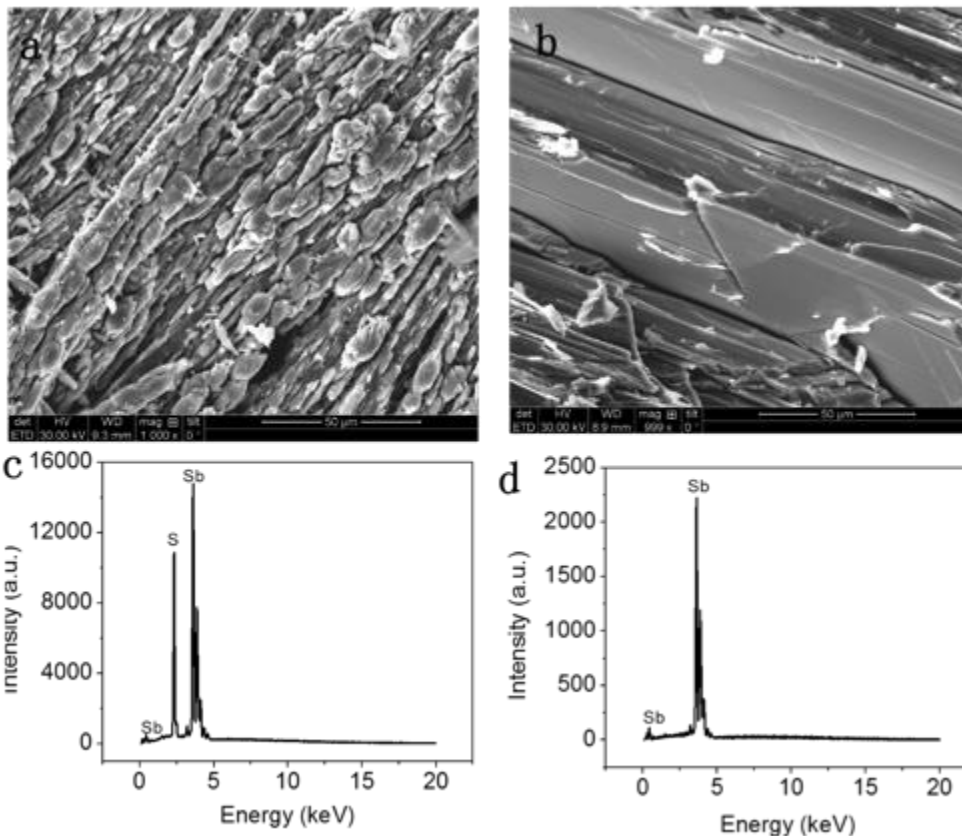


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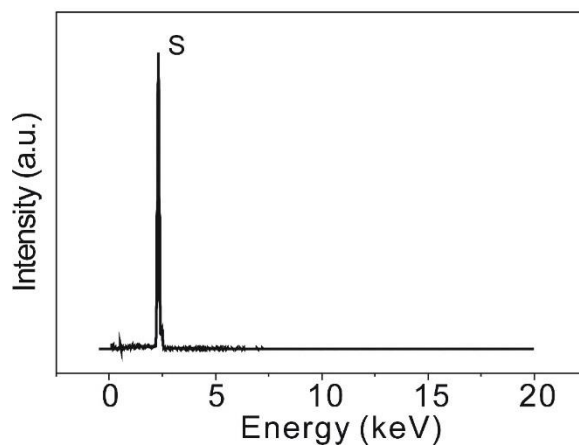
2 **Supplementary Figure 1| Direct observation of the NaCl-KCl-Na₂S melt in a transparent quartz cell.** Images

3 of NaCl-KCl-Na₂S: in molten state (a) and solid state (b).



4

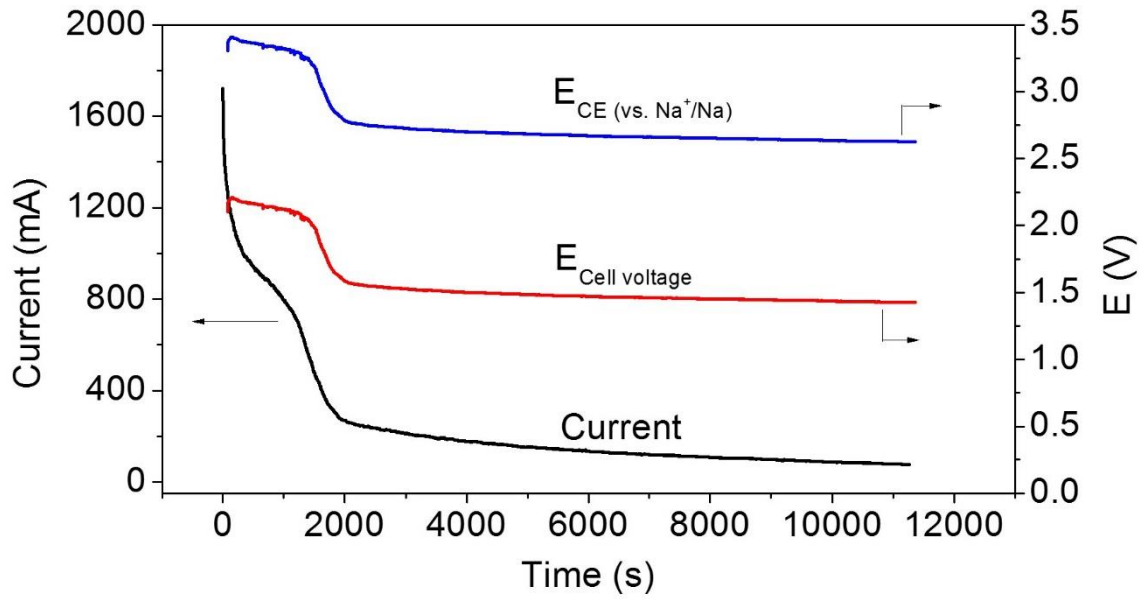
5 **Supplementary Figure 2| SEM and EDS analysis of the cathode metal product.** SEM images of Sb_2S_3 (a) and
 6 electrolytic Sb (b) obtained potentiostatically at 1.0V vs. Na^+/Na , and their corresponding spectra of EDS (c, d).



7

8 **Supplementary Figure 3| EDS analysis of anode product.** EDS spectrum of the yellow anode product on the side
 9 wall of the quartz cell

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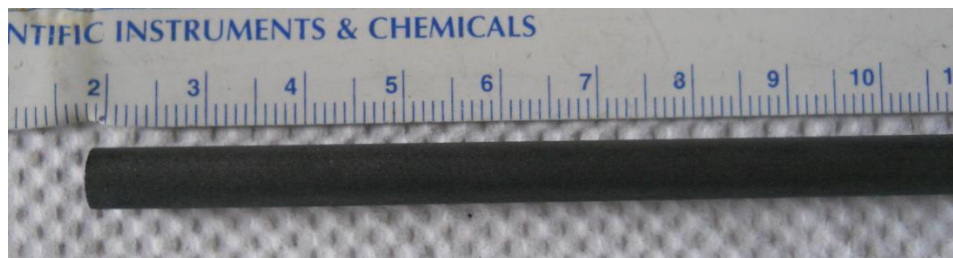


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12 **Supplementary Figure 4| Current and voltage profiles.** Voltage and current profiles vs time of the graphite
13 counter electrode and cell during potentiostatic electrolysis of Sb_2S_3 at 1.0 V vs. Na^+/Na .

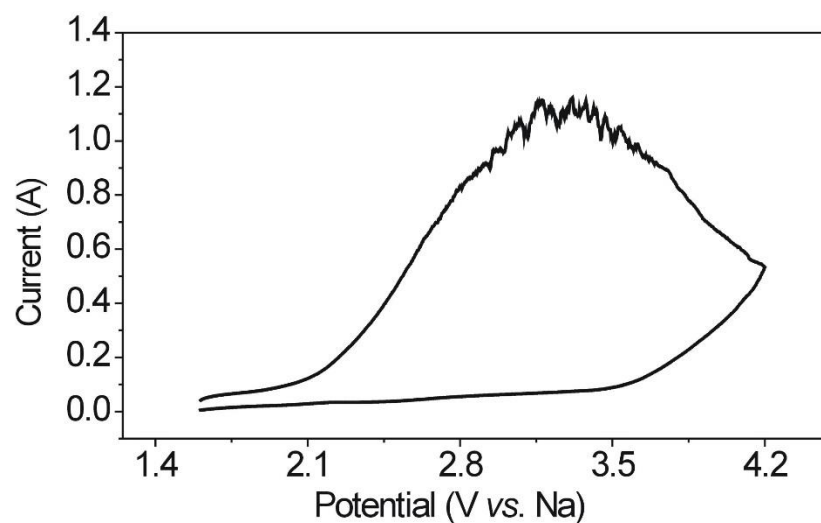
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17 **Supplementary Figure 5| Digital picture of anode.** Graphite anode after one week of service in $\text{NaCl-KCl-Na}_2\text{S}$.



18

19 **Supplementary Figure 6| Cyclic voltammogram of graphite electrode.** CV of graphite working electrode in
 20 NaCl-KCl-Na₂S at 700°C. Scan rate: 100 mV s⁻¹.

21

22

23 **Supplementary Table 1| Thermodynamic analysis.** Selected standard reduction potentials for the cathodes in
 24 molten chloride at 700°C, assuming all species to be in their standard state at unit activity (FactSage).

Reaction	E° (V)
$\text{Cl}_2(\text{g}) + 2 \text{e}^- = 2\text{Cl}^-$	3.3
$\text{S}_2(\text{g}) + 4\text{e}^- = 2\text{S}^{2-}$	1.55
$\text{Sb}_2\text{S}_3 + 6\text{e}^- = \text{Sb} + 3 \text{S}^{2-}$	1.3
$\text{Na}^+ + \text{e}^- = \text{Na}$	0

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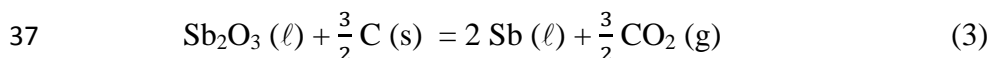
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29 **Supplementary Note 1**

30 **Pyrometallurgy and hydrometallurgy of antimony**

31 Antimony is a metalloid with main applications in flame-retardants, batteries and as
32 materials additive¹. It is found predominantly on earth as mineral stibnite (Sb₂S₃) from which
33 elemental Sb is extracted via traditional extractive methods such as pyro-metallurgy and
34 hydrometallurgy². A first pyro-metallurgical route converts Sb₂S₃ to volatile Sb₂O₃ by roasting,
35 which is then carbothermically reduced to Sb at temperatures exceeding 1200°C as shown in
36 reaction (3).



38 A second pyro-metallurgical route consists of chemical reduction of molten Sb₂S₃ with scrap
39 iron at temperatures ranging from 550 to 600°C (eq. 4). The metal obtained is subsequently
40 subjected to a purification step to dispose of iron and sulfur impurities².



42 Finally, hydrometallurgical routes usually consist of two steps, namely, leaching of the mineral
43 and subsequent electro-winning in aqueous solution² and poses additional efforts for product
44 recovery. In this manuscript, we demonstrate the method of an electron blocking secondary
45 sulfide ion conductive electrolyte and enable Sb to be processed in a simple, clean and energy
46 efficient manner via modern electrometallurgy.

47 **Results of Potentiostatic Electrolysis**

48 Potentiostatic electrolysis was employed to determine an appropriate current density to
49 conduct galvanostatic electrolysis while avoiding secondary electrolyte decomposition (chlorine

50 evolution). During potentiostatic electrolysis, the potential of the working electrode was held
51 constantly at 1V (vs Na/Na⁺), the potential of the counter electrode and the cell voltage were
52 monitored (Supplementary Fig. 4). In this experiment, features measured in the cell voltage are
53 attributed to the half reaction at the counter electrode. At the beginning of the electrolysis, we
54 observe that the counter electrode potential takes the value of 3.4 V (vs Na/Na⁺) and the current
55 density settles to ~1800 mA cm⁻² (Supplementary Fig. 4). Gradually, the potential of the counter
56 electrode decreased and was attended by a decrease of current density. After 2000 s the potential
57 of the counter electrode dropped to 2.8 V, and simultaneously the current density dramatically
58 decreased below 260 mA cm⁻², suggesting that most of the Sb₂S₃ had been converted to Sb. It is
59 desirable to avoid high polarization at both electrodes to suppress potential side reactions such as
60 chlorine evolution at the anode and co-deposition of sodium and / or potassium at the cathode.
61 As shown in Supplementary Fig. 4, at a current density of ~500 mA cm⁻², the potential at the
62 counter electrode floats to ~3.0 V, lower than the estimated potential for Cl₂ evolution at 3.3 V
63 (see Supplementary Table 1), and higher than the estimated potential for sulfur evolution at
64 1.55V.

65

66 **Supplementary References**

- 67 1. Buttermann, C. M. & Carlin, J. F. Mineral Commodity Profiles: Antimony. *United States Geological Survey*
68 (2003).
- 69 2. Anderson, C.G. The metallurgy of antimony. *Chemie der Erde*. **72**, 3-8 (2012).