Supplementary Information

Table S1. List of interatomic distances for Sb, Cu_2Sb and Na_3Sb phases.

Sb-Sb in R-3m Sb

	Label	Elmt	Fractional Coordinates x	y	z	Orthogonal Coordinates xor[Å]	yor[Å]	zor[Å]	Distance d[Å]
TARG.	Sb	Sb	0.0000	0.0000	0.2330	0.000	0.000	-2.627	
1.	Sb	Sb	-0.3333	-0.6667	0.1003	-1.244	2.154	-1.131	2.9029
2.	Sb	Sb	-0.3333	0.3333	0.1003	-1.244	-2.155	-1.131	2.9029
3.	Sb	Sb	0.6667	0.3333	0.1003	2.488	0.000	-1.131	2.9029
4.	Sb	Sb	-0.6667	-0.3333	0.4337	-2.488	-0.000	-4.890	3.3628
5.	Sb	Sb	0.3333	0.6667	0.4337	1.244	-2.155	-4.890	3.3628
6.	Sb	Sb	0.3333	-0.3333	0.4337	1.244	2.155	-4.890	3.3628
7.	Sb	Sb	-1.0000	-1.0000	0.2330	-3.732	2.154	-2.627	4.3090
8.	Sb	Sb	-1.0000	0.0000	0.2330	-3.732	-2.155	-2.627	4.3090
9.	Sb	Sb	1.0000	1.0000	0.2330	3.732	-2.154	-2.627	4.3090
10.	Sb	Sb	0.0000	-1.0000	0.2330	0.000	4.309	-2.627	4.3090
11.	Sb	Sb	0.0000	1.0000	0.2330	0.000	-4.309	-2.627	4.3090
12.	Sb	Sb	1.0000	0.0000	0.2330	3.732	2.155	-2.627	4.3090
13.	Sb	Sb	-0.6667	-0.3333	-0.1003	-2.488	-0.000	1.131	4.5071
14.	Sb	Sb	0.3333	-0.3333	-0.1003	1.244	2.155	1.131	4.5071
15.	Sb	Sb	0.6667	0.3333	0.5663	2.488	0.000	-6.385	4.5071
16.	Sb	Sb	-0.3333	-0.6667	0.5663	-1.244	2.154	-6.385	4.5071
17.	Sb	Sb	-0.3333	0.3333	0.5663	-1.244	-2.155	-6.385	4.5071
18.	Sb	Sb	0.3333	0.6667	-0.1003	1.244	-2.155	1.131	4.5071

Sb-X in P4/nmm Cu_2Sb

	Label	Elmt	Fractional Coordinates x	y	z	Orthogonal Coordinates xor[Å]	yor[Å]	zor[Å]	Distance d[Å]
TARG.	Sb	Sb	0.2500	0.2500	0.7000	1.000	-1.000	-4.273	
1.	Cu2	Cu	0.2500	0.2500	0.2700	1.000	-1.000	-1.648	2.6247
2.	Cu1	Cu	-0.2500	0.2500	1.0000	-1.000	-1.000	-6.104	2.7121
3.	Cu1	Cu	0.2500	-0.2500	1.0000	1.000	1.000	-6.104	2.7121
4.	Cu1	Cu	0.7500	0.2500	1.0000	3.001	-1.000	-6.104	2.7121
5.	Cu1	Cu	0.2500	0.7500	1.0000	1.000	-3.001	-6.104	2.7121
6.	Cu2	Cu	-0.2500	-0.2500	0.7300	-1.000	1.000	-4.456	2.8351
7.	Cu2	Cu	-0.2500	0.7500	0.7300	-1.000	-3.001	-4.456	2.8351
8.	Cu2	Cu	0.7500	0.7500	0.7300	3.001	-3.001	-4.456	2.8351
9.	Cu2	Cu	0.7500	-0.2500	0.7300	3.001	1.000	-4.456	2.8351
10.	Cu2	Cu	0.2500	0.2500	1.2700	1.000	-1.000	-7.752	3.4793
11.	Sb	Sb	-0.2500	-0.2500	0.3000	-1.000	1.000	-1.831	3.7370
12.	Sb	Sb	-0.2500	0.7500	0.3000	-1.000	-3.001	-1.831	3.7370
13.	Sb	Sb	0.7500	-0.2500	0.3000	3.001	1.000	-1.831	3.7370
14.	Sb	Sb	0.7500	0.7500	0.3000	3.001	-3.001	-1.831	3.7370
15.	Sb	Sb	-0.7500	0.2500	0.7000	-3.001	-1.000	-4.273	4.0010
16.	Sb	Sb	1.2500	0.2500	0.7000	5.001	-1.000	-4.273	4.0010
17.	Sb	Sb	0.2500	-0.7500	0.7000	1.000	3.001	-4.273	4.0010
18.	Sb	Sb	0.2500	1.2500	0.7000	1.000	-5.001	-4.273	4.0010

Cu-X in P4/nmm Cu_2Sb

Cu1

	Label	Elmt	Fractional Coordinates x	y	z	Orthogonal Coordinates xor[Å]	yor[Å]	zor[Å]	Distance d[Å]
TARG.	Cu1	Cu	0.7500	0.2500	0.0000	-2.386	0.027	2.076	
1.	Cu2	Cu	0.2500	0.2500	0.2700	-0.686	1.732	1.117	2.5919
2.	Cu2	Cu	0.7500	-0.2500	-0.2700	-3.001	-1.879	0.430	2.5919
3.	Cu2	Cu	0.7500	0.7500	-0.2700	-1.486	-1.330	4.092	2.5919
4.	Cu2	Cu	1.2500	0.2500	0.2700	-4.373	1.585	2.664	2.5919
5.	Sb	Sb	1.2500	0.2500	-0.3000	-4.071	-1.859	3.055	2.7121
6.	Sb	Sb	0.7500	0.7500	0.3000	-1.788	2.114	3.701	2.7121
7.	Sb	Sb	0.7500	-0.2500	0.3000	-3.303	1.565	0.039	2.7121
8.	Sb	Sb	0.2500	0.2500	-0.3000	-0.384	-1.712	1.508	2.7121
9.	Cu1	Cu	0.2500	0.7500	0.0000	0.214	0.375	3.133	2.8291
10.	Cu1	Cu	1.2500	-0.2500	0.0000	-4.987	-0.321	1.018	2.8291
11.	Cu1	Cu	1.2500	0.7500	0.0000	-3.473	0.228	4.680	2.8291
12.	Cu1	Cu	0.2500	-0.2500	0.0000	-1.300	-0.174	-0.529	2.8291
13.	Cu1	Cu	1.7500	0.2500	0.0000	-6.073	-0.120	3.623	4.0010
14.	Cu1	Cu	-0.2500	0.2500	0.0000	1.300	0.174	0.529	4.0010
15.	Cu1	Cu	0.7500	-0.7500	0.0000	-3.901	-0.522	-1.586	4.0010
16.	Cu1	Cu	0.7500	1.2500	0.0000	-0.872	0.576	5.738	4.0010

Cu2

	Label	Elmt	Fractional Coordinates x	y	z	Orthogonal Coordinates xor[Å]	yor[Å]	zor[Å]	Distance d[Å]
TARG.	Cu2	Cu	0.2500	0.2500	0.2700	-0.686	1.732	1.117	
1.	Cu1	Cu	0.7500	0.2500	0.0000	-2.386	0.027	2.076	2.5919
2.	Cu1	Cu	0.2500	-0.2500	0.0000	-1.300	-0.174	-0.529	2.5919
3.	Cu1	Cu	0.2500	0.7500	0.0000	0.214	0.375	3.133	2.5919
4.	Cu1	Cu	-0.2500	0.2500	0.0000	1.300	0.174	0.529	2.5919
5.	Sb	Sb	0.2500	0.2500	0.7000	-0.914	4.330	0.821	2.6247
6.	Sb	Sb	-0.2500	0.7500	0.3000	1.899	2.261	2.154	2.8350
7.	Sb	Sb	0.7500	-0.2500	0.3000	-3.303	1.565	0.039	2.8350
8.	Sb	Sb	-0.2500	-0.2500	0.3000	0.384	1.712	-1.508	2.8350
9.	Sb	Sb	0.7500	0.7500	0.3000	-1.788	2.114	3.701	2.8350
10.	Sb	Sb	0.2500	0.2500	-0.3000	-0.384	-1.712	1.508	3.4793
11.	Cu2	Cu	-0.2500	0.7500	0.7300	1.671	4.859	1.858	3.9860
12.	Cu2	Cu	-0.2500	-0.2500	0.7300	0.157	4.310	-1.804	3.9860
13.	Cu2	Cu	0.7500	0.7500	0.7300	-2.015	4.712	3.405	3.9860
14.	Cu2	Cu	0.7500	-0.2500	0.7300	-3.530	4.163	-0.257	3.9860
15.	Cu2	Cu	-0.7500	0.2500	0.2700	3.001	1.879	-0.430	4.0010
16.	Cu2	Cu	1.2500	0.2500	0.2700	-4.373	1.585	2.664	4.0010
17.	Cu2	Cu	0.2500	-0.7500	0.2700	-2.201	1.183	-2.545	4.0010
18.	Cu2	Cu	0.2500	1.2500	0.2700	0.829	2.281	4.779	4.0010

Sb-X in P63/mmc Na_3Sb

	Label	Elmt	Fractional Coordinates x	y	z	Orthogonal Coordinates xor[Å]	yor[Å]	zor[Å]	Distance d[Å]
TARG.	Sb1	Sb	0.3333	0.6667	0.2500	-2.318	3.124	-0.356	
1.	Na1	Na	0.0000	1.0000	0.2500	-1.786	4.762	-2.930	3.0978
2.	Na1	Na	0.0000	0.0000	0.2500	-2.333	0.027	-0.465	3.0982
3.	Na1	Na	1.0000	1.0000	0.2500	-2.835	4.581	2.329	3.0982
4.	Na2	Na	0.3333	0.6667	-0.0830	0.789	3.087	0.263	3.1685
5.	Na2	Na	0.3333	0.6667	0.5830	-5.425	3.160	-0.974	3.1685
6.	Na2	Na	0.6667	1.3333	0.0830	-0.745	6.201	0.065	3.4815
7.	Na2	Na	0.6667	1.3333	0.4170	-3.862	6.238	-0.556	3.4815
8.	Na2	Na	-0.3333	0.3333	0.0830	-0.242	1.647	-2.729	3.4815
9.	Na2	Na	-0.3333	0.3333	0.4170	-3.359	1.684	-3.350	3.4815
10.	Na2	Na	0.6667	0.3333	0.4170	-4.409	1.503	1.910	3.4824
11.	Na2	Na	0.6667	0.3333	0.0830	-1.292	1.467	2.530	3.4824
12.	Sb1	Sb	0.3333	-0.3333	0.2500	-2.865	-1.611	2.110	5.3660
13.	Sb1	Sb	0.3333	1.6667	0.2500	-1.771	7.858	-2.821	5.3660
14.	Sb1	Sb	-0.6667	-0.3333	0.2500	-1.815	-1.430	-3.149	5.3660
15.	Sb1	Sb	1.3333	1.6667	0.2500	-2.821	7.678	2.438	5.3660
16.	Sb1	Sb	-0.6667	0.6667	0.2500	-1.269	3.304	-5.615	5.3660
17.	Sb1	Sb	1.3333	0.6667	0.2500	-3.368	2.943	4.904	5.3660
18.	Sb1	Sb	0.6667	1.3333	-0.2500	2.362	6.165	0.683	5.6771
19.	Na1	Na	0.0000	1.0000	-0.2500	2.880	4.707	-2.001	5.6771
20.	Sb1	Sb	0.6667	1.3333	0.7500	-6.969	6.275	-1.175	5.6771
21.	Sb1	Sb	-0.3333	0.3333	-0.2500	2.865	1.611	-2.110	5.6771
22.	Sb1	Sb	-0.3333	0.3333	0.7500	-6.466	1.721	-3.968	5.6771
23.	Na1	Na	0.0000	1.0000	0.7500	-6.452	4.817	-3.859	5.6771
24.	Na1	Na	0.0000	0.0000	0.7500	-6.998	0.082	-1.394	5.6774
25.	Na1	Na	0.0000	0.0000	-0.2500	2.333	-0.027	0.465	5.6774
26.	Na1	Na	1.0000	1.0000	0.7500	-7.501	4.636	1.400	5.6774
27.	Na1	Na	1.0000	1.0000	-0.2500	1.830	4.526	3.258	5.6774
28.	Sb1	Sb	0.6667	0.3333	0.7500	-7.516	1.540	1.291	5.6776
29.	Sb1	Sb	0.6667	0.3333	-0.2500	1.815	1.430	3.149	5.6777

Table S2. Results obtained from fitting the Cu K-edge EXAFS of Cu_2Sb electrode films and several reference materials. 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. The values of R in parentheses are calculated based on the crystallographic structure, see Table S5.

Sample	Interaction	N	R (0.01)	σ^2	ΔE_0	R factor
Pristine Cu_2Sb film	Cu_1-Cu_2	4	2.58	0.010	2.3	0.001
	Cu_1-Sb	4	2.65			
	Cu_1-Cu_1	4	2.89			
	Cu_2-Cu_1	4	2.59			
	Cu_2-Sb	1	2.57			
	Cu_2-Sb	4	2.85			
Cu_2Sb powder	Cu_1-Cu_2	4	2.58 (2.59)	0.010	2.2	0.002
	Cu_1-Sb	4	2.65 (2.71)			
	Cu_1-Cu_1	4	2.90 (2.83)			
	Cu_2-Cu_1	4	2.59 (2.59)			
	Cu_2-Sb	1	2.57 (2.62)			
	Cu_2-Sb	4	2.85 (2.83)			
Cu_2Sb film charged at 1 V	Cu_1-Cu_2	3.2	2.58	0.017	1.7	0.05
	Cu_1-Sb	3.2	2.65			
	Cu_1-Cu_1	3.2	2.89			
	Cu_2-Cu_1	3.2	2.59			
	Cu_2-Sb	0.8	2.64			
	Cu_2-Sb	3.2	2.77			
	Cu-Cu	1.3	2.54	0.007	-0.4	
Cu_2Sb film discharged at 0 V	Cu-Cu	6.7 (0.5)	2.54	0.009	1.6	0.008
Cu foil	Cu-Cu	12	2.54	0.009	3.9	0.002

Table S3. Results obtained from fitting the Sb K-edge EXAFS of Cu_2Sb electrode films and several reference materials. 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	Interaction	N	R (0.01)	σ^2	ΔE_0	R factor
Pristine Cu_2Sb film	Sb-Cu_1	4	2.59	0.007	8.1	0.002
	Sb-Cu_2	1	2.53			
	Sb-Cu_2	4	2.85			
	Sb-Sb	4	3.65			
Cu_2Sb powder	Sb-Cu_1	4	2.70	0.012	6.9	0.003
	Sb-Cu_2	1	2.53			
	Sb-Cu_2	4	2.82			
	Sb-Sb	4	3.70			
Cu_2Sb film charged at 1 V	Sb-Cu_1	4	2.48	0.017	8.0	0.007
	Sb-Cu_2	1	2.69			
	Sb-Cu_2	4	3.45			
	Sb-Sb	4	3.64			
Cu_2Sb film charged at 2 V	Sb-Cu_1	4	2.75	0.002	8.7	0.001
	Sb-Cu_2	1	2.54			
	Sb-Cu_2	4	2.85			
	Sb-Sb	4	3.82			
Cu_2Sb film discharged at 0 V	Sb-Na_1	3	3.02	0.002	5.4	0.002
	Sb-Na_2	2	3.24			
	Sb-Na_2	6	3.43			
	Sb-Sb	6	5.36			
Sb powder	Sb-Sb	3	2.89	0.005	9.6	0.005
Na_3Sb powder	Sb-Na_1	3	3.06	0.003	3.4	0.003
	Sb-Na_2	2	3.27			
	Sb-Na_2	6	3.49			
	Sb-Sb	6	5.34			

Figure S1. Schematic representation of P4/nmm Cu_2Sb full unit cell. Gray, green and blue spheres represent Sb, Cu1 and Cu2 atoms.

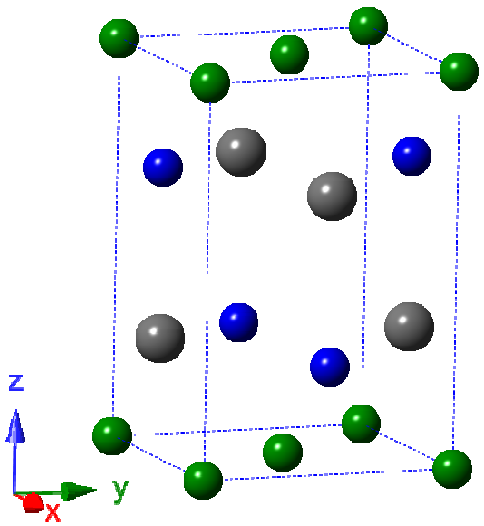

Figure S2. Discharge potential profiles of a 0.85 μm thick Cu_2Sb thin film cycled at 80 μA cm^{-2} from 0 to 1 V in a PC/FEC electrolyte as a function of cycling (see Figure 2a). Cycle numbers are indicated on the figure.

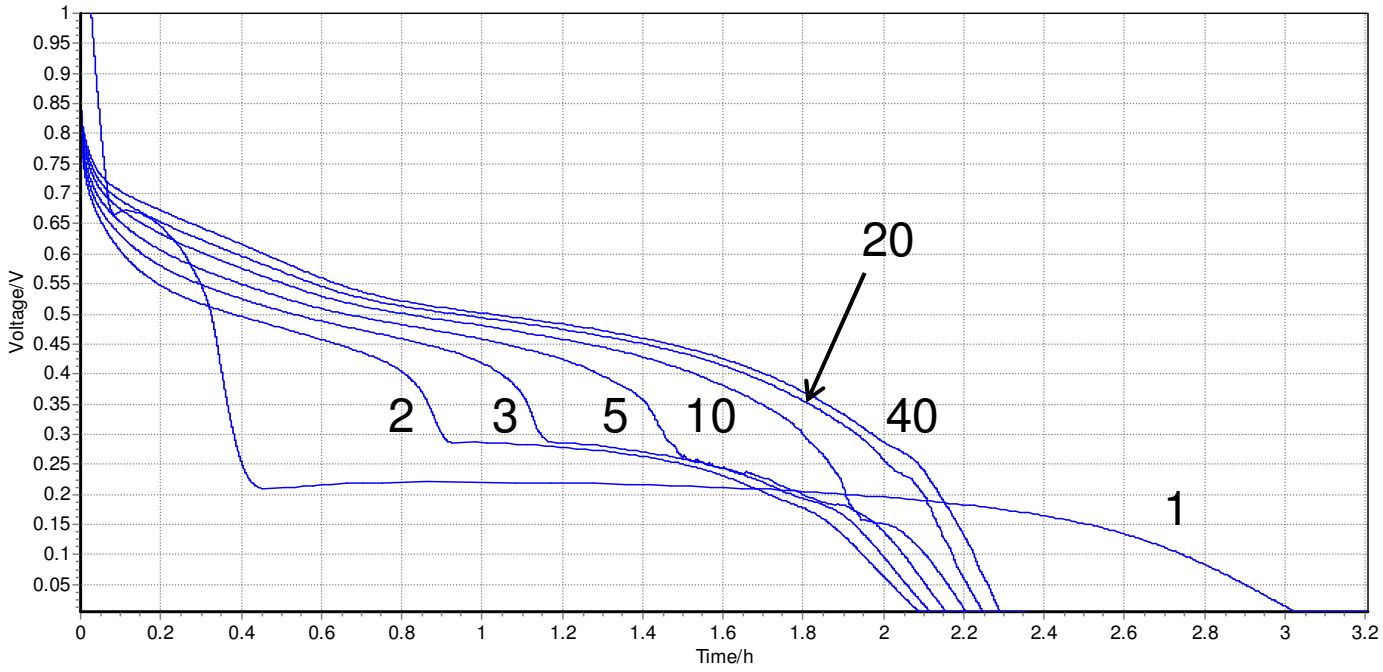

Figure S3. XRD patterns of Cu_2Sb electrodes marked A to F in Figure 2b. Red, blue and black bars indicate Na_3Sb, Cu_2Sb and Cu expected diffraction lines. The overlap of Cu_2Sb (112) strongest line (~19.7°) with the Cu (002) weak line around 19.5° is visible. Note that the Cu foil is strongly (022) preferentially oriented.

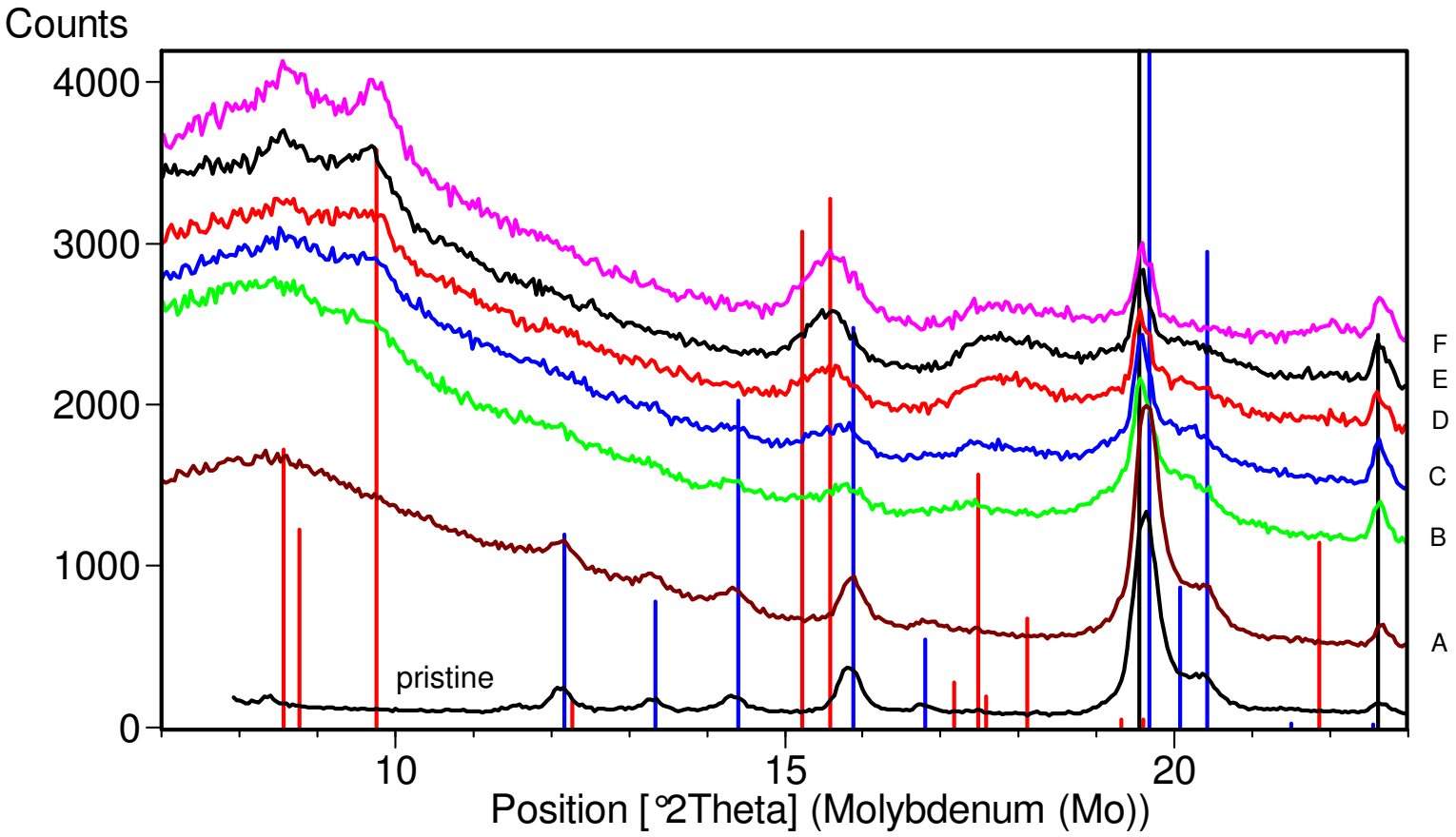

Figure S4. Schematic representations of the atomic surrounding of Sb in (top) R-3m Sb and (bottom) $P6_3/mmc$ Na_3Sb structures. Atoms are represented by gray (Sb), red (Na1) and orange (Na2) spheres.

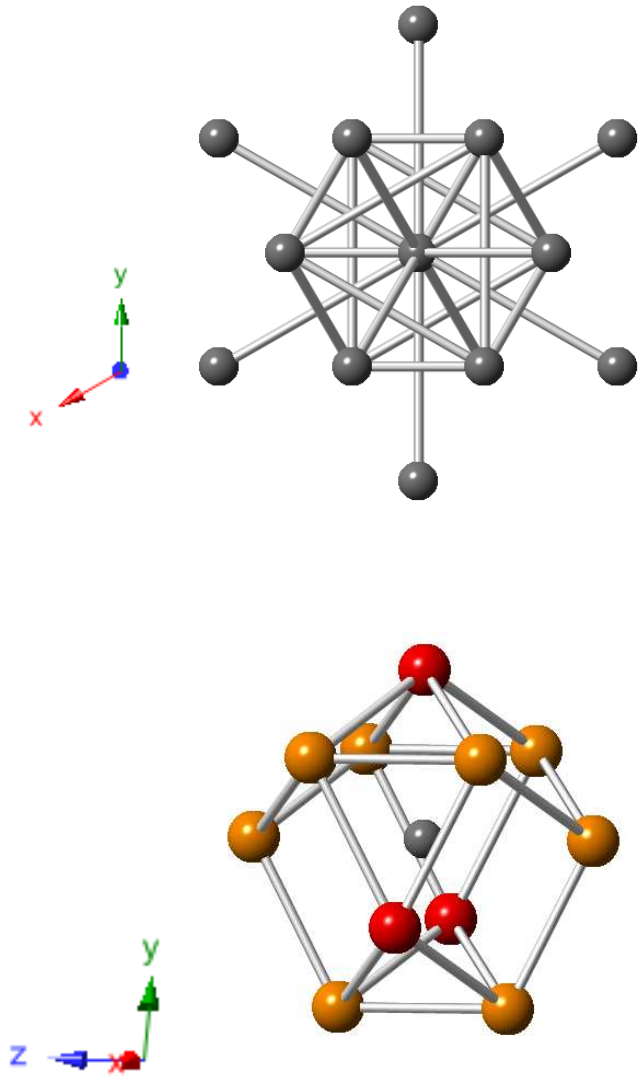

Figure S5. Sb K-edge XANES data for the pristine Cu_2Sb thin film and powder, electrode thin films discharged at 0 V and charged at 2 V, and for Sb and Na_3Sb powders.

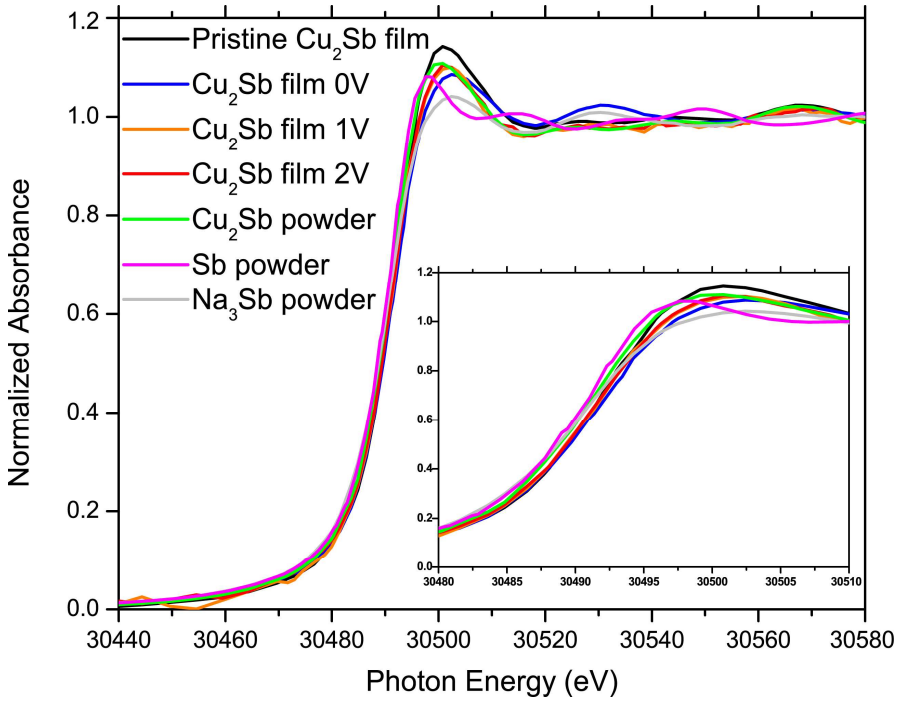
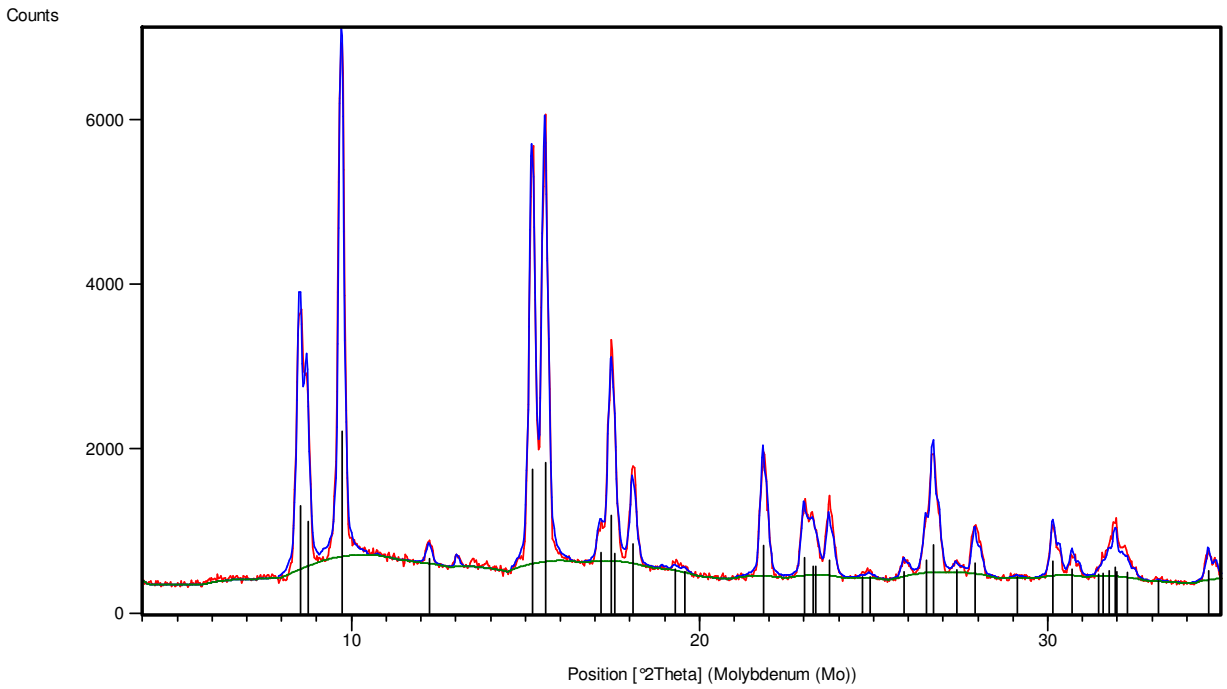
Figure S6. XRD pattern and Rietveld refinement for the Na_3Sb ($P6_3/mmc$) reference powder measured in a 0.5 mm sealed glass capillary with Mo K_α radiation. Refined lattice parameters are a = b = 5.3457 Å (±0.0006) and c = 9.4796 Å (±0.0014).