# Electronic Supplementary Information for "Synergic effect of Bi, Sb and Te for the increased stability of bulk alloying anodes for sodium-ion batteries"

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# Materials characterisation

**Table S1.** Refined structural parameters of  $Bi_{0.25}Sb_{1.75}Te_3$  (bulk-BST) obtained from Rietveld refinements of X-<br/>ray powder diffraction data collected at room temperature.

Space group	R - 3 m
a (Å)	4.2842(1)
c (Å)	30.433(2)
Volume (Å <sup>3</sup> )	483.74(3)
Te (I)	
Wyckoff position	За
$B_{\rm iso}({\rm \AA}^2)$	1.1(1)
Occupancy	1
Te(II)	
Wyckoff position	6c ( z = 0.21037(8) )
B <sub>iso</sub> (Å <sup>2</sup> )	1.1(1)
Occupancy	1
Sb(I)	
Wyckoff position	6c (z = 0.3990(1))
$B_{\rm iso}$ (Å <sup>2</sup> )	0.6(1)
Occupancy	0.89(2)
Bi(I)	
Wyckoff position	<i>6c</i> ( <i>z</i> = 0.3990(1))
$B_{\rm iso}$ (Å <sup>2</sup> )	0.6(1)
Occupancy	0.11(2)



Figure S1. Rietveld refinement of  $Bi_{0.25}Sb_{1.75}Te_3$  (bulk-BST). Final observed (red circles) and calculated (blue solid line) X-ray ( $\lambda = 1.5406$  Å) powder diffraction profiles. The lower solid line show the difference profile and the tick marks indicate the reflection positions ( $R_{wp} = 5.84\%$ ,  $\chi^2 = 1.12$ ). The refined structural parameters are listed in Table S1. Inset: schematic representation of the crystal structure of the ternary alloy: brown spheres represent Te(1), green spheres Te(2) and blue sphere the Sb and Bi statistically occupied position.



*Figure S2*. **Electrochemical performance of bulk Sb<sub>2</sub>Te<sub>3</sub> and nano Sb<sub>2</sub>Te<sub>3</sub>/C.** Galvanostatic cycling with current density 200 mA g<sup>-1</sup> in a potential window 0.01 - 2.0 V vs Na/Na<sup>+</sup>. The electrodes comprising both the micron sized powder and the C-nanocomposite of Sb<sub>2</sub>Te<sub>3</sub> were prepared in an identical manner as bulk-BST and nano-BST/C electrodes, respectively.

## Ex situ XRD measurements



*Figure S3.* **Structural changes in bulk-BST electrode.** *Ex situ* X-ray diffraction profiles of bulk Bi<sub>0.25</sub>Sb<sub>1.75</sub>Te<sub>3</sub> anode - pristine (black); sodiated at 0.01V (green) and desodiated at 2 V (blue)



Figure S4. Rietveld Refinement of  $Bi_{0.25}Sb_{1.75}Te_3$  (bulk-BST) electrode obtained *ex situ* after first full sodiation at 0.01 V. Final observed (red circles) and calculated (blue solid line) X-ray ( $\lambda = 1.5406$  Å) powder diffraction profiles are shown (the background from amorphous carbon is subtracted). The lower solid line shows the difference profile and the tick marks the reflection positions. The model used in the refinement comprises exclusively of a Na<sub>2</sub>Te crystalline phase (space group *F m*-3*m*, a = 7.350(2) Å,  $R_{wp} = 4.18\%$ ,  $\chi^2 = 1.38$ ).



Figure S5. **Rietveld Refinement of Bi**<sub>0.25</sub>**Sb**<sub>1.75</sub>**Te**<sub>3</sub> (bulk-BST) electrode obtained *ex situ* after 50 cycles at 3 V. Final observed (red circles) and calculated (blue solid line) X-ray ( $\lambda = 1.5406$  Å) powder diffraction profile are shown (the background from amorphous carbon was subtracted). The lower solid green line shows the difference profile and the tick marks the reflection positions. The model used in the refinement comprises y of three phases (i) Na<sub>2</sub>Te (space group *F m-3m, a* = 7.279(2) Å, phase weight fraction = 16.5(1) %), (ii) NaTe<sub>3</sub> (space group *P -3c*, a = 8.995(9) Å, c = 21.39(5) Å, phase weight fraction = 53.9(7) %) and (iii) Bi<sub>1-x</sub>Sb<sub>x</sub> (space group *R -3m, a* = 4.374(6) Å, *c* = 11.59(2) Å, phase weight fraction = 29.6(7) % ( $R_{wp} = 4.08\%$ ,  $\chi^2 = 1.44$ ). The obtained value of the cell volume for phase (iii) is smaller than that of pure Bi but larger than that of Sb substantiating the formation of a Bi<sub>1-x</sub>Sb<sub>x</sub> solid solution. Application of Vegard's law would result in a value of x~0.7.

#### Sodiation mechanism

The proposed whole charge/discharge mechanism of bulk-BST can be summarised as follows:

1<sup>st</sup> discharge:

$$Bi_{0.25}Sb_{1.75}Te_3 \rightarrow Na_2Te + Bi_{1-x}Sb_x \text{ (irreversible)}$$
$$Bi_{1-x}Sb_x \rightarrow Na_yBi_{1-x}Sb_x \text{ (y \le 3)}$$

1<sup>st</sup> charge:

$$Na_{y}Bi_{1-x}Sb_{x} \rightarrow Bi_{1-x}Sb_{x} + Sb$$
  
 $Na_{2}Te \rightarrow Na_{2}Te + NaTe_{3} + Te$ 

Following cycles:

$$NaTe_{3} + Te \leftrightarrow Na_{2}Te$$
$$Bi_{1-x}Sb_{x} + Sb \leftrightarrow Na_{y}Bi_{1-x}Sb_{x} + Na_{3-x}Sb_{x}$$

The proposed whole charge/discharge mechanism of nano-BST/C can be summarised as follows:

1<sup>st</sup> discharge:

$$Bi_{0.25}Sb_{1.75}Te_3 \rightarrow Na_2Te + Bi_{1-x}Sb_x + Sb \text{ (irreversible)}$$
$$Bi_{1-x}Sb_x + Sb \rightarrow Na_{2-x}Sb + Na_yBi_{1-x}Sb_x \text{ (y < 3)}$$

1<sup>st</sup> charge:

$$Na_yBi_{1-x}Sb_x + Na_{3-x}Sb \rightarrow Bi + Sb$$
  
 $Na_2Te \rightarrow NaTe_2 + Te$ 

Following cycles:

$$NaTe_3 + Te \leftrightarrow Na_2Te$$
  
 $Bi + Sb \leftrightarrow Na_3Bi + Na_{3-r}Sb$ 

#### Surface analysis

At fully sodiated state the SEI layer was too thick to allow XPS analysis of the active material, particularly in the case of the nano-BST/C anode. Nevertheless, upon charging the SEI layer partly dissolves allowing the characterisation of the electrode<sup>1–3</sup>. Due to the overlapping of Sb  $3d_{5/2}$  and O 1s core peaks, the Sb 3d spectrum is modelled to the Sb  $3d_{3/2}$  peak, with the Sb  $3d_{5/2}$  position and area defined by the expected spin orbit doublet splitting of 9.4 eV. The binding energies and atomic concentrations of Bi, Sb and Te are summarised in Table S2. In the fresh electrodes peaks consistent with Bi-Sb-Te alloys and surface metal oxides can be observed<sup>4–6</sup>. Due to difference in ionisation energy ( $I_{(Bi)} < I_{(Te)}$ ) the oxidation of Te atoms is much weaker than that of Sb and Bi<sup>4,7</sup>. Nevertheless, the relative concentration of oxides to alloy is much higher in the nano-BST/C, due to the much larger surface area. The surface oxide shell can cause the formation of Na<sub>2</sub>O, which can react with electrolyte to form carbonates, thus produce thicker and less ion conductive SEI layer<sup>8–10</sup>.

As observed in the *ex situ* HRTEM image the SEI layer is 10-15 nm thick at the fully charged state and the penetration depth of XPS surface analysis is only 10 nm. Therefore, to acquire full information on the anode material depth profiling was performed using a 5 keV Ar<sup>+</sup> ion beam. Indeed, before etching, in the nano-BST/C electrode the peaks of Sb are observed only at very low levels and the peak relative to Bi was absent. Furthermore, the carbon black wasn't detected on the surface of fully charged nano-BST/C electrode, whereas its presence was clear in the bulk-BST electrode. After ion bombardment concentration of CB increased in both electrodes. A small Te 3d peak at 571.5 eV was detected. The reported binding energy of Na<sub>2</sub>Te is 571.2 eV<sup>11</sup>, but this phase was not detected in the XRD measurements of fully charged electrode. Instead, the formation of NaTe<sub>3</sub> was confirmed in both the HRTEM and the XRD results. There is no literature on the binding energy of Te in NaTe<sub>3</sub>. However, it is known, that bonding with elements of lower electronegativity results in decreased binding energy<sup>12</sup>. As Te in NaTe<sub>3</sub> and Na<sub>2</sub>Te is in the same oxidation state (-2) it is expected that the binding energy would be close to that of Na<sub>2</sub>Te, but slightly higher due to smaller amount of the less electronegative Na. Therefore, the Te 3d peak could be assigned to Na-Te bonds in the NaTe<sub>3</sub>.

On the other hand, for the bulk-BST electrode, both Bi and Sb peaks are present before etching. This again suggests that after full charge the SEI layer is thicker on the nanocomposite. At this stage, in both materials a peak in the Sb 3d and O 1s envelope at around 527.6 eV appears. It is slightly shifted to lower values from the binding energy of Sb metal and is related to reduced Sb<sup> $\delta$ -</sup> species indicating Na–Sb bonds<sup>13,14</sup>. In the nano-BST/C electrode Sb peaks are shifted to more positive values, indicating higher intrinsic stresses.

In both electrodes etching revealed peaks not ascribed to  $NaTe_3$  or  $Na_xSb$  phase, i.e. at 157 eV (Bi 4f), at 529 eV (Sb 3d) and at 573 eV (Te 3d). The first two correspond to metallic bonds of Bi and Sb, respectively, in Bi-Sb mixture, while the latter can be ascribed to Te(0) metal<sup>5–7,12,15</sup>. Interestingly, small component of TeO<sub>2</sub> became apparent after 20 min of etching of the nano-BST/C, which is a clear sign that not all surface oxides were reduced in the first discharge.

The surface analysis also revealed variations in the SEI layer composition dependent on the size of the active material (Table S3). From O 1s, Na 1s, F 1s and C 1s peaks, the nature of the solid electrolyte interphase can be studied. In both electrodes, hydrocarbons constitute the largest fraction of top layer. Components 1071.4 eV, 531.3 eV and 684.3 eV of Na 1s, O 1s and F 1s respectively indicate that the other two major compounds present are Na<sub>2</sub>CO<sub>3</sub> and NaF<sup>2,16–18</sup>. After 20 min of ion bombardment fraction of C-C and C-H bonds decreases, however the drop is substantially more apparent in the nano-BST/C electrode. The Na 1s peak attributed mainly to NaF and Na<sub>2</sub>CO<sub>3</sub> increases with etching time in both materials. Another Na 1s feature at 1069.8 eV emerges after etching and it corresponds to Na<sub>2</sub>O<sup>2</sup>. Its concentration is higher on the surface of micron-sized material.

Therefore it is clear, that SEI layer on the nano-BST has high portion of inorganic carbonates underneath layer of hydrocarbons, while on the bulk-BST electrode it has homogenous structure of flexible organic matrix with inorganic precipitates. In both cases, on the surface of active material, small amount of sodium oxide was formed. It is worth noting that Na<sub>2</sub>O has higher ionic conductivity compared to Na<sub>2</sub>CO<sub>3</sub> in the whole working potential range<sup>10</sup>. High concentrations of poor ionic conductors such as carbonates and NaF lead to the inferior rate capability of nano-BST/C electrode<sup>10,19</sup>.



*Figure S6.* Surface analysis of fully charged nano-BST/C electrode. XPS plots of (a) Te 3d, (b) O 1s & Sb 3d, and (c) Bi 4f envelopes.

			bulk-BST fresh	bulk-BST 2 V	bulk-BST 2 V etched	nano-BST/C fresh	nano-BST/C 2 V	nano-BST/C 2 V etched
	Assignment	B.E. [eV]			A	t. %		
Te 3d	Bi <sub>0.25</sub> Sb <sub>1.75</sub> Te <sub>3</sub> (Te-Sb)	571.7 (bulk) 572.7 (nano)	0.29	-	-	0.45	-	-
	Bi <sub>0.25</sub> Sb <sub>1.75</sub> Te <sub>3</sub> (Te-Bi)	572.5 (bulk) 573.6 (nano)	0.09	-	-	0.12	-	-
	TeO2	575.8	0.34	-	-	1.41	-	0.05
	NaTe₃	571.5	-	0.32	0.54	-	0.52	1.53
	Те (0)	572.4	-	0.05	0.05	-	-	0.28
Sb 3d	Bi <sub>0.25</sub> Sb <sub>1.75</sub> Te <sub>3</sub>	528.1	0.07	-	-	-	-	-
	Sb <sub>2</sub> O <sub>3</sub>	530	0.40	-	-	1.77	-	-
	Na-Sb (Na <sub>x</sub> Sb)	527.3 (bulk) 528.2 (nano)	-	0.03	0.13	-	0.03	0.29
	Sb (Met.)	529	-	-	0.08	-	-	0.15
Bi 4f	Bi <sub>0.25</sub> Sb <sub>1.75</sub> Te <sub>3</sub>	157.1	0.07	-	-	0.02	-	-
	Bi <sub>2</sub> O <sub>3</sub>	158.8	0.09	-	-	0.51	-	-
	Bi (Met.)	156.9	-	0.03	0.07	-	-	0.09

**Table S2.** XPS atomic percentages and binding energy (B.E.) of Te, Sb and Bi elements in as coated bulk-BST and nano-BST/C electrodes, fresh and at fully charged state (2 V).

*Table S3.* XPS atomic percentages and binding energy (B.E.) of Na, F, O and C elements in as coated bulk-BST and nano-BST/C electrodes, fresh and at fully charged state (2 V).

			bulk-BST fresh	bulk-BST 2 V	bulk-BST 2 V etched	nano-BST/C fresh	nano-BST/C 2 V	nano-BST/C 2 V etched
		B.E. [eV]						
0 1s	C-O-C (Na <sub>2</sub> CO <sub>3</sub> /CMC)	531.3	6.16	7.34	4.16	8.53	14.51	10.73
	O-C=O (CMC)	533.0	12.56	2.65	1.4	14.65	1.49	0.58
	Metal oxides	529.8	1.36	-	-	3.96	-	-
	alkylcarbonates	530.4	-	1.42	6	-		4.91
C 1s	С-С, С-Н	284.8	14.48	45.56	33.11	16.78	54.51	27.8
	СВ	283.9	29.91	10.03	11.26	17.37	-	4.35
	CO- (NaOR and (-CH <sub>2</sub> -CH <sub>2</sub> -O-))	286.6	20.81	3.85	4.43	21.01	3.2	1.37
	CO₂- (NaCO₃R)	288.2	5.98	3.54	0.81	5.19	3.99	1.96
	CO₃- (Na₂CO₃ and NaCO₃R)	289.6	3.46	0.3	1.75	3.22	2.09	2.69
Na 1s	Na-CMC /Na <sub>2</sub> CO <sub>3</sub> +NaF	1071.4	3.94	13.82	22.69	5.02	11.35	31.05
	Na₂O	1069.8	-	-	3.26	-	-	0.5
F 1s	NaF and NaPO <sub>y</sub> F <sub>z</sub> ?	684.3	-	11.06	10.28	-	8.15	11.67

## Performance of Bi-Sb-Te anode



*Figure S7.* Comparison of capacity retention of various Bi/Sb/Te- based systems with  $Bi_{0.25}Sb_{1.75}Te_3$  anodes for SIBs. Discharge capacity retention of tested electrodes and some of recently researched Bi, Sb or Te based anodes. Capacity retention is calculated between  $2^{nd}$  and  $100^{th}$  cycle or in case of Bi-Sb and  $Sb_2Te_3$  alloys at  $50^{th}$  cycle. <sup>20-23</sup> Capacity retentions of  $Sb_2Te_3/C$  electrode studied in this work were very close to the one from ref<sup>23</sup>, however specific capacity was significantly higher and fast degradation is seen after 60 cycles (Fig. S2). Further studies are necessary to reconcile these small discrepancies.



*Figure S8.* **Raman spectra of prepared powders and carbon black.** Raman measurement were performed on Renishaw inVia spectrometer with excitation wavelenght 633 nm. The clearly visible in the nano-BST/C spectrum G and D bands indicate carbon coating of the alloy particles.

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