Large-scale synthesis of ternary Sn$_5$SbP$_3$/C composite by ball milling for superior stable sodium-ion battery anode

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Abstract
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Abstract

Alloy-based materials (i.e. Sn, Sb, P) are promising candidates for sodium-ion battery (SIB) anodes, but they suffer from capacity decay during charge/discharge cycling due to the pulverization caused by their huge volume change. Nanostructures can slow down the capacity fade, but most of the synthesis methods of such nanostructured anodes are difficult to scale-up. Herein, a ternary Sn$_2$SbP$_3$/C composite was fabricated by a green, low cost, one-step and easily scalable ball-milling of elementary Sn, Sb, P, and C. The microstructure of the ball-milled powders consists of micrometric agglomerates of active nano Sn$_4$P$_3$ and SnSb and Sn particles. Carbon in the composite acts as a conducting matrix, and it does not only benefit to the ball milling efficiency, but also benefit to the cycle life of the electrode. Each of the active Sn$_4$P$_3$ and SnSb and Sn phases in the composite functions mutually as a buffer for the others. As a result, this ternary composite anode delivers a good capacity of 352.2 mA h g$^{-1}$ at the current density of 2 A g$^{-1}$, which is notably higher than that of the binary Sn$_4$P$_3$/C and SnSb/C composites produced under the same conditions.

Key words: Sodium-ion battery, alloy anode, low cost, large-scale
1. Introduction

Sodium-ion batteries (SIBs) have been attracting great interest recently due to the low cost and abundance of sodium resources, especially for applications in stationary energy storage.[1-16] The successful commercialization of SIBs does not only calls for the development of electrode materials with enhanced performance, but also scalable synthesis protocols.[17] Alloy-based materials are believed to be very promising candidates for SIB anodes due to their high gravimetric and volumetric capacities, and slightly higher thermodynamic potential. [1, 18, 19] For instance, group 14 (Sn, Na$_{15}$Sn$_4$, 847 mA h g$^{-1}$) and 15 elements (P, Na$_3$P, 2596 mA h g$^{-1}$; Sb, Na$_3$Sb, 660 mA h g$^{-1}$) based alloys[14, 20, 21] have been intensively studied recently and have showed promising properties. Nevertheless, large volume changes (> 200 %) are inevitable for these alloy anodes during sodiation/desodiation. The huge volume expansion will lead to continuous pulverization, particle cracking, and subsequent separation of the active materials from the current collector and result in fast capacity fade.[1, 2, 22]

Nanomaterials with designed and optimized structures can slow down the capacity fade. The use of these nanosized materials by industry in the near future is unlikely, however, because of their complicated synthesis procedures, very high synthesis costs, high surface reactivity, low tap density, and difficulties for large-scale synthesis. In contrast, ball milling is a simple, cheap, and easily scalable synthesis method, and hence, it has a potential for industrial-scale application. Binary composite systems such as Sn$_4$P$_3$ and SnSb formed via ball milling have been shown to have significantly better electrochemical performance over pristine Sn, Sb, or P.\textsuperscript{20-3} The electrochemical performance of the ball milled binary Sn$_4$P$_3$ or SnSb is still far from adequate for practical applications, however, especially in terms of high rate
Herein, we report a ternary Sn\textsubscript{5}SbP\textsubscript{3}/C composite synthesized via ball-milling, which contains Sn\textsubscript{4}P\textsubscript{3}, SnSb and Sn nanoparticles (NPs), which are in intimate contact with each other and form heterojunctions in a conductive carbon matrix. The ternary composite displays superior electrochemical performance to the binary Sn\textsubscript{4}P\textsubscript{3}/C or SnSb/C composite. It was found that the Sn and SnSb in the composite facilitate the electron transfer and Sn\textsubscript{4}P\textsubscript{3} provides high sodium storage capacity. The SnSb phase also promotes a superior stable cycling performance by the formation of an intermediate amorphous phase Na\textsubscript{x}Sb.[23, 27-29] It seems that the superior electrochemical performance of the ternary Sn\textsubscript{5}SbP\textsubscript{3}/C composite is resulted from a synergetic effect of the multi phased nanostructure on a conductive network. Importantly ball milling is a scalable process and a large volume of composite architecture electrodes can be easily produced for practical applications.

2. Experimental Section

Preparation of Sn\textsubscript{5}SbP\textsubscript{3}/C ternary composite

Sn\textsubscript{5}SbP\textsubscript{3}/C powder was directly synthesized by ball milling the raw materials of Sn (Aldrich, ≥99.8%), Sb (Aldrich, ≥99.5%), red phosphorus (Aldrich, ≥99%) and carbon black. The weight ratio of Sn: Sb: P: C in the composite is 64.26:13.18:10.06:12.5. The ball milling was conducted in a planetary QM-1SP2 ball mill for 30 h at 500 rpm. A stainless steel jar and stainless steel balls of 10 mm in diameter are used. The powder-to-ball weight ratio was 1:30. For comparison, binary composites SnSb/C and Sn\textsubscript{4}P\textsubscript{3}/C were also synthesized under the same conditions. The weight ratios are Sn: Sb: C= 43.19: 44.31: 12.5 and Sn: P: C = 73.11: 14.39: 12.5 in the binary composites SnSb/C and Sn\textsubscript{4}P\textsubscript{3}/C respectively. The storage and handling of all the samples were performed in an Ar filled glovebox (MBraun Unilab).

Materials characterization

The phasic composition and information of the as-prepared powders were characterized by
powder X-ray diffraction (XRD) on a GBC MMA diffractometer with a Cu $K_\alpha$ radiation at a scanning rate of $1^\circ \ min^{-1}$. The particle morphology and size of the prepared powder materials were characterized on a JEOL JSM-7500FA field-emission scanning electron microscope (FESEM) and on a JEOL ARM-200F cold field emission and aberration-corrected transmission electron microscope (TEM).

**Electrochemical measurements**

Electrodes were fabricated using a slurry-coating method. The synthesized materials ($\text{Sn}_5\text{SbP}_3/C$, $\text{Sn}_4\text{P}_3/C$ and $\text{SnSb}/C$) were mixed with Super P carbon black and carboxymethyl cellulose (CMC) in the weight ratio of 8:1:1 to form slurry with deionized (DI) water. Then, the slurry was coated on copper foil and dried in a vacuum oven at 80 °C for 12 h. Coin-type (CR2032) cells were assembled in an argon-filled glove box ($\text{H}_2\text{O} < 0.1 \ \mu\text{g}$, $\text{O}_2 < 0.1 \ \mu\text{g}$), with 1 M NaClO$_4$ in a mixture of propylene carbonate (PC) with 5 wt. % fluoroethylene carbonate (FEC) as the electrolyte. Cyclic voltammetry (CV) tests were conducted on a Bio-logic VMP-3 electrochemical workstation at a scan rate of 0.05 mV s$^{-1}$. The cells were galvanostatically charged-discharged between 0.01 and 2.0 V versus Na/Na$^+$ at various current densities on a Land battery tester. The mass loading of active material ($\text{Sn}_5\text{SbP}_3$, $\text{Sn}_4\text{P}_3$ and $\text{SnSb}$) was over 0.78 mg cm$^{-2}$. The specific capacity was calculated based on the weight of pure $\text{Sn}_5\text{SbP}_3$, $\text{Sn}_4\text{P}_3$ and $\text{SnSb}$ active materials.

**3. Results and discussion**

Fig. 1a presents the X-ray diffraction (XRD) patterns of the ternary $\text{Sn}_5\text{SbP}_3/C$ and the binary $\text{Sn}_4\text{P}_3/C$ and $\text{SnSb}/C$ composites. The ternary $\text{Sn}_5\text{SbP}_3/C$ composite contains three intermetallic and metallic phases: $\text{Sn}_4\text{P}_3$ (ICSD#15014), $\text{SnSb}$ (ICSD#52303) and Sn (ICSD#40037). In contrast, only $\text{Sn}_4\text{P}_3$ or $\text{SnSb}$ was observed in the binary composite $\text{Sn}_4\text{P}_3/C$ or $\text{SnSb}/C$, respectively. The carbon black is not observed in the XRD patterns due to
its amorphous features, but it can be clearly identified by Raman analysis, as shown in Fig. S1 in the Supporting Information. Also, no bonds of C with Sn, Sb, and/or P are observed in X-ray photoelectron spectroscopy (XPS) analysis (Fig. S2). Fig. 1b presents the a Rietveld refinement profile for the Sn₅SbP₃/C composite, performed by using the GSAS-II software package.[30] All the peaks in the XRD pattern of the ternary Sn₅SbP₃/C can be indexed those of hexagonal Sn₄P₃ (R ̅3m), cubic SnSb (F m̅ 3m), and tetragonal Sn (I4₁/ amd). The lattice parameters obtained from the Rietveld refinement are \( a = 4.0283 \) Å, \( c = 35.6999 \) Å for the Sn₄P₃, \( a = 6.1278 \) Å for the SnSb and \( a = 5.8456 \) Å, \( c = 3.1903 \) Å for the Sn respectively. The amount of each phase in the Sn₅SbP₃ was calculated as 65.75 ± 3.14 wt% Sn₄P₃, 18.54 ± 0.62 wt% SnSb, and 15.71 ± 0.67 wt% Sn.

![Fig.1. a) XRD patterns of Sn₅SbP₃/C composite, Sn₄P₃/C and SnSb/C; b) Rietveld refinement profile for the Sn₅SbP₃/C composite.](image)

The as-milled Sn₅SbP₃/C, Sn₄P₃/C and SnSb/C powders were characterized by SEM and the results are shown in Fig 2. It can be seen that the powders in all three samples show irregular shapes in their morphology. The agglomerated and micro sized particles are the main constituent of the powders, and there are also numerous primary nanoparticles about 50 nm - 100 nm in size (Figs. 2a, b, c). The mixed structure of the micro- and nano- particles may allow full contact of the electrolyte with the active materials and hence facilitate an efficient
ion transportation.[31] It can also be seen that Sn, Sb, and P are distributed uniformly in the Sn$_5$SbP$_3$/C composite according to the energy dispersive X-ray spectroscopy (EDX) (Fig. 2d). EDX results for the Sn$_4$P$_3$/C and SnSb/C are shown in Fig. S3 and the compositions of the three different powders are listed in Table S1.

**Fig.2.** SEM images of a) Sn$_5$SbP$_3$/C composite, b) Sn$_4$P$_3$/C, c) SnSb/C powders; d) EDX mappings of Sn$_5$SbP$_3$/C composite.

Fig. 3 shows a TEM image, and a HRTEM image taken from a micron particle of the Sn$_5$SbP$_3$/C composite. The micron particle is composed of nanoparticles with the size ranging from 20 to 100 nm (Fig. 3a). These nanoparticles are composed of Sn$_4$P$_3$, SnSb and Sn and they are intimately mixed and uniformly distributed in the amorphous carbon matrix (Fig. 3b). The microscale particle size could make the power easy to handle and a higher tapped density, while the nanostructure provides short and fast ion diffusion path during sodiation and desodiation cycling. Figure 3b shows a HRTEM image of such a nanoparticle and the inset shows the indexed fast Fourier transform (FFT) pattern. From this pattern the lattice fringes were indexed and the spacings of the fringes were measured to be about 0.283 nm for the $(10\bar{7})$ planes and 0.309 nm for the $(01\bar{5})$ planes. These values are in good agreement with the $d_{10\bar{7}}$ and $d_{01\bar{5}}$ of Sn$_4$P$_3$. The Sn$_4$P$_3$ particle is about 20 nm in size and is also
surrounded by a few minor Sn and SnSb particles. The HRTEM observations are consistent with the XRD results and further confirm the coexistence of the three phases: Sn₄P₃, SnSb and Sn in the Sn₅SbP₃. It also should be noted that the phosphorus containing phase is sensitive to the electron beam and unstable at high voltages and at room temperature. Therefore, the lowest available voltage of 80 kV and a liquid nitrogen holder were used during the HRTEM measurements.

**Fig. 3.** a) TEM image of the Sn₅SbP₃/C composite, b) HRTEM image of the Sn₅SbP₃/C composite, with the inset showing the FFT pattern of the zone outlined in red.

The electrochemical performance in terms of sodium storage of the Sn₅SbP₃/C composite was systematically investigated. Fig. 4a displays cyclic voltammograms (CV) of the Sn₅SbP₃/C composite. During the first cathodic scan, a weak peak occurred at around 0.8 V, but it reduced slowly and disappeared in the following four cycles. This peak reduction may be attributed to the sodiation of amorphous phosphorus at the surface of the Sn₅SbP₃/C composite. The apparent reduction band at around 0.01-0.1 V may be attributed to the formation of Na₁₅Sn₄ and Na₃P, Na₃Sb (Eq. 1). In the second and subsequent cathodic scans, this large reduction band has obviously shrunken and another new reduction peak appeared at around 0.2-0.7 V. These two reduction bands at 0.18-0.69 V and 0.01-0.16 V can be attributed
to the Na-Sn, Na-Sb and Na-P alloying reactions (Eqs. 2, 3 and 4), according to the CV results for the Sn₄P₃/C and SnSb/C electrodes (Figs. S4a and b). During the anodic scans, the oxidation peaks at around 0.29 and 0.8 V are mainly attributed to the Na-Sn and Na-P dealloying reactions (Eqs. 3 and 4), and the Na-Sn and Na-Sb de-alloying reactions (Eqs. 2 and 4), respectively. The main peak at around 0.6 V is due to the desodiation of Na₃P, although some overlap of the Na-Sn and Na-Sb de-alloying reactions may also be present. Therefore, it is likely that the sodiation and desodiation mechanism may proceed as follows:

During the initial charging (Na insertion) process

$$Sn_4P_3 + SnSb + Sn + 34.5Na^+ + 34.5e^- \rightarrow 1.5Na_{15}Sn_4 + 3Na_3P + Na_3Sb \quad (1)$$

In the subsequent discharging (sodiation) and charging (desodiation) processes

$$Sb + 3Na^+ + 3e^- \leftrightarrow Na_3Sb \quad (2)$$

$$P + 3Na^+ + 3e^- \leftrightarrow Na_3P \quad (3)$$

$$Sn + 3.75Na^+ + 3.75e^- \leftrightarrow Na_{3.75}Sn \quad (4)$$

The theoretical capacity of Sn₃SbP₃, Sn₄P₃ and SnSb could be calculated as 996.3, 1130.5 and 753.8 mA h g⁻¹, respectively. Fig. 4b shows the rate performance of the three electrodes (Sn₃SbP₃/C, Sn₄P₃/C and SnSb/C) at current densities of 100, 250, 500, 1000 and 2000 mA g⁻¹. Clearly, the rate performance of the Sn₃SbP₃/C is better than that of those Sn₄P₃/C or SnSb/C. Moreover, it seems that the superior sodium storage performance of the ternary composite to the binary composites becomes even more outstanding at the higher current densities. For example, a capacity of 352.2 mA h g⁻¹ is obtained for the Sn₃SbP₃/C at the current density of 2 A g⁻¹, which is much larger than those of the two binary composite at the same current density. The capacity retention ratio of the Sn₃SbP₃/C composite electrode is 57.9 % which is also higher than 42.02% of the Sn₄P₃/C and 48.96% of the SnSb/C at the same current density of 2 A g⁻¹, as shown in Fig. 4c.

To better understand the reasons for the superior performance of the Sn₃SbP₃/C electrode, electrochemical impedance spectroscopy (EIS) was also conducted on the three electrodes.
and compared, as shown in Fig. 4d. The EIS curves contain a depressed semicircle in the high frequency region, and a straight sloping line in the low frequency region. The resistor $R_{ct}$ in parallel with the constant phase element (CPE) in the equivalent circuit is the charge-transfer resistance at the electrode/electrolyte interface, which is calculated from the depressed semicircle. Clearly, the $R_{ct}$ of the Sn$_5$SbP$_3$/C electrode (110 $\Omega$) is much lower than those of the binary electrodes (468 $\Omega$ for Sn$_4$P$_3$/C and 1439 $\Omega$ for SnSb/C). The lower the $R_{ct}$ value is, the faster the ion transportation. Thus, the Sn$_5$SbP$_3$/C electrode has the fastest reaction kinetics among the three electrodes.

![Fig. 4.](image)

**Fig. 4.** (a) Cyclic voltammograms (CVs) of Sn$_5$SbP$_3$/C composite for the first 5 cycles, tested at a scanning rate of 0.05 mV s$^{-1}$, b) rate performance of the three electrodes at current densities from 100 mA g$^{-1}$ to 2000 mA g$^{-1}$, c) average discharge capacity retention for the 3 electrodes at current densities from 100 mA g$^{-1}$ to 2000 mA g$^{-1}$, and d) EIS spectra of the three electrodes.
To further explore the superior electrochemical performance of the Sn₅SbP₃/C composite, the long-term cycling stability of the three samples was investigated and compared, as shown in Fig. 5. The Sn₅SbP₃/C electrode exhibits a relatively more stable cycling performance at 500 mA g⁻¹ (Fig 5a). A capacity of 431.6 mA h g⁻¹ is delivered by the Sn₅SbP₃/C after the 200 cycles, which is higher than 346.4 mA h g⁻¹ of the Sn₄P₃/C and 269.5 mA h g⁻¹ of the SnSb/C after the same number of cycles. Meanwhile, the retention rates with respect to their second cycle capacities are 77.65% and 69.74%, for the Sn₄P₃/C and SnSb/C respectively and they are much lower than that of Sn₅SbP₃/C electrode (95.2% of the second cycle capacity). Accordingly, the discharge-charge profiles of the three electrodes at the current density of 500 mA g⁻¹ at the 1ˢᵗ, 2ⁿᵈ, 5₀ᵗʰ, 1₀₀ᵗʰ and 2₀₀ᵗʰ cycles are presented in Figs. 5b-d, respectively. The profiles display a long plateau at around 0.01-0.3 V (Sn₅SbP₃/C), 0.01-0.5 V (Sn₄P₃/C) and 0.2-0.3 V (SnSb/C), respectively, in their first discharge process. The plateaus are mainly due to the formation of the SEI layer. Several discharge and charge plateaus are observed after cycling, however. These results are in agreement with the CV results (Fig. 4a, Fig. S4a, b), and reflect the stepwise alloy phase transition reactions (Eqs. 2-4). The Sn₅SbP₃/C composite electrode also exhibits higher and more stable capacities than the binary composite electrodes at the higher current density (1 A g⁻¹), as shown in Fig. 5e. A capacity of 370.5 mA h g⁻¹ is delivered by the Sn₅SbP₃/C composite in the 2₀₀ᵗʰ cycle, which is higher than 251.5 mA h g⁻¹ of the Sn₄P₃/C and 1₀₆ mA h g⁻¹ of the SnSb/C in the same number of cycles.
Fig. 5. (a) Cycling performance and Coulombic efficiency of three different materials tested at a current density of 500 mA g\(^{-1}\) in the range of 0.01-2V (vs. Na\(^+\)/Na). Galvanostatic charge-discharge curves of (b) Sn\(_5\)SbP\(_3\)/C composite, (c) Sn\(_4\)P\(_3\)/C and (d) SnSb/C for the 1\(^{st}\), 2\(^{nd}\), 50\(^{th}\), 100\(^{th}\) and 200\(^{th}\) cycles tested at current density of 500 mA g\(^{-1}\) in the range of 0.01-2V (vs. Na\(^+\)/Na). (e) Cycling performance and Coulombic efficiency of Sn\(_5\)SbP\(_3\)/C, Sn\(_4\)P\(_3\)/C and SnSb/C tested at a current density of 1000mA g\(^{-1}\) in the range of 0.01-2V (vs. Na\(^+\)/Na).

It is well known that one of the deadly problems for alloy-based anodes in SIBs is the huge
volume expansion during charging/discharging, which leads to continuous pulverization upon cycling[32, 33]. Therefore, the morphology changes before and after 100 cycles were examined by SEM, as shown in Figs. 6 a-f. The Sn5SbP3/C composite electrode shows no obvious morphological change and only a few micro cracks were observed after 100 cycles. The Sn4P3/C and SnSb/C electrodes, however, show not only more cracks, but these cracks are also much coarser. Some of the cracks can be as wide as 5 μm and hundreds of micrometers long after 100 cycles. The results indicate that the volume changes are alleviated effectively in the ternary composite, and hence, it has the superior electrochemical performance.

Fig. 6. FESEM image of a) fresh Sn5SbP3/C electrode, b) Sn5SbP3/C composite after 100
cycles at 1000 mA g⁻¹, c) fresh Sn₄P₃/C electrode, d) Sn₄P₃/C composite after 100 cycles at 1000 mA g⁻¹, e) fresh SnSb/C electrode, and f) SnSb/C composite after 100 cycles at 1000 mA g⁻¹.

The superior electrochemical performance of the ternary Sn₅SbP₃/C composite can be attributed to its unique structure, where the Sn₄P₃, SnSb and Sn nanoparticles (NPs) are in intimate contact with each other and form heterojunctions in the conductive carbon matrix. The three phases may play different and complementary roles in the ternary Sn₅SbP₃/C composite electrode because that the Sn₄P₃ phase has a high capacity but a very low electrical conductivity, the Sn and SnSb should have good electric conductivity. (Table S2). Therefore the Sn and SnSb phases together with the conductive carbon matrix could form continuous conductive networks for faster diffusion of electrons[23] which in turn improves the electrochemical performance of the Sn₄P₃. The Sn₄P₃ and SnSb have different reaction potentials according to the CV results (Fig. 4a and S4). Therefore it is expected that the reaction products of NaₓSn, NaᵧSb and NaᵦP in the ternary composite electrode would act as buffers to support each other and moderate the volume expansion during cycling.[23, 25, 34] Furthermore, the three phases can form heterojunctions in the interfacial areas (Fig. 3), which will induce an electric field within the nanocrystals, and hence encourage a rapid interfacial ion/electron transfer.[17] In addition to the three active phases, the carbon in the composite can play an important role as well. The effect of the carbon content in the ternary Sn₅SbP₃/C composite on the Sn₅SbP₃/C composite was also investigated and the results are shown in Fig. S5. It seems that that the optimum carbon addition in the ternary Sn₅SbP₃/C composite is 12.5 wt. %. Considering that the carbon black only delivers a capacity of around 100 mA h g⁻¹ (Fig. S6), the capacity in the Sn₅SbP₃/C composite is largely attributed from the three active phases. Nevertheless, the addition of carbon can benefit the cycle life due to its good electric conductivity and buffer effect (Fig. S5). The last, but still important, benefit brought by the
nano sized multiphase structure of the Sn$_5$SbP$_3$/C electrode is efficient Na ion transportation, which in turn enhances the performance of the electrode. All these factors synergistically contribute to better capacity and cycling performance and high rate capability by offering high electrical conductivity, fast ion transportation and high structure strength.

4. Conclusions

In summary, Sn$_5$SbP$_3$/C composite was successfully synthesized by a facile ball-milling technique. When tested as anode in sodium-ion batteries, the Sn$_5$SbP$_3$/C shows a superior electrochemical performance to the binary Sn$_4$P$_3$/C or SnSb/C electrode, especially at higher current densities (500 mA g$^{-1}$ and 1000 mA g$^{-1}$). The excellent electrochemical performance of the Sn$_5$SbP$_3$/C electrode arises from a synergetic effect, which is due to the mutual buffering effect of the multiple phases, the fine grain size of the active phases, the conductive carbon matrix which enhances the integrity and the good electrical conductivity of the electrode. Our results encourage the exploration of superior cycle stable alloy based anode materials through the low-cost, eco-friendly, and scalable ball milling method for rechargeable batteries.

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References
Large-scale synthesis of Sn$_8$SbP$_3$/C composite by ball milling for superior stable sodium-ion battery anode

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Fig.S1 Raman spectra of Sn₅SbP₃/C, Sn₄P₃/C and SnSb/C powder
Fig. S2 a) Typical XPS survey spectra of the Sn₅SbP₃/C and the corresponding b) Sn 3d c) Sb 3d d) P 2p and e) C 1s XPS spectra
Fig. S3 EDS mapping of a) Sn₄P₃/C, b) SnSb/C powders
Fig. S4 Cyclic voltammograms of a) Sn₄P₃/C, b) SnSb/C electrodes tested at a scanning rate of 0.05 mV/s
Fig. S5 a) X-ray diffraction (XRD) patterns and b) Cycling performance at the current density of 1A g⁻¹ of SnₓSbP₃-12.5% carbon black (CB), SnₓSbP₃-no carbon, SnₓSbP₃-5% carbon and SnₓSbP₃-20% carbon
Fig. S6 Cycling performance of carbon black (CB) at the current density of 100 mA g⁻¹
Fig. S7 Cycling performance at the current density of 1A g$^{-1}$ of Sn$_5$SbP$_3$/C, SnSbP/C and Sn$_4$SbP$_4$/C
Fig. S8 FESEM images (1000X) of a) Sn$_3$SbP$_3$/C, b) Sn$_4$P$_3$/C, c) SnSb/C after 100 cycles at 1000 mA g$^{-1}$. 
Fig. S9 Cycling performance at the current density of 1 A g$^{-1}$ of Sn$_5$SbP$_3$/C, Sn$_4$P$_3$/C, SnSb/C and Sn$_4$P$_3$/C+SnSb/C
Table S1 EDS mapping composition of three different powders in wt.%

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Table S2 Comparison electrical conductivity of Sn, Sb and P

<table>
<thead>
<tr>
<th>Element</th>
<th>Electrical conductivity (S cm⁻¹)</th>
<th>Theoretical capacity (mA h g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn</td>
<td>9*10⁴</td>
<td>847</td>
</tr>
<tr>
<td>Sb</td>
<td>2.5*10⁴</td>
<td>660</td>
</tr>
<tr>
<td>P</td>
<td>1*10⁻¹⁴</td>
<td>2596</td>
</tr>
</tbody>
</table>