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Abstract

Metal-ion batteries are promising for large-scale energy storage. Their potential commercialization not only depends on their superior electrochemical performance, but also on the large-scale synthesis cost of electrode materials. In the conventional industrial technology for producing non-oxides, argon protection is required to avoid oxidation, leading to additional costs and extra processing. We demonstrate, without protection gas, that ball milling in air with a small amount of Ti additive can be a cost-effective approach for preparing high-performance alloy anodes. Ti consumes the oxygen, forming TiO_2 ($< 10 \text{ nm}$) in situ with high ionic conductivity, while also preventing oxidation and sustaining the electrical conductivity of carbon. This strategy effectively promotes the rate capability (61% capacity retention from 60 to 3000 mA g^{-1}) of SnSb/carbon-nanotube anode (over 204% better than without Ti additive).

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Creating fast ion conducting composites via in-situ introduction of Titanium as oxygen getter

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KEYWORDS

oxygen getter, ion conductivity, high rate capability, sodium ion batteries

Abstract

Metal-ion batteries are promising for large-scale energy storage. Their potential commercialization not only depends on their superior electrochemical performance, but also on the large-scale synthesis cost of electrode materials. In the conventional industrial technology for producing non-oxides, argon protection is required to avoid oxidation, leading to additional costs and extra processing. We demonstrate, without protection gas, that ball milling in air with a small amount of Ti additive can be a cost-effective approach for preparing high-performance alloy anodes. Ti consumes the oxygen, forming TiO_2 (< 10 nm) in situ with high ionic conductivity, while also preventing oxidation and sustaining the electrical conductivity of carbon. This strategy effectively promotes the rate capability (61% capacity retention from 60 to 3000 mA g^{-1}) of SnSb/carbon-nanotube anode (over 204% better than without Ti additive).

1. Introduction

Owing to the rapid developments of electronic devices, electric vehicles, and energy storage systems, low-cost, highly-efficient and large-scale methods of preparing materials for energy storage are urgently needed^{1,2}. By offering energy storage with high energy density and long cycle life, lithium- and sodium-ion batteries (LIBs and SIBs) have attracted great attention for the past decades³⁻¹⁰. Benefiting from their competitive costs, SIBs have been considered a better candidate than LIBs for grid-scale applications. Among all the currently available electrode materials, alloy-based materials have been proven to be promising anodes for SIBs due to their high gravimetric and volumetric capacities^{11,12}. Alloy electrodes undergo enormous volume

change and continuous pulverization, and therefore show relatively poor cycle performance. Numerous strategies to overcome the degradation of electrodes, such as employing unique nanostructures or introducing a conductive matrix (e.g. carbon) to buffer the volume changes, have been studied in recent years^{13,14}. Nevertheless, the effects are hitherto barely satisfactory.

For industrial applications, the synthesis of alloy-based electrodes must be scalable, simple, and low-cost. Various scalable synthesis methods, such as solid-state reaction¹⁵, electrospinning¹⁶, glycothermal approach¹⁷, ball milling¹⁸, etc., have been studied. Amongst, ball milling is the most appealing large-scale synthesis technique¹⁹ because of its environmental friendliness (without a solvent involved) and easy operability. In some cases, the preparation of precursors for solid-state synthesis definitely needs the assistance of the ball-milling technique²⁰, taking advantages of the ability of ball milling to make small and homogeneous particles. Ball milling requires the protection of argon gas, to avoid unwanted oxidation or other side reactions^{15, 19, 20}. Undoubtedly, the use of argon gas will not only increase the cost, but also multiply the complexity of operation processes. Inspired by the use of Ti as an oxygen getter in alloy melting^{21,22} and the excellent ionic conductivity of TiO₂ in metal-ion batteries²³, Ti may be used in the ball milling of alloy electrode materials to form TiO₂ as well as protecting the electrode materials from oxidation. Thus, there is a possibility to create an electrode material that combines the merits of a high-capacity alloy-based material with the rapid ion conductivity of TiO₂ in a simpler synthesis process. SnSb is one of the most promising anode materials for SIBs due to its high theoretical capacity (754 mA h g⁻¹) and stepwise reaction mechanism²⁴. Although different strategies have been applied to SnSb anodes for improving their electrochemical performance in recent years, the long-term cycling performance of SnSb electrodes at high rates

has rarely been reported so far, especially for SnSb fabricated via large-scale synthesis techniques.

Herein, taking SnSb anode material as an example, we used Ti as an oxygen getter for the SnSb fabrication via the ball milling of Sn and Sb in air. Without argon protection, this one-step approach will be favourable for the ease of handling and the significantly-reduced synthesis cost. In order to buffer the volume change of SnSb anode material during cycling in SIBs, untreated commercial multi-wall carbon nanotubes (MWCNTs) were also added to create a conductive buffering matrix. The TiO_2 (< 10 nm) with high ionic conductivity and the carbon matrix with good electronic conductivity synergistically improve the high-rate capability ($326.9 \text{ mA h g}^{-1}$ at 3 A g^{-1}) and cycling stability (63.7% capacity retention after 300 cycles at 1.2 A g^{-1}).

2. Results and discussions

Figure 1 (a) XRD and (b) NPD data (enlargement of unfitted peaks in inset) of the as-prepared powders, (c) the XPS analysis of Ti 2p peak from SnSb-3% Ti (air) and (d) C 1s peaks from SnSb-3% Ti (air) and SnSb (air), (e) edge-model for MWCNT, (f) formation energy of various X-O (X: Ti, C, Sn, Sb) bond per oxygen atom. (SnSb- $x\%$ Ti (air or argon) denotes the SnSb sample containing x wt.% Ti and 12.5 wt.% MWCNT prepared in air or argon.)

As depicted in Figure 1a, all the well-defined major peaks in the X-ray diffraction (XRD) patterns can be indexed to the hexagonal $R\text{-}3m$ SnSb structure. With the addition of Ti, several weak peaks that appear to belong to Ti were observed in the SnSb-5% Ti (air) and SnSb-3% Ti (argon), but not in the SnSb-3% Ti (air). It is possible that most of Ti in SnSb-3% Ti (air) was oxidised so that the amount of residual Ti was under the detection limit of XRD. The MWCNT are not observed in XRD, but they can be identified by Raman spectroscopy (Figure S1) and high-resolution neutron powder diffraction (NPD) data (Figure 1b). The Raman spectra clearly show the disordered (D) band and graphitic (G) band of MWCNTs, and the 3 broad peaks at $2\theta = 26, 42, \text{ and } 84^\circ$ in the NPD pattern of the SnSb-3% Ti (air) are due to MWCNTs. Through careful Rietveld analysis of the NPD pattern, the $R\text{-}3m$ SnSb structure was confirmed, as shown in Table S1. There are still unfitted parts, which are highlighted by green rectangles in the inset of Figure 1b. Using the exact same instrumental parameters (from SnSb NPD dataset), a simulated NPD pattern of rutile TiO_2 with a particle size of 3 nm, (estimated using transmission electron microscopy (TEM), with details to be shown later) is shown in Figure S2, showing 2 major peaks at the same positions as in the unfitted parts of the NPD spectrum. It is reasonable to believe that those unfitted parts might be due to the contribution of nanocrystalline rutile TiO_2 . Gibbs free formation energy of oxides (Figure S3) estimated using Thermal-Calc suggests rutile is likely to be formed.

Figure 1c shows the X-ray photoelectron spectroscopy (XPS) spectrum of SnSb-3% Ti (air) in Ti 2p. The Ti $2p_{3/2}$ (458.5 eV) and Ti $2p_{1/2}$ (464.6 eV) peaks can be assigned to the chemical valence of Ti^{4+} , and this observation is consistent with the NPD simulation. XPS spectra for C

1s, O 1s, Sb 3d, and Sn 3d are presented in Figure 1d, Figures S4 and S5, respectively. The Sb 3d_{5/2} (528.3 eV), Sb 3d_{3/2} (537.7 eV), Sn 3d_{5/2} (485.2 eV), and Sn 3d_{3/2} (493.6 eV) peaks show the metallic nature of Sn and Sb. In all the C 1s XPS spectra, typical C-C (284.8 eV), C-O-C (286 eV), and O-C=O (288.5 eV) peaks were detected. It was found that the ratio of the C-O-C to the C-C peak was 0.185 and 0.393 for the SnSb-3% Ti (air) and SnSb (air) samples; while the ratio of the O-C=O to the C-C peak was 0.032 and 0.116 for the two samples, respectively. It appears that the oxidation of carbon was significantly reduced by Ti, implying Ti works effectively as an oxygen getter that competitively reacts with oxygen during ball milling. Similar results were also observed for other Ti-added samples, such as SnSb-5% Ti (air) and SnSb-3% Ti (argon)) (Figure S4a). It was also evident that all the Ti-free samples, including the untreated pure commercial MWCNTs and SnSb (with 12.5 wt. % MWCNTs), both ball-milled in argon, have higher C-O-C and O-C=O to C-C bond ratios than the Ti-containing samples (Figure S4b). The XPS studies above suggest that oxygen preferentially reacts with Ti and forms TiO₂. Density functional theory (DFT) calculations were used to estimate the magnitudes of oxygen affinity for the different elements (Figures 1e and f). C-O and C=O carbon-oxygen bonds were simulated, and the formation energies of various X-O bonds were also calculated for comparison, where X is C, Ti, Sn or Sb. It is clear that Ti-O has the lowest formation energy among all the X-O bonds, which agree well with the XPS results. The formation energies of C-O (-1.504 eV) and C=O (-1.508 eV) bonds are lower than those of Sn-O (-1.063 eV) and Sb-O (-0.928 eV), suggesting that MWCNT will be oxidized if there is no Ti present during ball milling, thus reducing its electrical conductivity²⁵.

Figure 2 Microscopic characterization of the SnSb-3% Ti (air) powder. (a) FESEM and (b) TEM images (enlargement in inset), (c) HRTEM image and SAED pattern (inset), with the red outlines indicating the sizes of TiO_2 particles, (d-h) STEM mapping, (i-j) STEM images and (k) EELS analysis of the Ti L-edge and O K-edge for the selected area in (j)

Figure 2a shows a field-emission scanning electron microscope (FESEM) image showing the morphology of irregular agglomerated micro-sized particles, and Figure 2b presents a low magnification TEM image of the SnSb-3% Ti (air) sample. A high resolution TEM (HRTEM) image and corresponding selected area diffraction (SAED) pattern of the SnSb-3% Ti (air) powder are given in Figure 2c. The first and faint diffraction ring of the SAED pattern can be indexed as the (110) reflection of TiO_2 . The second ring with stronger intensity is indexed as the (101) reflection of SnSb. TiO_2 nanoparticles (circled in red) are distributed evenly in the carbon matrix, and their sizes are in the range of 3-6 nm. The lattice fringes of the particles have the

spacing ~ 0.3247 nm, which corresponds to the (110) planes of rutile TiO_2 . It has been reported that ultrafine TiO_2 with particle size below 10 nm could significantly increase capacitive charge storage and enhance the discharge/charge kinetics due to the faradaic reactions on the surfaces of the materials²⁶. Figures 2d-k shows X-ray mapping results, scanning TEM (STEM) images, and the electron energy loss spectrum (EELS) of the SnSb-3% Ti (air) sample. Clearly, the elements Ti, Sn, Sb, C, and O are distributed uniformly in the composite material. The fine structures near the Ti-L3, Ti-L2, and O-K edges match those of rutile TiO_2 . The EELS result is consistent with the NPD, SAED, and HRTEM results given earlier.

Figure 3. Electrochemical performance of SIBs. (a) Rate capabilities and (b) capacity retention of cells at various current densities. Galvanostatic discharge and charge profiles of (c) SnSb-3% Ti (air) and (d) SnSb (air) electrodes at different current densities. (e) Long-term cycling tests of the cells at the current density of 1.2 A g⁻¹.

The rate performance was investigated at various current densities in the range of 60 to 3000 mA g⁻¹. Figures 3a and 3b show that the SnSb-3% Ti (air) electrode exhibits the best rate performance among all the compared electrodes. It delivered 538, 509, 484, 442, 381, and 327 mA h g⁻¹ at the current densities of 60, 150, 300, 600, 1200, and 3000 mA g⁻¹, respectively, and had the highest capacity retention of 60.8% at 3 A g⁻¹. In order to further investigate the effect of TiO₂ formed during ball-milling, we employed SnSb-3% Ti (argon) electrode, in which less TiO₂ can be formed due to limited oxygen source only from functional group of MWCNTs not from air. It can be found that the capacity of the SnSb-3% Ti (argon) electrode maintained 48.3% at 3 A g⁻¹, which is lower than that of the SnSb-3% Ti (air) electrode. Both of the SnSb-3% Ti (air) and SnSb-3% Ti (argon) electrodes can sustain the electrical conductivity due to the reduction of the functional group of CNTs. However, the 3% Ti in the SnSb-3% Ti (air) electrode, can also scavenge oxygen from air to form more TiO₂ than that in the SnSb-3% Ti (argon) electrode, demonstrating that TiO₂ formed enhanced the rate capability for the electrodes, due to the higher ion conductivity.

In addition, the SnSb (argon) electrode exhibits better rate performance compared to the SnSb (air) electrode. The SnSb (argon) maintains 216 mA h g⁻¹ at 3 A g⁻¹ with a capacity retention of 39.9% compared with that at 60 mA g⁻¹, while the SnSb (air) electrode has a relatively lower capacity retention of 29.7% at 3 A g⁻¹, which may be ascribed to the partial oxidation of the MWCNTs during the ball-milling process, where the generation of numerous C-O and C=O bonds on the carbon nanotubes (CNTs) decreases the electrical conductivity. The SnSb-5% Ti (air) and SnSb-3% Ti (argon) electrodes show slightly reduced capacities. Even with a similar amount of TiO₂, the reduced capacity in SnSb-5% Ti (air) is believed to be due to the excess of unreacted Ti and less SnSb active materials.

On comparing the discharge-charge profiles of the SnSb (air) and SnSb-3% Ti (air) electrodes at different current densities (Figures 3c and 3d), it was found that the latter showed significantly lower polarization than the former. The discharge-charge potential difference for the SnSb-3%Ti (air) electrode changed very slightly with increasing current density. In contrast, for the SnSb (air) electrode, the discharge-charge potential difference was boosted significantly with increasing current density, indicating a higher polarization in the SnSb (air) electrode. The enlarged polarization of the SnSb (air) is mainly ascribed to the sluggish diffusion dynamics due to the lack of TiO_2 phase and the oxidation of the MWCNTs. Electrochemical impedance spectroscopy measurements (Figure S7) show SnSb-3% Ti (air) electrode has a lower charge-transfer and electrode resistances than those of SnSb (air).

The SnSb-3% Ti (air) electrode also shows excellent long-term cycling stability (Figure 3e). Except for the initial low coulombic efficiency due to the formation of the solid electrolyte interphase layer, the coulombic efficiency remains above 99% for all electrodes in the first 300 cycles (Figure S8), indicating good reversibility during cycling. After 300 cycles, the SnSb-3% Ti (air) electrode maintains the capacity of 246 mA h g^{-1} , which represents reversible capacity of 63.7%. In contrast, the capacity of the SnSb (air) electrode drops quickly to 55 mA h g^{-1} after 150 cycles, corresponding to 21.1% capacity retention with a large capacity fading of 0.263% per cycle. Furthermore, TiO_2 could effectively assist the transport of ion even after 100 cycles (Figures S10 and S11). It is believed that the electrochemical performance could be further improved via electrode and electrolyte optimization for industrial application.

Scheme 1. Schematic illustration of the one-step preparation process and the enhanced electrochemical performance mechanism.

Scheme 1 illustrates the one-step and scalable method for electrode materials: During the ball-milling process in air, the oxygen will be preferentially captured by Ti and form TiO₂, which is distributed uniformly in the active materials and carbon matrix. It appears that 3% Ti will be sufficient to take out all the oxygen in the chamber and some oxygen from the function groups on the CNT edges. Consequently, Ti prevents oxidation of the active alloy elements and reduces the oxidation of CNT, thus maintaining the electrical conductivity of the SnSb composite electrode. During cycling, the TiO₂ provides fast ionic conductivity, while the CNT acts as a good electrical conductor and buffering matrix to accommodate volume changes and synergistically maintain the charge transfer and the structural integrity. The cyclic voltammetry measurements at various scanning rates (Figures S12 and S13) confirm the Na diffusivity in the Ti-containing electrodes are notably higher than those of the other electrodes. In particular, the SnSb-3% Ti (air) electrode shows a superior rate capability compared with the other ball-milled alloy-based electrodes reported in the literature (Figure S14). To obtain detailed insight into the

high diffusion coefficient, we studied the process of Na ion migration in TiO₂ by DFT calculations (Figure S15). Na ions can either diffuse in the channel along the *c*-direction (path A) or move to the neighbouring channel along the [110] direction (path B). The energy barriers calculated by the nudged elastic band (NEB) method are 0.23 eV and 1.2 eV for paths A and B, respectively. The lower diffusion barrier for path A indicates that Na ion migration in rutile TiO₂ involves one-dimensional diffusion along the *c*-direction. At room temperature (300 K), the diffusion coefficient is 10⁻⁷ cm² s⁻¹, representing a significantly higher diffusion coefficient than those in other anodes (Table S2). Therefore, TiO₂ component promotes Na diffusivity in the composite electrode and significantly improves the electrochemical performance of the SnSb electrode. Figure S16 shows the SnSb (air) sample has the lowest electrical conductivity among all samples. SnSb-3% Ti (air), SnSb-5% Ti (air) and SnSb-3% Ti (argon) powders have the higher electrical conductivity than the powders without Ti additive.

3. Conclusions

In summary, for the first time we have utilized the concept of an oxygen getter and designed a strategy which not only simplifies the ball milling process, but also enhances the electrochemical performance of alloy-based anodes. Owing to the merits of the strong oxygen affinity of Ti and the fast ionic conductivity of TiO₂, this method could be promising for emerging applications of ball milling in energy storage. It is expected that our findings will provide new avenues for the improvements of ball-milling techniques and pave the way to reducing the costs for preparing large-scale electrode materials under air for industrial applications down to a practical level.

Supporting Information.

Additional details on synthesis, characterization, computational calculations, electrochemical measurements, Raman spectra, simulated NPD results, thermodynamic calculations, XPS analysis, STEM results of cycled electrode, diffusion coefficient tests and calculations, additional electrochemical measurements.

Conflicts of interest

There are no conflicts to declare

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Creating fast ion conducting composites via in-situ introduction of Titanium as oxygen getter

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Methods

Synthesis of electrode materials

SnSb- $x\%$ Ti (air or argon) powders were synthesised by a facile one-step approach. In a typical ball-milling procedure, elemental Sn (Sigma-Aldrich, $\geq 99.8\%$), Sb (Sigma-Aldrich, $\geq 99.8\%$) and multi-wall carbon nanotubes (MWCNTs) were used without further purification as the raw materials in the weight ratio of Sn: Sb: MWCNTs = 43.2: 44.3: 12.5 (with Sn and Sb in the molar ratio of 1:1, respectively). The ball-milling was conducted in a planetary QM-1SP2 ball mill for 30 h, and the elemental mixture was milled at 500 rpm using stainless steel balls 10 mm in diameter with a powder-to-ball weight ratio of 1:30. All sample storage and handling took place under air atmosphere. SnSb (air) powders were prepared without the addition of Ti. By adding 3% Ti or 5% Ti (Sigma-Aldrich, $\geq 99.8\%$) powders in situ into the ball-milling jar, SnSb-3% Ti (air) and SnSb-5% Ti (air) powders were prepared to optimize the proper ratio of Ti. For comparison purposes, SnSb (argon) and SnSb-3% Ti (argon) powders were prepared in an argon filled glove box (MBraun Unilab).

The volume of the ball-milling vial we used is 100 mL. The approximately oxygen content can be calculated as 100 mL *21% (volume of oxygen in air) =21 mL (~0.028g). Based on the equation ($\text{Ti} + \text{O}_2 = \text{TiO}_2$), 0.03g O_2 could be consumed by ~0.042g Ti, which is corresponding to ~2.7 wt.% in the total amount (0.648g Sn+ 0.665g Sb+ 0.187g carbon nanotubes) of the powder. Besides, the extra Ti will react with partial C-O and C=O bonds existed on multi-wall carbon

nanotubes (MWCNTs). Therefore, the total amount for removing the entire O during ball-milling is around 3%.

The electrical conductivity was measured by means of a static DC method using an Ozawa RZ2001i. The resultant fine powders were densified by a cold isostatic pressing (CIP) instrument under an axial compressive stress of 60 MPa for 5 min. The obtained highly dense pellets were cut and polished into rectangular bars with dimensions of $\sim 6 \times 2 \times 2 \text{ mm}^3$, and then annealed for 12 h at 300 °C. The measurement of the electrical conductivity was conducted on an Ozawa RZ2001i (Japan) instrument under helium atmosphere at 323K.

Characterization

The crystal structures of the as-prepared powders were characterized by powder X-ray diffraction (XRD, Rigaku D/max 2500) with a Cu K α source ($\lambda = 1.54056 \text{ \AA}$) at a scanning rate of 8° min^{-1} . Raman spectra were collected on a JobinYvon HR800 Raman spectrometer. High-resolution neutron powder diffraction (NPD) data of the as-prepared SnSb sample were collected using the high-resolution neutron powder diffractometer, namely, ECHIDNA¹, at the Open Pool Australian Light-water (OPAL) research reactor at the Australian Nuclear Science and Technology Organization (ANSTO). The as-prepared SnSb-3% Ti (air) was loaded into a 9-mm vanadium can, and the neutron beam wavelength used was $1.6219(2) \text{ \AA}$, which was confirmed using the La¹¹B₆ National Institute of Standards and Technology (NIST, USA) standard reference material (SRM) 660b. NPD data were recorded for the 2θ range from 6.5 to 164° with a step size of 0.125° . X-ray photoelectron spectroscopy (XPS) was conducted on an AXIS ultra DLD. The morphology of the synthesized powders was characterized on a JEOL JSM-7500FA field-emission scanning electron microscope (FESEM) and on a transmission electron

microscope (TEM, JEOL 2010F). The elemental mapping and EELS spectra were collected with a scanning TEM (STEM, ARM-200F).

Computational details

DFT calculations were performed by using the Quickstep module implemented in the CP2K program² with the Perdew-Burke-Ernzerhof (PBE) functional³ and Geodecker-Teter-Hutter (GTH) pseudopotentials⁴. The double-zeta valence plus polarization (DZVP) basis set was employed⁵. Brillouin zone integration was performed at the gamma point. An energy cut-off of 800 Ry and the convergence criterion of 10^{-7} Ha were used for all calculations. The nudged elastic band method (NEB)⁶ implemented in CP2K was used to calculate the diffusion energy barriers. Fifteen images were used for each NEB calculation. The calculated lattice constants for rutile TiO_2 (Space group number 136) are $a = b = 4.62 \text{ \AA}$ and $c = 2.98 \text{ \AA}$, which are in good agreement with the experimental values $a = b = 4.60 \text{ \AA}$, $c = 2.98 \text{ \AA}$. The possible sites for Na ions in the TiO_2 structure are the octahedral sites (0.5, 0, 0) and (0, 0.5, 0). Supercells consisting of $2a \times 2b \times 3c$ unit cells containing 24 formula units (TiO_2) were used. After one Na was added, the length of the a - and b -axis parameters changed from $4.62 \text{ \AA}$ to $4.72 \text{ \AA}$ and $4.76 \text{ \AA}$, respectively, while the c -axis parameter decreased from $2.98 \text{ \AA}$ to $2.97 \text{ \AA}$. Under the assumption that the local diffusion of Na ions does not perturb the shape of the overall crystal structure, those new lattice constants were used in the NEB calculations, with full relaxation of the internal coordinates.

In this paper, the enthalpy of formation per oxygen atom was calculated as follows:

$$\Delta H_f = \frac{E_{CNT+nO} - E_{CNT} - nE_O}{n}$$

where $E_{\text{CNT+O}}$, E_{CNT} , and E_{O} are the calculated electronic energies of CNT-O compound, CNT, and an O atom, respectively.

The diffusion coefficient can be calculated from the energy barriers along the diffusion path using transition state theory. The diffusion coefficient can be written as:

$$D = \Gamma d^2$$

where Γ is the rate of jumping to a neighbouring site and d is the diffusion distance. This jumping rate can be written as:

$$\Gamma = \nu e^{-\Delta E/k_b T}$$

Where ΔE is the diffusion energy barrier, k_b is Boltzmann's constant, T is the absolute temperature, and ν is the effective frequency associated with atomic vibration, which can be assumed to be a constant, $1 \times 10^{13} \text{ Hz}$ ⁷.

The Gibbs free energy and enthalpy of selected phases in the Sn-O, Sb-O, and Ti-O binary systems were calculated using Thermal-Calc software⁸. For a binary system, ΔG_m (where ΔG_m represents the nucleation driving force of the crystallization process) of Φ phase could be calculated by Equation (1):

$$\Delta G_m = x_A^\Phi \bar{G}_A^L + x_B^\Phi \bar{G}_B^L - G^\Phi \quad (1)$$

where x_A^Φ, x_B^Φ are the mole fractions of A and B in Φ phase, G^Φ is the Gibbs free energy of Φ phase. $\bar{G}_A^L$ and $\bar{G}_B^L$ are the Gibbs free energy values of A and B in the liquid state. The enthalpy, ΔH_m , could be calculated in a similar way.

Electrochemical measurements

The working electrodes were fabricated using a slurry-coating method. The synthesized materials were mixed with Super P carbon black and carboxymethyl cellulose (CMC) in the weight ratio of 8:1:1, respectively. Deionized (DI) water was used as the dispersing agent. Then, the slurry was coated on copper foil and dried in a vacuum oven at 80 °C overnight, followed by pressing at 300 kg cm⁻². Coin-type (CR2032) cells were assembled in an argon-filled glove box with oxygen and water content lower than 0.1 ppm. Na half-cells were assembled with sodium metal as the counter electrode, glass fibre as separator, and 1 M NaClO₄ in propylene carbonate (PC) with 5% fluoroethylene carbonate (FEC) additive as electrolyte. The mass loading of active material (SnSb-*x*% Ti) was over 0.99 mg cm⁻², corresponding to a total mass loading of 1.41 mg cm⁻². Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) tests were conducted on a VMP-3 electrochemical workstation. The cells were galvanostatically charged-discharged between 0.01 and 2.0 V versus Na/Na⁺ at various current densities on Neware battery test systems. The specific capacity was calculated based on the weight of SnSb-*x*% Ti.

Figure S1. Raman spectra of the as-prepared powders.

Figure S2. Simulated NPD results for rutile TiO_2 .

Figure S3. Thermodynamic calculations of the selected phases in the Ti-O, Sn-O, and Sb-O systems. (a) Gibbs free energy calculations; (b) enthalpy formation energy calculations.

The Gibbs formation energies of titanium oxides, Sn oxides, and Sb oxides were calculated and the results are given in Figure S3, where rutile TiO_2 exhibits the lowest Gibbs formation energy and the lowest formation enthalpy among all three polymorphs of titanium oxide (anatase, brookite, and rutile), suggesting that rutile TiO_2 is the most stable binary compound in the Ti-O system. The calculated results also show that Ti has a stronger oxygen affinity than Sn and Sb with increasing temperature, which is consistent with the DFT calculation results above.

Figure S4. XPS analysis of the as-prepared samples. (a) Sb 3d and O 1s peaks; (b) Sn 3d peaks.

Figure S5. C 1s XPS analysis of the as-prepared samples. (a) SnSb-5% Ti (air) and SnSb-3% Ti (argon) samples; (b) commercial MWCNTs and SnSb (argon) samples.

Figure S6. Galvanostatic discharge-charge profiles of a) SnSb-5% Ti (air), b) SnSb-3% Ti (argon), and c) SnSb (argon) electrodes at different current densities in the range of 60 to 3000 mA g^{-1} .

Figure S7. Electrochemical impedance spectroscopy comparison of all the electrodes before cycling.

Electrochemical impedance spectroscopy (EIS) measurements were also performed to evaluate all the electrodes. As shown in Figure S7, the high-frequency semicircle of the SnSb-3% Ti (air) cell is clearly the smallest among all the cells, suggesting that the SnSb-3% Ti (air) electrode has a lower charge-transfer resistance.

Figure S8. Coulombic efficiency comparison of the as-prepared electrodes.

Figure S9. Long-term cycling tests of the cells at the current density of 1.2 A g^{-1} .

The SnSb-1% Ti (air) electrode show a slighter higher capacity and better cycling performance than that in the SnSb (air) electrode at 1.2 A g^{-1} , which is possibly due to the less amount of TiO_2 formed during ball-milling. 1% Ti can only partially scavenge the oxygen in the ball-milling jar, indicating the ion conductivity and electrical conductivity could not be improved significantly.

Figure S10. STEM-mapping of SnSb-3% Ti (air) electrode after 100 cycles.

Figure S11. STEM image (left) and EELS spectrum (right) for the selected area of SnSb-3% Ti (air) electrode after 100 cycles.

X-ray mapping and EELS were carried out to identify the Ti-containing phase in the SnSb-3% Ti (air) electrode after 100 cycles, as shown in Figures S10 and S11. The fine structure near the Ti-L3, Ti-L2, and O-K edges matches that of rutile TiO₂. This suggests that the rutile TiO₂ is stable and capable of effectively assisting the transport of ions even after 100 cycles.

Figure S12. CV curves at different scan rates. (a) SnSb (air); (b) SnSb-3% Ti (air); (c) SnSb-5% Ti (air); (d) SnSb-3% Ti (argon); and (e) SnSb (argon) electrodes.

Figure S13. Peak currents versus $v^{0.5}(v^{0.5}s^{-0.5})$, where v is the scan rate and s the time, and the corresponding linear fits. (a) The cathodic reaction adopted from A1-E1; (b) the anodic reaction adopted from A2-E2.

The average sodium-ion diffusion coefficient (D_{Na^+}) can be calculated based on the Randles-Sevcik equation:

$$i_p = 0.4463nF \sqrt{\frac{nFD}{RT}} AC \sqrt{v}$$

Where i_p represents the peak current, n is the number of electrons, F is the Faraday constant, R is the gas constant, T is the temperature, A is the surface area of the electrode, D is the diffusion coefficient, C stands for the concentration of sodium-ions in the electrolyte, and v is the voltage scanning rate.

Figure S14. Comparison of capacity retention of SnSb-3% Ti (air) electrode in this work with SnSb composites prepared by other methods and other alloy-based anodes synthesised by ball-milling methods^{9, 10, 11, 12, 13, 14, 15}.

Figure S15. Na diffusion pathways in (a) *c*-axis view and (b) *a*-axis view. Path A represents the diffusion of Na along a channels parallel to the *c*-direction. Path B represents diffusion of Na to the next channel along the [110] direction. Ti: red; O: blue; Na: orange; TiO₆ octahedra: red.

Figure S16. The electrical conductivity comparison of the as-prepared powders

Figure S16 shows the SnSb (air) sample has the lowest electrical conductivity among all samples. SnSb-3% Ti (air), SnSb-5% Ti (air) and SnSb-3% Ti (argon) powders have the higher electrical conductivity than the powders without Ti additive.

Besides, SnSb-3% Ti (air) powder has a lower electrical conductivity than SnSb-3% Ti (argon) and SnSb-5% Ti (air) powders, however, the SnSb-3% Ti (air) electrode shows the best rate capability, further demonstrating that the introduction of Ti oxygen getter not only helps sustain the electrical conductivity, but also forming TiO₂ which facilitate sodium ion diffusion to some extent, and enhance the rate capability.

Figure S17. The Cycling performance of the as-prepared electrodes at 60 mA g⁻¹.

All the as-prepared electrodes have high reversible capacities over 520 mA h g⁻¹ at 60 mA g⁻¹. After we carefully compared the capacities of the various electrodes, the SnSb (air) electrode exhibited a slightly higher specific capacity than the other electrodes around 550 mA h g⁻¹ at 60 mA g⁻¹.

Figure S18. The Cycling performance of the TiO₂ electrode at 60 mA g⁻¹.

The TiO₂ electrode maintained a reversible capacity of around 110 mA h g⁻¹ at 60 mA g⁻¹. In this work, 3 wt. % Ti has been added to scavenge oxygen from the air and the C-O or C=O groups to form TiO₂, indicating that the content of TiO₂ would be no more than 3 wt. %. Therefore, the capacity contribution from TiO₂ itself would be lower than 3.3 mA h g⁻¹, which can be ignored.

Although the capacity contribution from TiO₂ is negligible, TiO₂ can enhance the rate capability of the electrodes due to its high ionic conductivity. In addition, the Ti can also scavenge oxygen from air to sustain the electrical conductivity (avoiding the oxidation of CNTs). Hence, the rate capability of the electrodes containing TiO₂ is still higher than for those without TiO₂, especially at high current rate.

Table S1. Crystallography of SnSb determined from Rietveld analysis of high-resolution NPD spectrum.

SnSb (space group = R-3m) a = b = 4.345(5) Å, c = 5.285(3) Å						
Atom	Wyckoff site	x	y	z	Uiso	Occupancy
Sb	6c	0	0	0.49(2)*	0.013(2)**	0.5~
Sn	6c	0	0	0.49(2)*	0.013(2)**	0.5~

*,** constrained to be same. ~ fixed.

Table S2. Diffusion coefficient comparison with other anode materials.

Electrode materials	Lithium or sodium ion batteries (LIBs or SIBs)	Diffusion coefficient ($\text{cm}^2 \text{s}^{-1}$)	Reference
Rutile TiO_2	SIBs	10^{-7}	This work
Sn	LIBs	1.8×10^{-11}	16
Sb	LIBs	1.1×10^{-11}	16
SnSb	LIBs	4×10^{-12}	17
graphite	LIBs	1.12×10^{-10}	18
Si	LIBs	5.1×10^{-12}	19
CoP	SIBs	$\sim 3 \times 10^{-13}$	20
Ge	SIBs	$\sim 10^{-13}$	21
TiS_2	SIBs	$\sim 10^{-12}$	22

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