Electronic Supplementary Information

Na-Ion Storage Performance of Amorphous Sb₂S₃ Nanoparticles: Anode for Na-Ion Batteries and Seawater Flow Batteries

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Experimental details

Sample preparation: SbCl₃ (10 mM, Alfa Aesar) powder and thioacetamide (TAA, 50 mM, Alfa Aesar) powder were separately dissolved in ethylene glycol (Alfa Aesar) to form two clear solutions, each with a volume of 200 ml. The two solutions were reacted by slowly pouring the TAA solution into the SbCl₃ solution and then gently stirring for 12 h at room temperature. As the stirring proceeded, the solution mixture turned orange and finally red. The red precipitates were acquired by repeated centrifugation at 8000 rpm and sonication in absolute ethanol and then dried in a vacuum oven at 80 °C. For the phase analysis, the assynthesized powder was heat-treated at 250 °C for 1 h for crystallization under Ar atmosphere.

Sample characterization: The thermal behavior of the as-synthesized powder was probed

by TG-DTA (TA, Q500) in the temperature range of 30 to 700 °C at a ramping rate of 5 °C · min⁻¹ under N₂ flow. The morphology and microstructure of the as-synthesized and heat-treated powders were observed by electron microscopy, i.e., SEM (Verios 460, FEI Company, 10 kV) and/or TEM (JEM-2100F, JEOL, 200 kV). The phases were identified by using an X-ray diffractometer (D/Max, Rigaku apparatus) equipped with a Cu-K α X-ray source and by Raman spectroscopy (Alpha300S, 785 nm laser, WITec). The chemical bonding states were analyzed by XPS (K-alpha, Thermo Fisher, UK) with a Mg-K α X-ray source. The chemical composition was examined by using inductively coupled plasma-optical emission spectrometry (ICP-OES, Varian, 700-ES) and an elemental analyzer (Flash2000, Thermo).

Electrochemical measurements: The electrochemical properties of the anodes were investigated by using 2032 coin-type half-cells. The electrodes were prepared by coating a slurry containing the active material (60 wt%), conducting agent (Super-P, 20 wt%), and carboxymethyl cellulose binder (CMC, 20 wt%) dissolved in deionized water onto Al foil. Subsequently, the electrodes were dried in a convection oven, roll-pressed under a pressure of 180 kg·cm⁻², and finally dried at 80 °C for 10 h in a vacuum oven. The loading levels of the active material were 1.0-1.5 mg cm⁻². Assembly of the coin cells was carried out in a glove box under high-purity Ar (O₂ and H₂O less than 1 ppm). Na metal (Aldrich) and Whatman GF/D microfiber filter paper were used as the reference/counter electrodes and separator, respectively. The electrolyte comprised 1 M NaClO₄ dissolved in a mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) at a volume ratio of 1:1 with a fluoroethylene carbonate (FEC, 5 wt%) additive. The coin cells were galvanostatically discharged and charged with a constant current of 50 mA \cdot g⁻¹ in the voltage window of 0.01–2.5 V (vs. Na⁺/Na) for 100 cycles. The rate capability was examined at various current densities of 50 mA·g⁻¹ to 3000 mA·g⁻¹. Cyclic voltammetric (CV) analysis of the coin cells was performed with a VSP-300 potentiostat (BioLogic) at a potential scan rate of 0.1 mV·s⁻¹. For comparison, the

electrochemical properties of a commercially available, crystalline Sb_2S_3 particle (Alfa Aesar) anode were evaluated under the same conditions.

Prior to application of the *a*-Sb₂S₃ electrode as the anode for seawater flow battery fullcells, the cathode half-cells (Na|seawater) were tested by galvanostatic charge-discharge processes at a current density of 0.05 mA·cm⁻². To improve the reaction kinetics at the cathode during discharging, such as the oxygen reduction reaction (ORR), and hence, the discharge voltage, commercially available Pt/C (50 wt%, Alfa Aesar) powder was used as the electrocatalyst for the cathode of the seawater flow cells. The Pt/C-loaded air-electrode was fabricated by mixing Pt/C powder (90 wt%) and poly(vinylidene fluoride) (PVDF, 10 wt%, Sigma Aldrich) binder in *N*-methyl-2-pyrrolidone (NMP, Sigma Aldrich) and coating the mixture onto carbon felt with a diameter of 16 mm and a thickness of 3 mm, followed by drying in an oven at 80 °C. The loading amount of the Pt/C catalyst was 20 mg. NASICON-type ceramic electrolytes (Na_{1+x}Zr₂Si_xP_{3-x}O₁₂, x = 2, NZSP) with a diameter of 16 mm and a thickness of 0.8 mm were used as the Na⁺ ion-conducting membrane and the separator between the anode (Na metal or *a*-Sb₂S₃) and cathode (seawater) compartments, as schematically illustrated in Fig. 3. The ionic conductivity of the NZSP discs was measured to be approximately 8 × 10⁻⁴ S·cm⁻¹ at room temperature.

Seawater flow cells (*421Energy Co., Ltd*) were assembled in the following manner. First, the anode compartment was assembled by mounting the NZSP ceramic disc onto the openstructured top part of the anode and then sealed with the bottom part of the anode; the non-aq. electrolyte comprising 1 M NaClO₄ dissolved in a mixture of EC/DEC (1:1) with 5 wt% FEC additive and an anode of either Na metal (99.9%, Sigma Aldrich) or *a*-Sb₂S₃ electrode were used. The assembly process was performed in a glove box under high-purity Ar atmosphere (O₂ and H₂O <1 ppm). The assembled anode compartment and the air-electrode were immersed in natural seawater and electrically connected to a measurement system (WBCS 3000 battery cycler, WonATech). Natural seawater from IIsan beach, Ulsan, Republic of Korea (GPS 35.497005, 129.430996) was used after filtration. The pH of the seawater was determined to be around 8. The anions and cations in the natural seawater were quantitatively analyzed by ion chromatography (ICS-3000 for anions, ICS-1600 for cations, Dionex) and the results are summarized in Table S3. The electrochemical properties of the cathode half-cells (Na | seawater) and full-cells (*a*-Sb₂S₃ | seawater) were evaluated at a current density of 0.05 mA·cm⁻²_{NASICON, exposed area} (16 mm in diameter) with a capacity cut-off of 550 mAh·g⁻¹_{anode} upon charging and at a voltage cut-off of 0.4 V upon discharging. To evaluate sodiation of the *a*-Sb₂S₃ anode by natural seawater, the cell was disassembled after the 15th charge process and the *a*-Sb₂S₃ anode was exposed to ambient air for 50 h. The anode surface was then examined by XRD. In addition, both sides of the NASICON ceramic (the organic electrolyte side and the seawater side) were investigated to evaluate the phase stability before and after cycling.



Fig. S1. TG/DTA curves of the as-synthesized Sb₂S₃ nanoparticles obtained under N₂ atmosphere. Two prominent endothermic peaks were found in the DTA curve. The former, which accompanied an abrupt weight loss at ~198 °C, followed by a gradual weight loss up to ~300 °C (total weight loss ~7.9%), was probably due to vaporization of small amounts of ethylene glycol solvent (T_m ~197 °C) and pyrolysis of the other organic residues remaining within the as-synthesized Sb₂S₃ nanoparticles. The latter corresponded to melting of the Sb₂S₃. No signal relating to sulfur vaporization at 145–150 °C was detected.

Table S1. Chemical composition of the as-synthesized Sb_2S_3 nanoparticles determined byelemental analysis

	С	Н	Ν	S	0	Sb	S/Sb
Measured wt%	1.58	0.31	0.24	28.74	1.73	-	-
Calculated at%	6.53	15.40	0.84	44.43	5.35	27.45*	1.62

*The atomic percentage of Sb was calculated by subtracting the sum of all the percentages of measured elements from 100 (at%), assuming that Sb accounts for the remainder of the analyzed sample. Hence, the relative ratio of S to Sb is calculated to be 1.62.



Fig. S2. SEM images after heat-treatment of the as-synthesized powder at 250 °C for 1 h in an Ar atmosphere. The inset shows a magnified image.



Fig. S3. XPS Sb 3d (a) and S 2p (b) spectra. The peak marked by '+' in (a) indicates the possible existence of small amounts of Sb–O bonds.



Fig. S4. CV curves of the half-cell containing the amorphous Sb_2S_3 anode $(Na|a-Sb_2S_3)$ for the first 6 cycles (a) and 6th to 20th cycles (b). Noticeable peaks arose during the cathodic scan and anodic scan as marked by symbols 'C_x' and 'D_x', respectively. The speculated reactions corresponding to all the indexed peaks are summarized in Table S2.

Scan direction	Marks	Reactions	Ref.	
Cathodic	C ₁ '	insertion $(^{a}SbS_{y} + xNa \rightarrow ^{a}Na_{x}SbS_{y})$ & SEI formation	[S1,S2]	
	C ₁ "	<i>insertion</i> $(^{a}SbS_{y} + xNa \rightarrow ^{a}Na_{x}SbS_{y})$	[S1,S2]	
	C ₂ ' / C ₂ "	<i>conversion</i> ($^{a}Na_{x}SbS_{y}+2-xNa \rightarrow yNa_{2/y}S + Sb$)	[S1,S2]	
	C ₃ ' / C ₃ " C ₃ "'/ C ₃ "	alloying $(Sb + xNa \rightarrow {}^{a}Na_{x}Sb;$ ${}^{a}Na_{x}Sb + 3-xNa \rightarrow Na_{3}Sb)$		
	C_4	extra-sodiation (interface storage)	[S4,S5]	
Anodic	A_1	<i>extraction</i> ($^{a}Na_{x}SbS_{y} \rightarrow ^{a}SbS_{y} + xNa$)	[S1]	
	A_2	<i>reconversion</i> ($yNa_{2/y}S + {}^{a}Sb \rightarrow {}^{a}Na_{x}SbS_{y} + 2-xNa$)	[S1,S2]	
	A ₃ ' / A ₃ "	<i>dealloying</i> (Na ₃ Sb \rightarrow ^{<i>a</i>} Na _{<i>x</i>} Sb + 3- <i>x</i> Na; ^{<i>a</i>} Na _{<i>x</i>} Sb \rightarrow ^{<i>a</i>} Sb + <i>x</i> Na)		
	A_4	desodiation (from the interface)	[S4,S5]	

Table S2. Expected reactions during cathodic and anodic scans

^{*a*}amorphous phase

References

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Fig. S5. Galvanostatic charge-discharge voltage profiles of the amorphous Sb_2S_3 anode halfcell (Na|*a*-Sb₂S₃) at a current rate of 50 mA·g⁻¹ during 100 cycles.



Fig. S6. XRD pattern (a), SEM image (b), and electrochemical properties (c, d) of the commercial Sb_2S_3 particle anode. Galvanostatic charge-discharge voltage profiles at a current rate of 50 mA·g⁻¹ during 70 cycles (c), and rate capability at different current rates from 50 mA·g⁻¹ to 3000 mA·g⁻¹ (d). The inset in (d) shows the charge-discharge voltage profiles at different current rates.

Components	Na ²⁺	Cl-	SO4 ²⁻	Mg ²⁺	Ca ²⁺	K ⁺	Total
Concentration	10,188	19,543	2,754	1,266	406	385	34,541
(mg/kg)							

 Table S3. Ionic species in natural seawater, detected by ion chromatography



Fig. S7. Charge-discharge voltage profiles of the cathode half-cells (Na|seawater) using only carbon felt or Pt/C-loaded carbon felt current collectors at a current density of 0.05 mA·cm⁻². The voltage gaps between the charge and discharge curves (ΔV) were measured to be ~1.01 V and ~0.56 V for the carbon felt and Pt/C-loaded samples, respectively.



Fig. S8. XRD patterns of the NASICON solid electrolytes before and after 70 cycles. The bottom panel shows the reference pattern (JCPDS No.35-0412). No significant change of the NASICON phase was found.