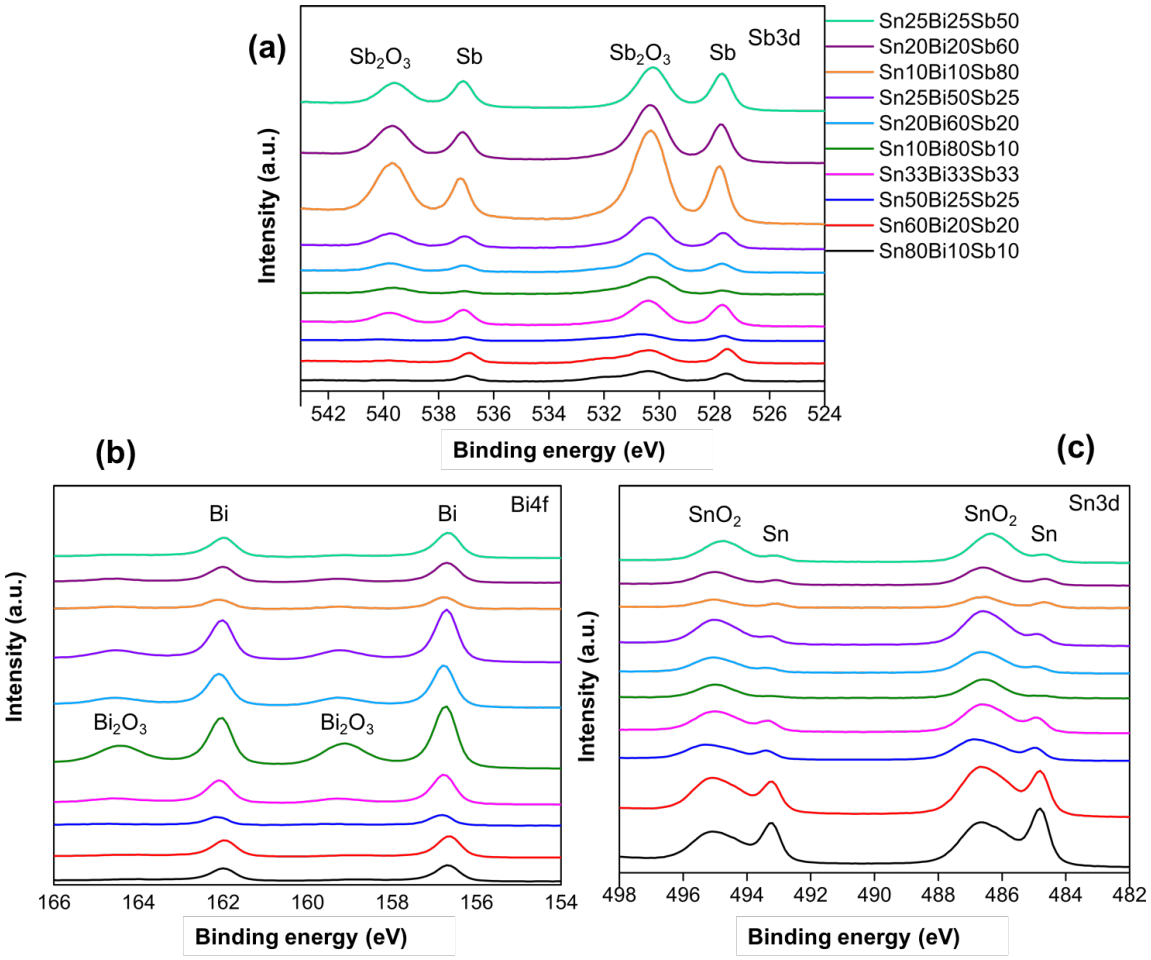

Fig. S2 High resolution XPS spectra of Sb3d, Sn3d, and Bi4f of as-deposited thin films for all the alloy compositions investigated in this work.

Table S1 Average weight and standard deviation for each composition based on 6 different samples

Sample	Average weight (mg)	Standard deviation (mg)
Sn	0.0485	0.0004
Sn80 Bi10Sb10	0.0538	0.0014
Sn60 Bi20Sb20	0.0590	0.0006
Sn50 Bi25Sb25	0.0586	0.0005
Bi	0.0830	0.0012
Sn10**Bi80**Sb10	0.0742	0.0013
Sn20**Bi60**Sb20	0.0715	0.0019
Sn25**Bi50**Sb25	0.0692	0.0009
Sn33Bi33Sb33	0.0621	0.0012
Sb	0.0499	0.0004
Sn10Bi10**Sb80**	0.0563	0.0008
Sn20Bi20**Sb60**	0.0559	0.0023
Sn25Bi25**Sb50**	0.0580	0.0010

Table S2 Sample compositions of as-deposited alloy electrodes, derived from XPS spectra.

Sample	Sn (at%)	Bi (at%)	Sb (at%)
Sn80 Bi10Sb10	76	13	11
Sn60 Bi20Sb20	62	20	18
Sn50 Bi25Sb25	57	22	21
Sn10**Bi80**Sb10	33	36	31
Sn20**Bi60**Sb20	12	75	13
Sn25**Bi50**Sb25	23	55	22
Sn33Bi33Sb33	26	50	24
Sn10Bi10**Sb80**	11	88	81
Sn20Bi20**Sb60**	17	25	58
Sn25Bi25**Sb50**	26	27	46

Table S3 Grain sizes of all phases in as-deposited films (as determined by XRD using the Scherrer equation).

Sample	(Sn) grain size (nm)	(Bi) grain size (nm)	(Sb) grain size (nm)	β-SnSb grain size (nm)
Sn	89			
Sn80 Bi10Sb10	88	85		99
Sn60 Bi20Sb20	90	87		91
Sn50 Bi25Sb25	77	85		81
Bi		95		
Sn10**Bi80**Sb10		41		47
Sn20**Bi60**Sb20		42		47
Sn25**Bi50**Sb25		42		46
Sn33Bi33Sb33		50		50
Sb			40	
Sn10Bi10**Sb80**			36	
Sn20Bi20**Sb60**			27	
Sn25Bi25**Sb50**		9.3	22	42

Table S4 Grain sizes of all phases after 100 constant current charge/discharge cycles

Sample	(Sn) grain size (nm)	(Bi) grain size (nm)	(Sb) grain size (nm)	β-SnSb grain size (nm)
Sn	95			
Sn80 Bi10Sb10	54	11		60
Sn60 Bi20Sb20	19	21		44
Sn50 Bi25Sb25				53
Bi		47		
Sn10**Bi80**Sb10		17		
Sn20**Bi60**Sb20		16		9.2
Sn25**Bi50**Sb25		11		15
Sn33Bi33Sb33		7.1		19
Sb			16	
Sn10Bi10**Sb80**		33	8.9	
Sn20Bi20**Sb60**		11	8.2	
Sn25Bi25**Sb50**		10	11	

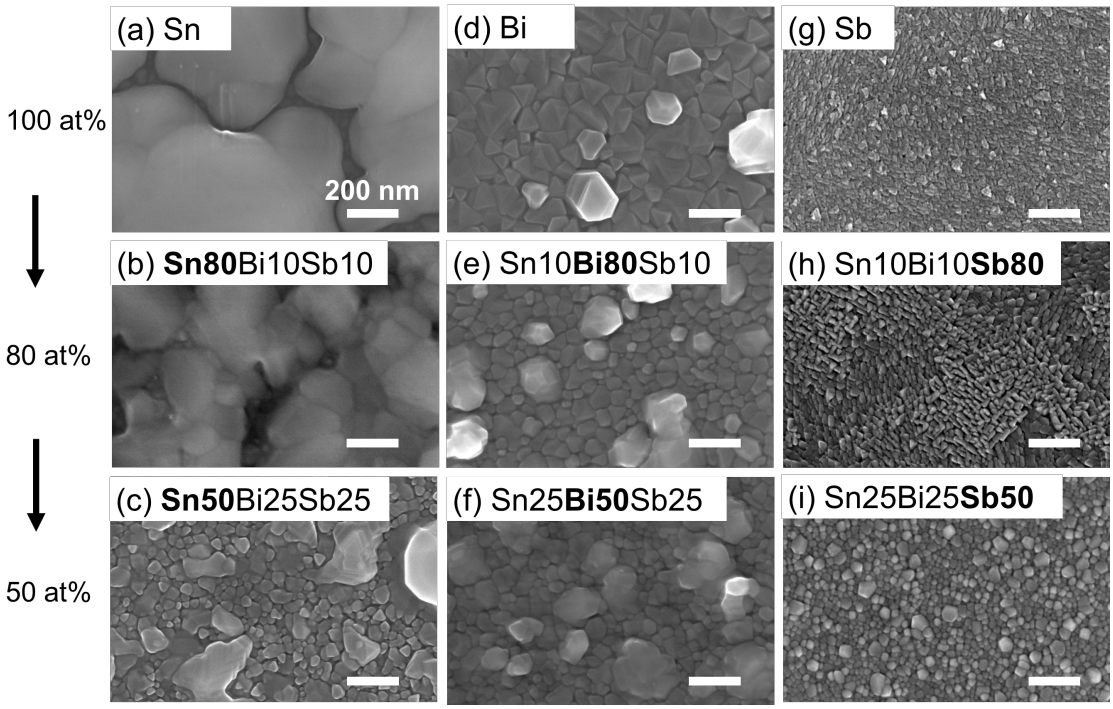

Fig. S3 SEMs of as-deposited elemental films and alloys. (a) Sn, (b) **Sn80**Bi10Sb10, (c) **Sn50**Bi25Sb25, (d) Bi, (e) Sn10**Bi80**Sb10, (f) Sn25**Bi50**Sb25; (g) Sb, (h) Sn10Bi10**Sb80**, (i) Sn25Bi25**Sb50**. All scale bars are 200 nm. The numbers following the elements represent the molar percent of elements in the film.

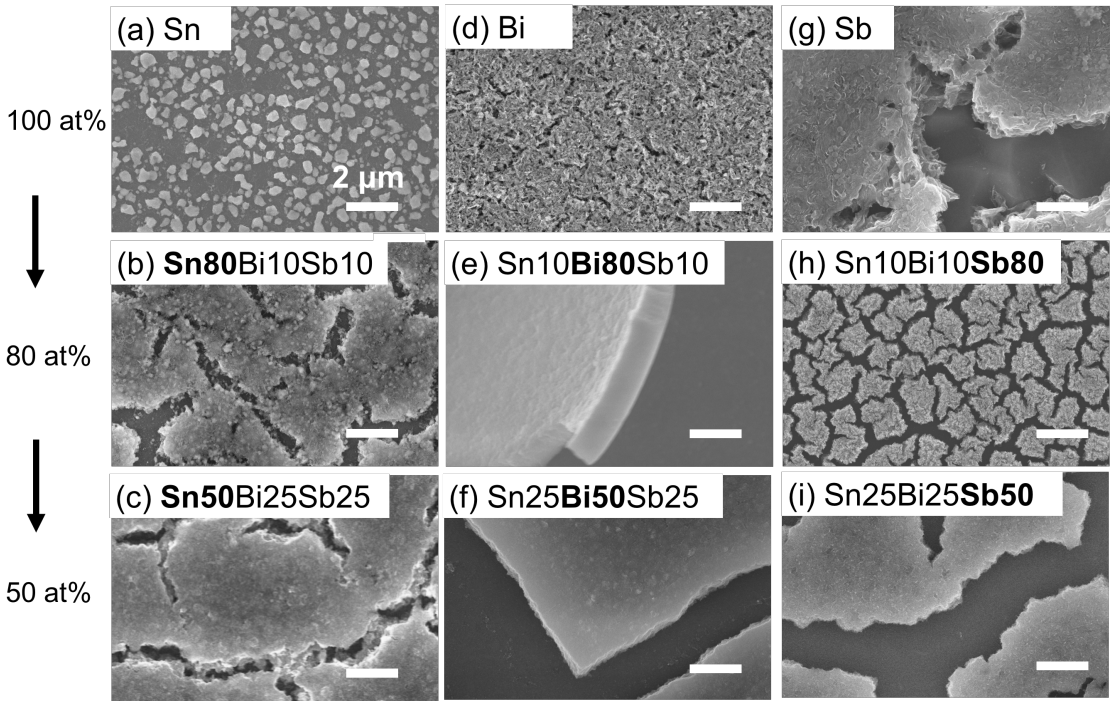

Fig. S4 SEM micrographs of the cycled elemental films and alloys. (a) Sn (b) **Sn80**Bi10Sb10, (c) **Sn50**Bi25Sb25; (d) Bi, (e) Sn10**Bi80**Sb10, (f) Sn25**Bi50**Sb25; (g) Sb, (h) Sn10Bi10**Sb80**, (i) Sn25Bi25**Sb50**. Pure Sn and Bi were cycled 50 times, and all other electrodes 100 times. All scale bars are 2 µm.

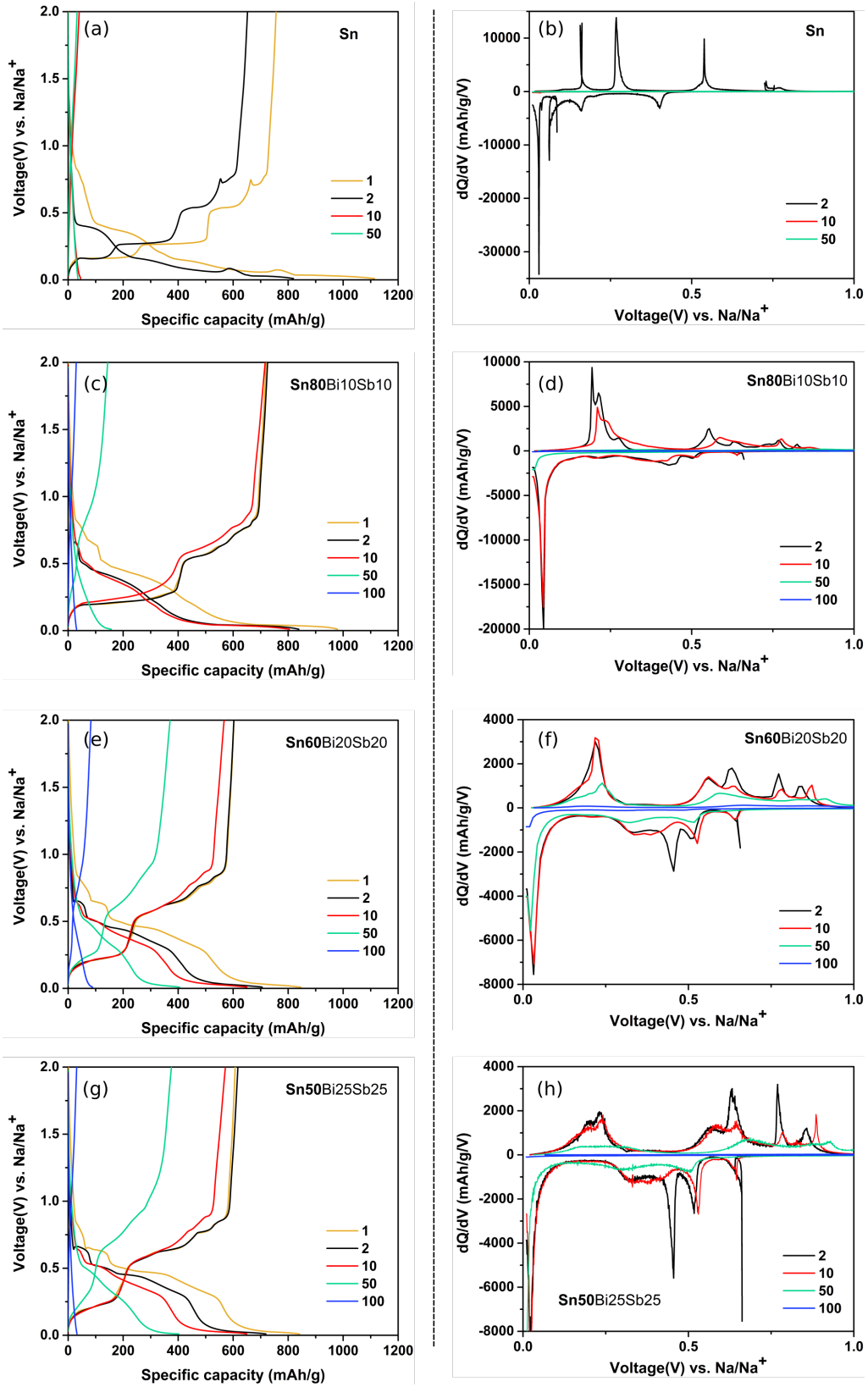

Fig. S5 Voltage profiles (left) and corresponding dQ/dV plots (right) for (a,b) elemental Sn, (c,d) Sn**80**Bi10Sb10, (e,f) Sn**60**Bi20Sb20 and (g,h) Sn**50**Bi25Sb25.

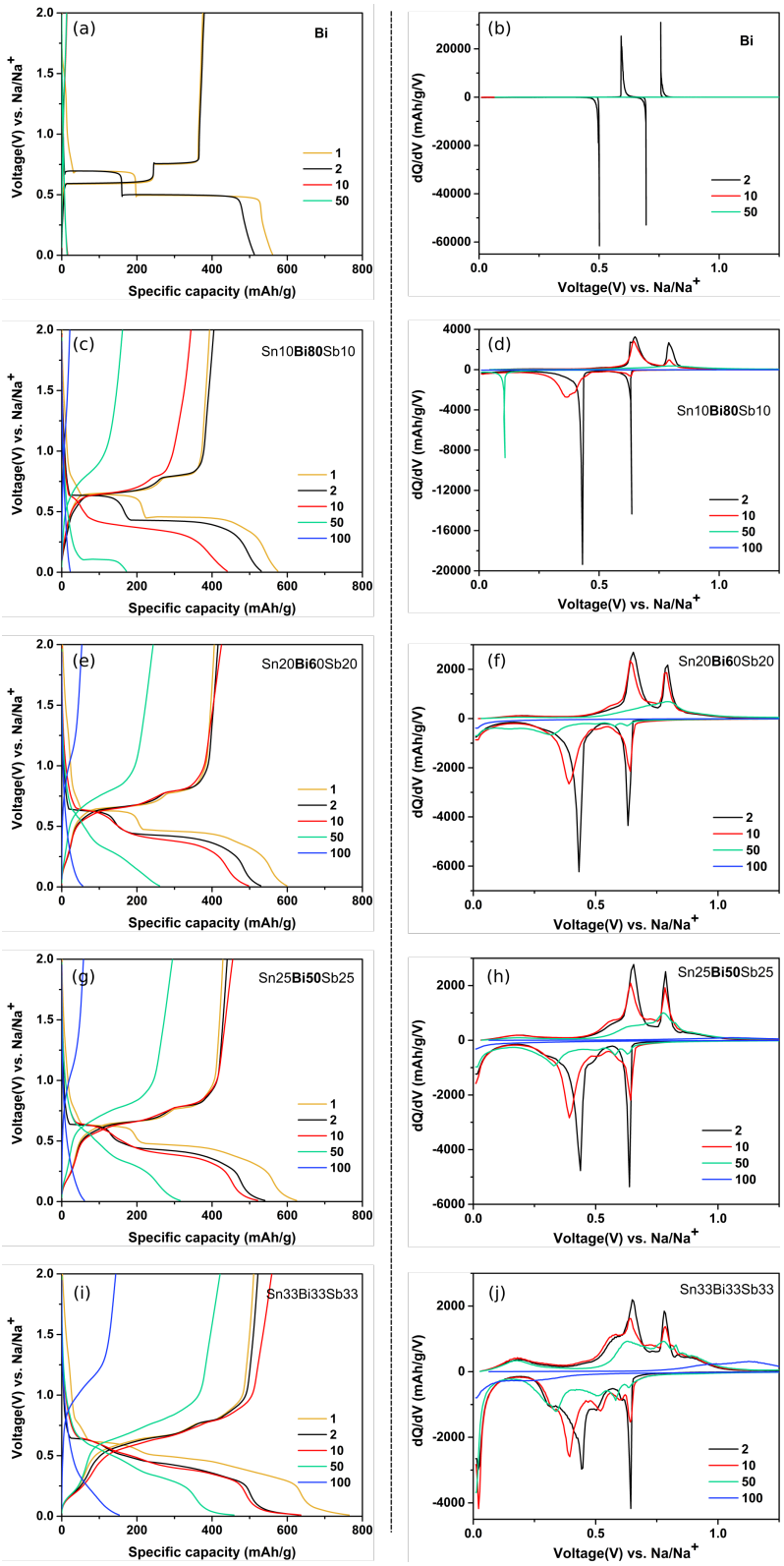

Fig. S6 Voltage profiles (left) and corresponding dQ/dV plots (right) for (a,b) elemental Bi, (c,d) Sn10Bi**80**Sb10, (e,f) Sn20Bi**60**Sb20, (g,h) Sn25Bi**50**Sb25 and (i,j) Sn33Bi33Sb33.

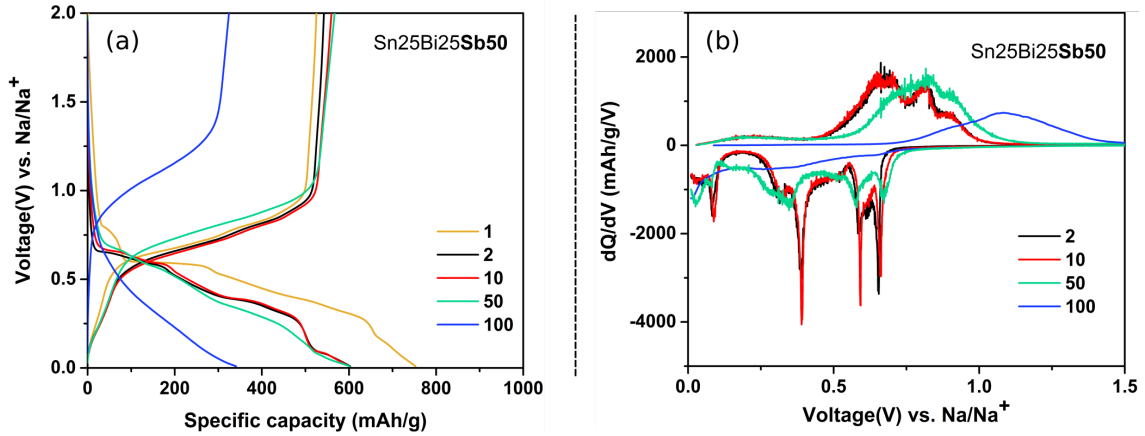

Fig. S7 Voltage profile (a) and corresponding dQ/dV plot (b) for Sn25Bi25**Sb50**.

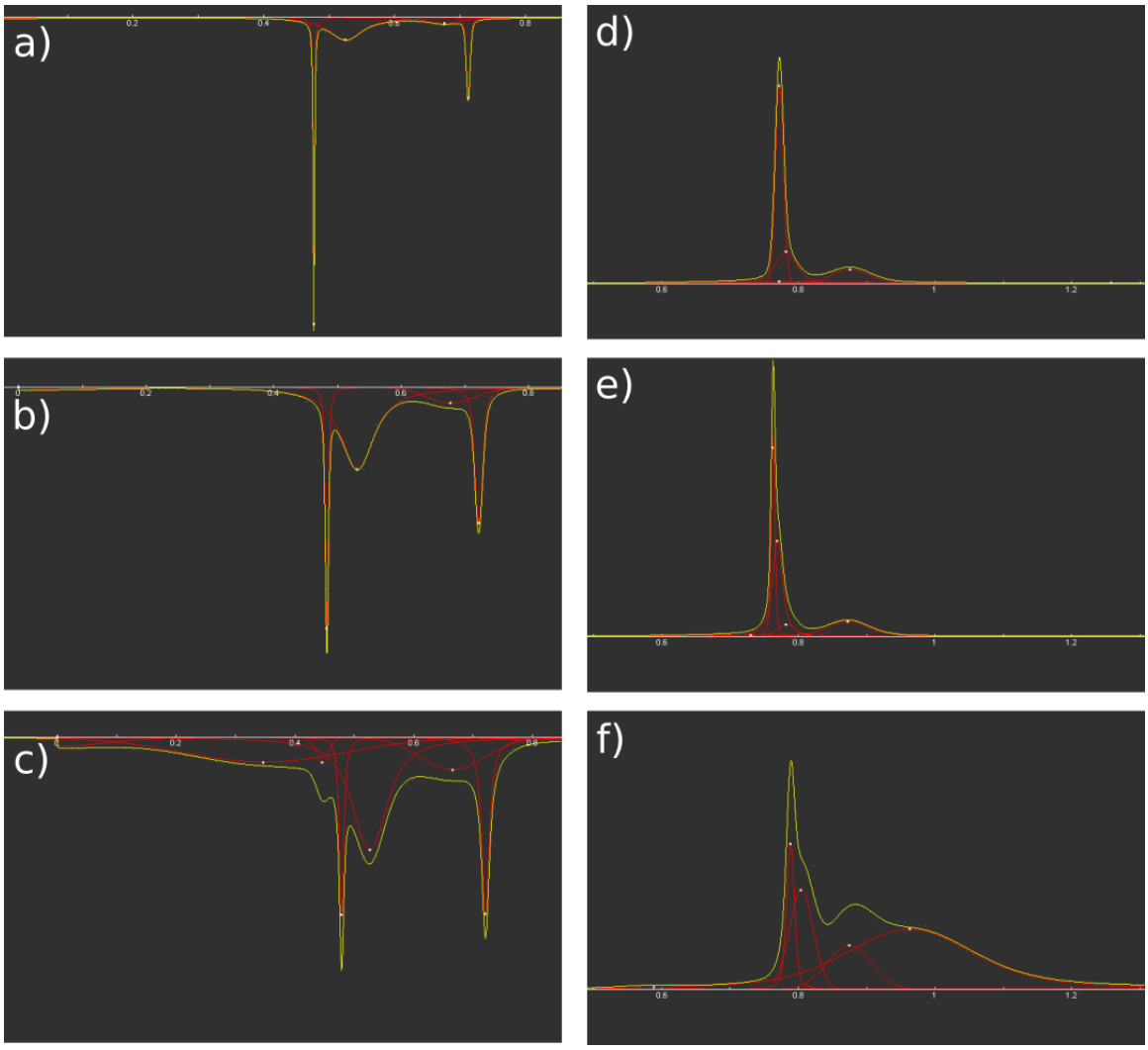

Fig. S8 Curve fitting of dQ/dV the sodiation/desodiation profiles of pure Sb. (a-c) sodiation curves for cycles 2,10 and 35. (d-f) desodiation curves for cycles 2, 10 and 35.

Table S5 Peak fit parameters dQ/dV curves of pure Sb films.

Sb - sodiation

Cycle	Center (V)	Width (mV)	Area (%)
2	0.00	165	3.3
2	0.48	4	23.4
2	0.52	97	46.0
2	0.68	101	12.6
2	0.71	9	14.5
2	0.90	78	0.3
10	0.00	139	2.6
10	0.48	8	13.1
10	0.53	97	54.7
10	0.68	96	10.6
10	0.72	20	18.2
10	0.87	107	0.8
35	0.00	105	2.8
35	0.35	345	24.9
35	0.45	27	2.0
35	0.48	13	6.8
35	0.53	104	34.1
35	0.67	139	13.0
35	0.72	24	12.2
35	0.93	454	4.3

Sb - desodiation

Cycle	Center (V)	Width (mV)	Area (%)
2	0.77	15	59.3
2	0.77	344	12.3
2	0.88	80	15.6
2	1.25	1324	12.9
10	0.73	317	8.1
10	0.77	18	59.4
10	0.87	91	18.2
10	1.41	1485	14.4
35	0.59	111	0.8
35	0.79	17	22.8
35	0.87	82	12.0
35	0.96	288	56.1
35	1.59	1149	8.3

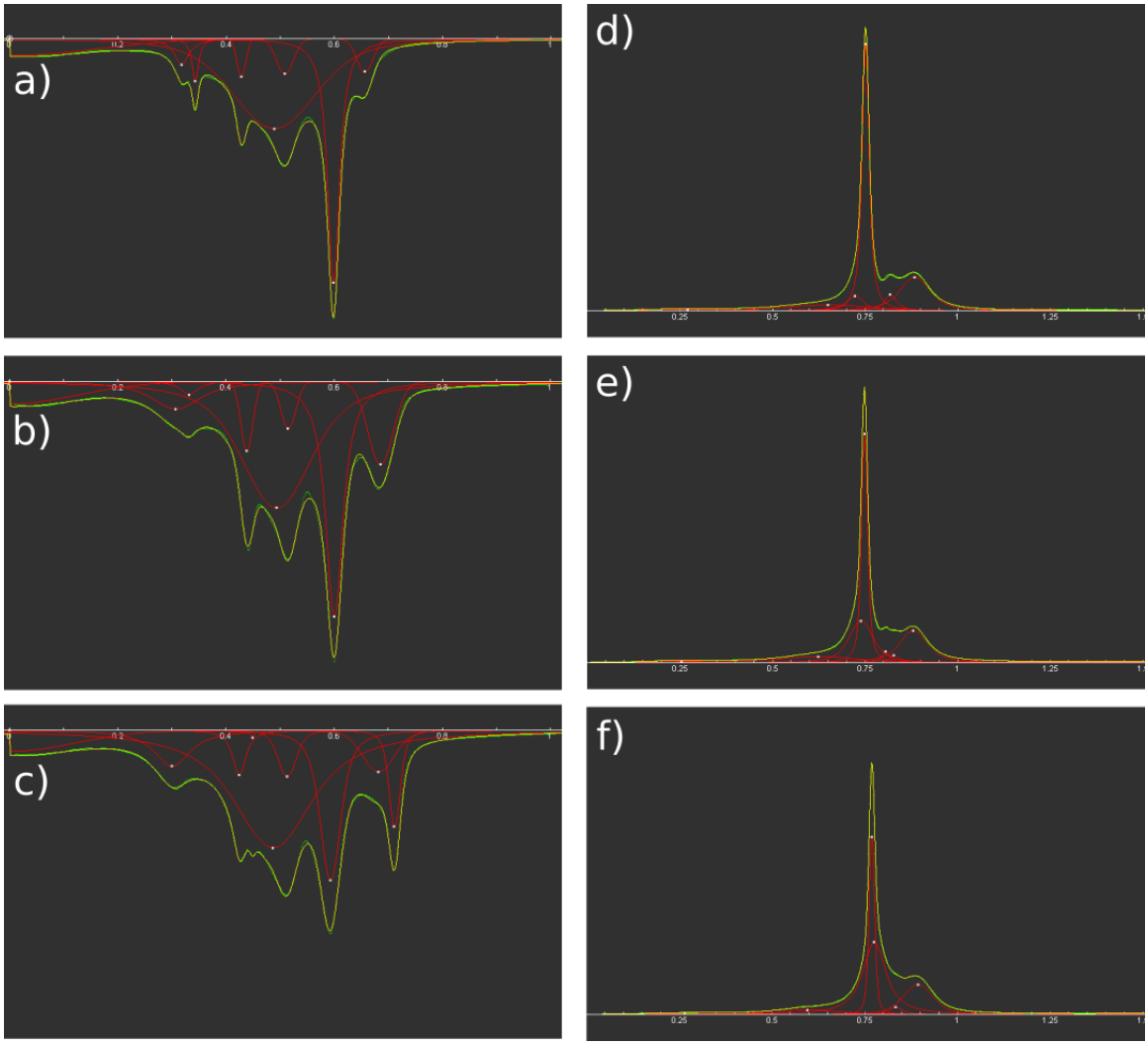

Fig. S9 Curve fitting of dQ/dV the sodiation/desodiation profiles of Sn10Bi10**Sb80**. (a-c) sodiation curves for cycles 2,10 and 50. (d-f) desodiation curves for cycles 2, 10 and 50.

Table S6 Peak fit parameters dQ/dV curves of Sn10Bi10**Sb80** films.

Sn10Bi10**Sb80** - sodiation

Cycle	Center (V)	Width (mV)	Area (%)
2	0.00	201	8.5
2	0.32	50	3.2
2	0.34	21	2.2
2	0.43	21	2.0
2	0.49	235	49.3
2	0.51	59	6.3
2	0.60	41	25.0
2	0.66	40	3.4
10	0.00	157	6.1
10	0.31	165	7.8
10	0.33	60	1.4
10	0.44	28	3.4
10	0.49	212	46.1
10	0.52	35	2.8
10	0.60	59	23.8
10	0.69	59	8.5
50	0.00	152	5.6
50	0.30	126	7.8
50	0.42	45	3.5
50	0.45	11	0.2
50	0.49	260	50.9
50	0.51	51	5.0
50	0.59	63	15.4
50	0.68	82	5.8
50	0.71	33	5.8

Sn10Bi10**Sb80** - desodiation

Cycle	Center (V)	Width (mV)	Area (%)
2	0.27	292	2.9
2	0.65	318	9.5
2	0.72	53	6.3
2	0.75	33	44.6
2	0.82	64	5.2
2	0.88	137	23.2
2	1.54	1637	8.3
10	0.25	228	1.7
10	0.62	386	12.5
10	0.73	107	17.0
10	0.75	29	33.5
10	0.81	58	4.3
10	0.88	128	19.9
10	1.62	1938	11.1
50	0.26	265	1.6
50	0.60	309	7.4
50	0.77	23	19.9
50	0.78	114	40.6
50	0.83	71	2.6
50	0.89	124	18.5
50	1.75	127	9.6

Correction for instrumental broadening for grain size determination by XRD

Due to instrumental factors such as beam width, beam divergence, emission profile, filter and monochromators, the measured peak widths from an XRD spectra will always have a non-zero amount of broadening which is not the result of grain size or atomic strain. This instrumental broadening can be described mathematically as convolution.[1]

$$h(2\theta) = f(2\theta) \otimes g(2\theta) = \int_{-\infty}^{\infty} f\,(2\theta)g(2\theta - x)dx$$

Where $f(2\theta)$ is the true sample peak profile, $g(2\theta)$ is the instrumental line profile (or system impulse response) and $h(2\theta)$ is the measured peak profile. The instrumental line profile can be estimated by the measurement of the XRD spectrum of a known single crystal sample.

The true sample line profile, $f(2\theta)$, can be estimated via deconvolution, which was performed using an inversion scheme of non-negative least-squares with Tikhonov regularization.[2] Briefly, both the measured sample line profile, $h(2\theta)$, and instrumental line profile, $g(2\theta)$ are expressed as discrete vectors e.g.

$$\mathbf{h} = [h_1 \quad h_2 \quad \dots \quad h_n]$$

Next the forward convolution operation can be reformulated as matrix multiplication

$$G\mathbf{f} = \mathbf{h}$$

Where G is the Toeplitz matrix

$$G = \begin{bmatrix} h_1 & 0 & \dots & 0 & 0 \\ h_2 & h_1 & \dots & \vdots & \vdots \\ h_3 & h_2 & \dots & 0 & 0 \\ \vdots & h_3 & \dots & h_1 & 0 \\ h_{n-1} & \vdots & \dots & h_2 & h_1 \\ h_n & h_{n-1} & \vdots & \vdots & h_2 \\ 0 & h_n & \dots & h_{n-2} & \vdots \\ 0 & 0 & \dots & h_{n-1} & h_{n-2} \\ \vdots & \vdots & \vdots & h_n & h_{n-1} \\ 0 & 0 & 0 & \dots & h_n \end{bmatrix}$$

From this matrix equation we can use standard non-negative least-squares with regularization, where the estimated true sample line profile is given by

$$\min \| G\mathbf{f} - \mathbf{h}|_2^2 + \lambda^2 \| \mathbf{f} \|_2^2$$

Subject to

$$\mathbf{f} > 0$$

Where λ is the regularization constant, which is minimized using a χ^2 test. Generally the regularization parameter was made a small as possible, but sufficiently large to damp unphysical ringing.

Prior to deconvolution both the peaks of the corundum standard and the sample of interest were fit to a Voigt function. These peak fits are then discretized and utilized in the deconvolution algorithm. Shown in Fig. S8a is the measured instrumental profile, the measured sample profile of a 100 nm thick film of as-deposited Sn and the deconvolved sample profile. The integral breadth of this deconvolved sample profile is then measured and used in the Scherrer equation to calculate the grain size. Also shown in Fig. S8b is both the measured sample profile and simulated sample profile, which is calculated via convolution of the instrumental profile and the deconvolved sample profile.

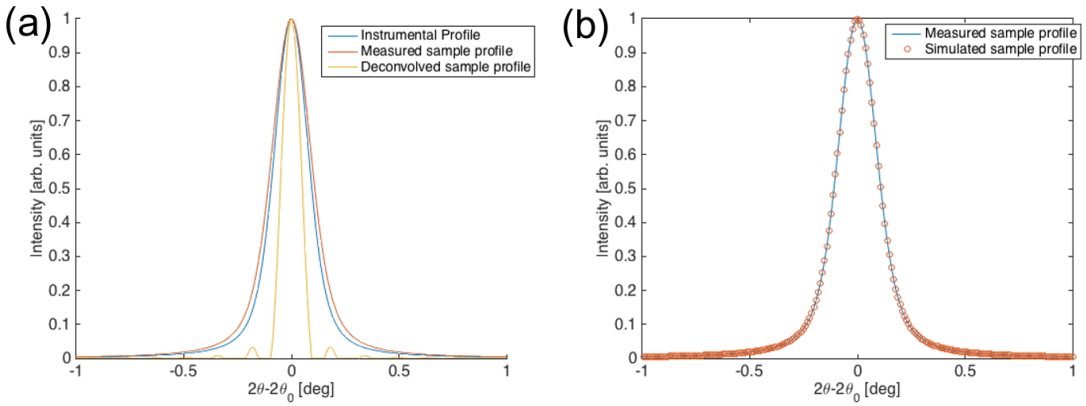

Fig. S10 (a) measured instrumental profile, the measured sample profile of a 100 nm thick film of as-deposited Sn and the deconvolved sample profile. (b) Measured sample profile and simulated sample profile, which is calculated via convolution of the instrumental profile and the deconvolved sample profile.

From these data we can see the necessity of correcting for instrumental broadening as the measured grain size would be 36 nm without deconvolution and 89 nm after deconvolution (which agrees well with the SEM data).

References

1 M. Birkholz, *Thin Film Analysis by X-Ray Scattering*, Wiley-VCH, Weinheim, 2005.

2 R. C. Aster, B. Borchers and C. H. Thurber, *Parameter Estimation and Inverse Problems*, Academic Press, Waltham, MA, 2nd edition., 2012.