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Multi-geometric carbon encapsulated SnP₃ composite for superior lithium/potassium ion batteries†

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Tin phosphide has gained extensive attention as a prospective anode for lithium/potassium ion batteries because of its high theoretical capacity. Nevertheless, the fast capacity fading, which is induced by the huge volume expansion and poor electrical conductivity during cycling, severely restricts its practical applications. In this work, a SnP₃-CNTs/KB composite with a SnP₃ content as high as 90 wt% was successfully synthesized by a two-step ball milling method. SnP₃ nanoparticles were tightly encapsulated in multi-geometric composite carbon layers to efficiently relieve the volume changes and enhance conductivity. Specifically, the resulting SnP₃-CNTs/KB anode showed a specific capacity up to 998.6 mA h g⁻¹ after 100 cycles at 50 mA g⁻¹ and 810.4 mA h g⁻¹ after 500 cycles at 1000 mA g⁻¹ for lithium ion batteries. For potassium ion batteries, a high reversible capacity of 200.2 mA h g⁻¹ was achieved after 200 cycles at 1000 mA g⁻¹. This work affords a new insight for exploring excellent support structures of tin phosphide-based anodes.

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1. Introduction

Lithium-ion batteries (LIBs) have been dominating the lugable energy storage field, but limited availability of lithium resources has increasingly turned out to be a major factor inhibiting the widespread use of LIBs.^{1,2} Compared with LIBs, potassium-ion batteries (PIBs) have the potential to be used as low-cost and high-voltage batteries because of the abundant potassium resources and the low standard redox potential of potassium in a non-aqueous electrolyte, and therefore they are receiving increasing attention.^{3,4} However, similar to LIBs, PIBs are faced with the problem of limited energy density and poor cycling performance of anode materials, which severely restricts their application.^{5,6}

Among all types of anode materials for LIBs and PIBs, tin phosphides (e.g., Sn₄P₃ and SnP₃) have high theoretical capacities comparable to phosphorus, but have relatively lower

volume expansion due to the incorporation of tin, which is an emerging anode candidate for LIBs/PIBs.^{7,8} Nevertheless, the inherent low electrical conductivity, coupled with huge volume expansion during alloying/de-alloying with lithium and potassium, results in rapid capacity degradation and inferior rate capability of pure tin phosphides.⁹

To enhance the performance of tin phosphides, many efforts have been devoted to alleviate volume expansion of tin phosphides and enhance electrode conductivity.¹⁰⁻¹³ Current research mainly focuses on constructing tin phosphide-carbon composites, in which carbon not only improves the structural stability of tin phosphides but also provides convenient channels for electrons/ions.¹⁴⁻¹⁶ Despite these advances, the dominant structure required to solve the two key problems of poor electrical conductivity and huge volume expansion of tin phosphide-based anodes to achieve the desired performance is not clear. Moreover, previous studies have mainly involved carbon support materials with a single-geometric structure, and few reports are available about the preparation of tin phosphide/carbon composites by combining various carbon materials with multi-geometric structures as support materials.

In this work, carbon nanotubes (CNTs) and Ketjen black (KB) were used to construct a multi-geometric composite carbon support for tin phosphide using a ball milling method. As the anode of LIBs, the SnP₃-CNTs/KB composite provided a high capacity of 810.4 mA h g⁻¹ after 500 cycles at

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1000 mA g⁻¹. When used as the anode for PIBs, SnP₃-CNTs/KB exhibited a high specific capacity up to 200.2 mA h g⁻¹ after 200 cycles at 1000 mA g⁻¹.

2. Experimental

2.1. Chemicals

Red phosphorus (98.5%) was bought from Energy Chemicals. Tin particles (99.8%) were bought from 3A Chemicals. Multi-walled carbon nanotubes (CNTs, >95%) were bought from Aladdin. Ketjen black (KB, Carbon ECP) was bought from DodoChem.

2.2. Preparation of SnP₃ particles

SnP₃ particles were made by ball milling tin particles and red phosphorus under an argon atmosphere in a 1 : 3 molar ratio. A 20 : 1 weight ratio of milling balls to particles was used and the speed of the mill was set at 400 rpm for 40 h.

2.3. Preparation of the SnP₃-CNTs/KB composite

SnP₃ particles (90 wt%), CNTs (5 wt%) and KB (5 wt%) were milled under an argon atmosphere to prepare the SnP₃-CNTs/KB composite. A 20 : 1 weight ratio of milling balls to particles was used and the speed of the mill was set at 400 rpm for 24 h. The SnP₃-CNTs composite was made by milling SnP₃ particles (90 wt%) with CNTs (10 wt%), and the SnP₃-KB composite was made by milling SnP₃ particles (90 wt%) with KB (10 wt%).

2.4. Characterization

X-ray diffraction (XRD) patterns were recorded on an X-ray diffractometer (Rigaku SmartLab). Transmission electron microscopy (TEM) images were captured using a Tecnai F30 TEM system (300 kV). Scanning electron microscopy (SEM) images were obtained using a SEM system (Hitachi SU8010). X-ray photoelectron spectroscopy (XPS) spectra of materials were obtained with an XPS spectrometer (Thermo ESCALAB 250XI).

2.5. Electrochemical measurements

The electrochemical properties of the samples were evaluated by assembling CR2032 button half cells using 16 mm lithium discs or potassium discs as counter/reference electrodes. Copper foil was utilized as a collector and coated with a slurry of the active material and carboxymethyl cellulose in a weight ratio of 9 : 1. 12 mm diameter discs with a typical loading of 0.6–1.0 mg cm⁻² of the active material were used as working electrodes, and the battery capacity was calculated based on the mass of the active material. For LIBs, Celgard2325 acted as the separator, and 1.0 M LiPF₆ in EC/DMC (5% FEC) was used as the electrolyte. For PIBs, glass fiber acted as the separator, and 1.0 M KFSI in EC/DEC was used as the electrolyte. Cyclic voltammetry (CV) and discharge-charge tests were conducted within 0.01–3.0 V (vs. Li⁺/Li) and 0.01–2.0 V (vs. K⁺/K), respectively.

3. Results and discussion

The preparation process of the SnP₃-CNTs/KB composite is shown in Fig. 1. Tin and red phosphorus were first ball-milled to form SnP₃ nanoparticles. After further ball-milling with CNTs and KB, a dual-carbon conducting network structure was formed around the SnP₃ nanoparticles, in which the SnP₃ content was as high as 90 wt%. This structure not only favors the shortening of transport distances of ions and electrons, but also alleviates large volume changes during charging/discharging, thus boosting the rate and cycling performance.¹⁷

Fig. 2 depicts the XRD patterns of the as-synthesized composites, all of which fit well with the hexagonal structure of SnP₃ (JCPDS no. 72-0853). The main peaks at 21.9°, 24.1° and 32.8° belong to the (012), (110), and (202) planes of SnP₃, respectively, suggesting that the crystal structure of SnP₃ was not damaged during the milling process. However, characteristic peaks were not observed for CNTs or KB due to their low loading contents (10 wt%) and reduced crystallinity.

The morphologies of the composites are shown in Fig. 3a–c. Under the action of the shear force generated during the high-energy ball milling (HEBM) process, CNTs and KB achieved

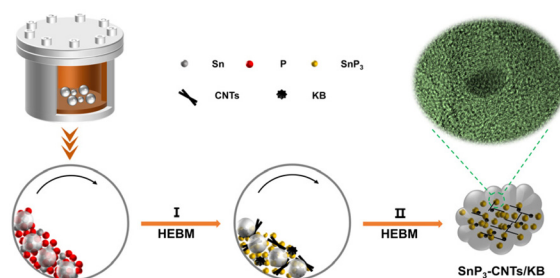


Fig. 1 Schematic diagram of the fabrication process of the SnP₃-CNTs/KB composite.

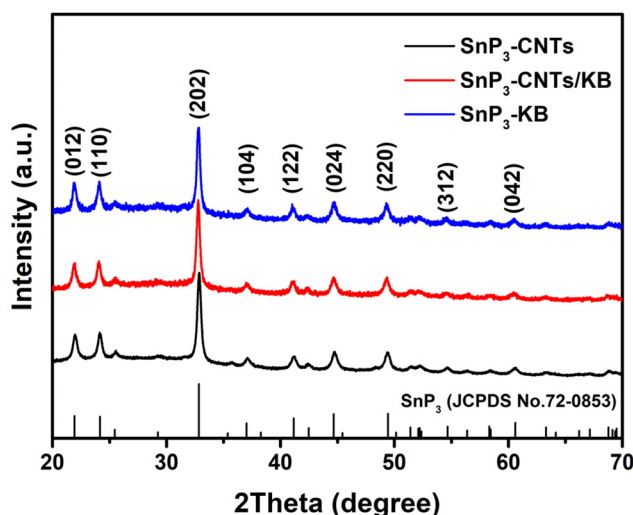


Fig. 2 XRD patterns of the as-synthesized composites.

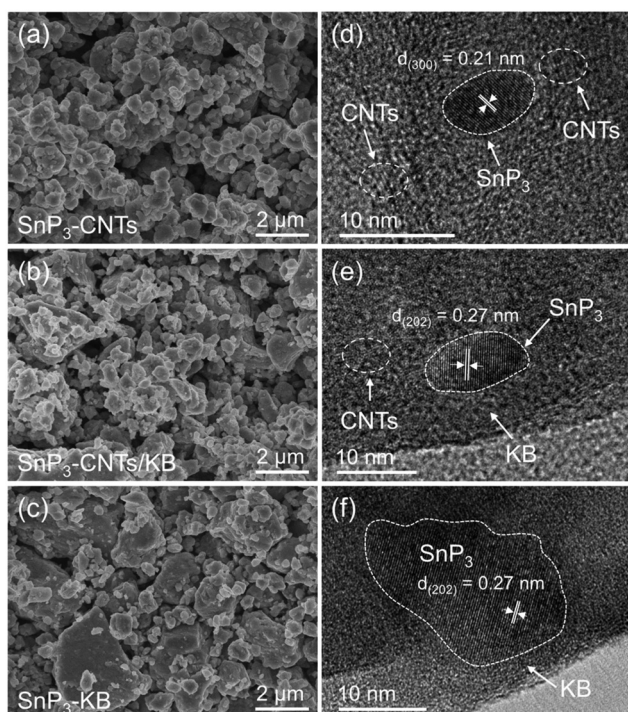


Fig. 3 SEM and HRTEM images of the (a and d) SnP₃-CNTs, (b and e) SnP₃-CNTs/KB, and (c and f) SnP₃-KB composites.

homogeneous mixing with the SnP₃ particles. The HRTEM image displays an interplanar distance of 0.21 nm (Fig. 3d), corresponding to the (300) plane of SnP₃ (JCPDS no. 72-0853). In Fig. 3e and f, the interplanar distance of 0.27 nm can be indexed to the (202) plane of SnP₃.

Moreover, SnP₃ particles were surrounded by the CNTs/KB-formed multi-geometric network (Fig. 3e), beneficial for relieving the volume expansion of SnP₃ and promoting charge transfer during the charging/discharging process.¹⁸ The obtained SnP₃-CNTs and SnP₃-KB composites exhibited structures similar to that of the SnP₃-CNTs/KB composite, but only with a single-geometric carbon structure.

The surface component and valence states of the SnP₃-CNTs/KB composite were investigated using XPS. Sn, P, O, and C elements were detected from the composite surface (Fig. 4a). For the high-resolution spectra of Sn 3d (Fig. 4b), 496.0 and 487.6 eV belong to Sn 3d_{3/2} and Sn 3d_{5/2}, respectively.¹⁹ For the P 2p spectrum (Fig. 4c), 130.6 and 129.8 eV are attributed to P 2p_{1/2} and P 2p_{3/2}, respectively, while 133.9 eV is attributed to the phosphate species formed on the surface of SnP₃ when it was exposed to air. In Fig. 4d, 284.4, 285.7, and 288.8 eV are assigned to C-C, C-O-C, and O-C=O bonds, respectively.²⁰

The surface areas and pore structures of the SnP₃-CNTs/KB composite, CNTs, and KB were studied through N₂ adsorption/desorption isotherms. It is observed from Fig. S1(a-c)† that all samples display a representative type-IV isothermal curve, revealing the mesoporous feature. The calculated BET surface areas and dominant pore diameters of the SnP₃-CNTs/KB composite, CNTs, and KB are 30.567 m² g⁻¹ (3.86 nm),

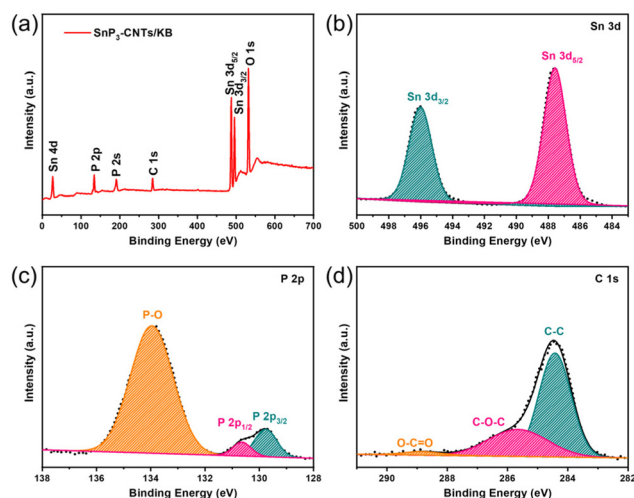
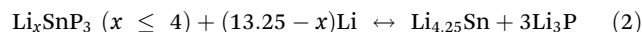
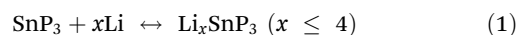


Fig. 4 (a) Survey XPS spectrum and high-resolution XPS spectra of (b) Sn 3d, (c) P 2p, and (d) C 1s in the SnP₃-CNTs/KB composite.

184.468 m² g⁻¹ (3.44 nm), and 810.815 m² g⁻¹ (3.85 nm), respectively (Fig. S1(d-f)†). The porous structure and high specific surface area are conducive to providing more available channels for ion transport and rich active sites for ion insertion, thereby improving electrochemical lithium/potassium storage performance.

The electrochemical behavior of SnP₃ particles and the SnP₃-CNTs/KB composite as anodes for LIBs was investigated by CV in half cells. As shown in Fig. S2a,† reduction peaks at 0.3 and 0.7 V as well as oxidation peaks at 0.75 and 1.45 V were observed in the CV curves of SnP₃ particles, attributed to the reversible intercalation/conversion reactions:²¹



In subsequent cycles, the intensity of these redox peaks gradually decreased, indicating that the electrochemical reaction of pure SnP₃ particles is less reversible (Fig. S2a†). In contrast, these peaks of the SnP₃-CNTs/KB composite can be repeated and approximately overlapped after the first cycle (Fig. S2b†), showing greatly improved reversibility, which was also confirmed by its overlapped galvanostatic charge/discharge curves (Fig. S2c†).

Fig. 5a presents the rate performance of the SnP₃-CNTs/KB composite. Compared to SnP₃-CNTs and SnP₃-KB (Fig. S3†), the SnP₃-CNTs/KB composite electrode exhibited a superior rate capability and delivered capacities of 1230.5, 1086.3, 898.0, 804.9, and 715.2 mA h g⁻¹ at 50, 100, 200, 500, and 1000 mA g⁻¹, respectively. After 100 cycles at 50 mA g⁻¹ (Fig. 5b), the SnP₃-CNTs/KB composite electrode displayed a capacity as high as 998.6 mA h g⁻¹ with a coulombic efficiency close to 100%, higher than those of SnP₃-KB and SnP₃-CNTs (Fig. S4 and S5†). After 500 cycles at 1000 mA g⁻¹, the SnP₃-CNTs/KB electrode presented a specific capacity up to 810.4 mA h g⁻¹ (Fig. 5c). EIS Nyquist plots of the composites

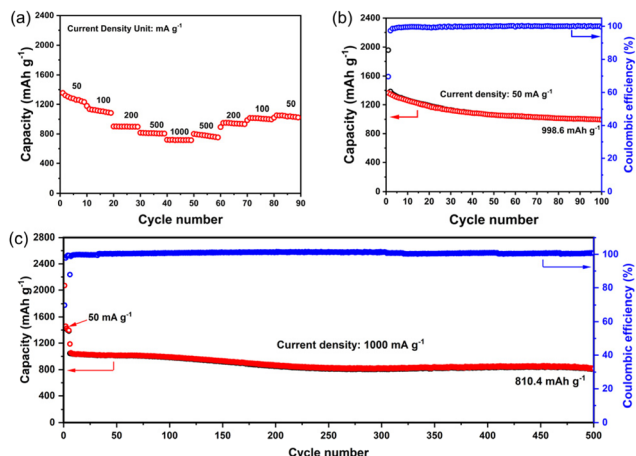


Fig. 5 Electrochemical performance for LIBs: (a) rate performance of the SnP₃-CNTs/KB composite. (b) Cycling performance of the SnP₃-CNTs/KB composite at 50 mA g⁻¹. (c) Long-term cycling performance of the SnP₃-CNTs/KB composite at 1000 mA g⁻¹.

are shown in Fig. S6.† It is obvious that SnP₃-CNTs/KB exhibited a smaller charge-transfer impedance (R_{ct}) than SnP₃-CNTs and SnP₃-KB, demonstrating the faster charge transfer kinetics of SnP₃-CNTs/KB. To our knowledge, the lithium storage capacity of the SnP₃-CNTs/KB electrode after long cycling is significantly higher than those of some tin phosphide-based anodes reported in the previous literature (Table 1).^{20–28}

The pseudocapacitive charge storage and electrochemical transport kinetics of SnP₃-CNTs/KB were further explored by CV measurements with different sweep rates (Fig. 6a). The relationship between the peak current and scan rate can be calculated according to eqn (3) and (4).²⁹

$$i = av^b \quad (3)$$

$$\log(i) = b \log(v) + \log(a) \quad (4)$$

$$i = k_1v + k_2v^{0.5} \quad (5)$$

In the equations, i is the peak current, v is the scan rate, and a and b are adjustable parameters. The pseudocapacitive

Table 1 Summary of cycling performances of some tin phosphides for LIBs

Materials	Current density (mA g ⁻¹)	Cycle number	Capacity (mAh g ⁻¹)	Ref.
Sn ₄ P ₃ -NC	1000	400	506.9	22
SnP/C	1000	500	610	23
Sn ₄ P ₃ /C	200	100	727	23
MWCNTs/Sn ₄ P ₃ @C	1000	1000	569.5	24
Sn ₄ P ₃ /C composite	1000	400	760	20
SnP ₃ /C	100	100	395	21
Sn ₄ P ₃ nanoparticles	1000	90	207	25
Mn-doped Sn ₄ P ₃	1000	200	255	26
Sn ₃ P ₄ /Sn ₄ P ₃ @C	1000	100	513	27
Sn ₃ P ₃ /C-2	1000	300	366	28
SnP ₃ -CNTs/KB	1000	500	810.4	This work

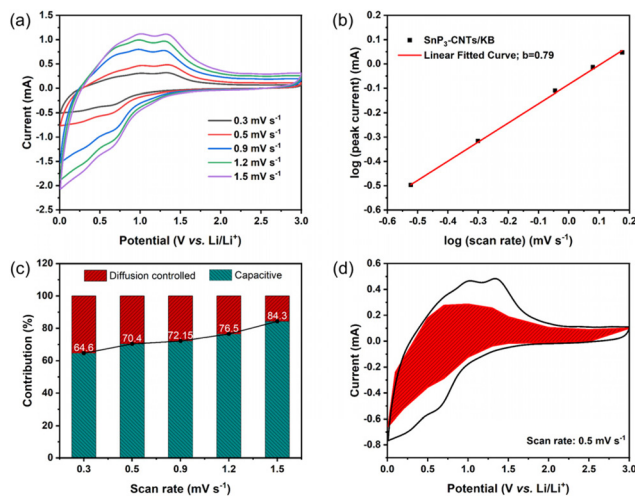


Fig. 6 (a) CV curves of the SnP₃-CNTs/KB composite at different scan rates. (b) The b value obtained by plotting $\log i$ vs. $\log v$ lines. (c) Histograms of capacitive contribution to the total capacity of the SnP₃-CNTs/KB composite at different scan rates. (d) Illustration of charge contribution from capacitive and diffusion-controlled processes of the SnP₃-CNTs/KB composite at 0.5 mV s⁻¹.

contribution is further estimated quantitatively according to eqn (5),²⁹ where k_1 and k_2 are the adjustable parameters. In Fig. 6b, the calculated b value corresponding to the anodic peak at ~ 1.32 V was about 0.79, indicating that the SnP₃-CNTs/KB electrode exhibited both pseudocapacitance and diffusion control behavior.³⁰

Fig. 6c summarizes the pseudocapacitive contributions of SnP₃-CNTs/KB, which are 64.6%, 70.4%, 72.15%, 76.5%, and 84.3% at 0.3, 0.5, 0.9, 1.2, and 1.5 mV s⁻¹, respectively. Fig. 6d shows the detailed pseudocapacitive fraction of SnP₃-CNTs/KB compared to the whole current at 0.5 mV s⁻¹. Therefore, the contribution of pseudocapacitance may be part of the reason for the outstanding electrochemical performance of SnP₃-CNTs/KB electrodes.

The electrochemical properties of the SnP₃-CNTs, SnP₃-CNTs/KB, and SnP₃-KB composites as anodes for PIBs were tested in half cells. The storage behavior of potassium ions was evaluated by CV. As shown in Fig. S7,† a major peak at around 0.01 V was observed in the initial cathodic scan. In the anodic scan, a broad peak centered at 0.75 and a weak peak at 1.4 V can be observed, assigned to the depotassiation processes of K-Sn/K-P.³¹ Fig. 7a presents the rate performance of the composites. Compared to SnP₃-CNTs and SnP₃-KB, the SnP₃-CNTs/KB composite electrode exhibited a superior rate capability and delivered capacities of 395.3, 386.5, 332.2, 281.6, and 220.2 mA h g⁻¹ at 50, 100, 200, 500, and 1000 mA g⁻¹, respectively. The initial charge/discharge voltage profiles of the composites at 50 mA g⁻¹ are depicted in Fig. 7b. After 200 cycles at 1000 mA g⁻¹, the SnP₃-CNTs/KB electrode displayed a specific capacity up to 200.2 mA h g⁻¹ (Fig. 7c).

Fig. 7d shows the initial coulombic efficiency (ICE) of the composites at 1000 mA g⁻¹. The ICE values of the SnP₃-CNTs,

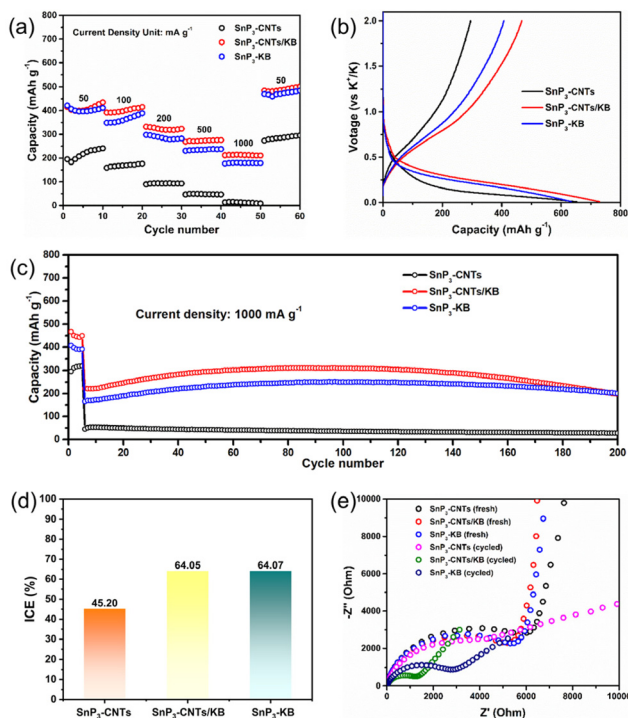


Fig. 7 Electrochemical performance for PIBs: (a) rate performances of the composites. (b) Initial charge/discharge voltage profiles of the composites at 50 mA g^{-1} . (c) Long-term cycling performances of the composites at 1000 mA g^{-1} . (d) Comparison of the initial coulombic efficiency (ICE) of the composites at 1000 mA g^{-1} . (e) EIS Nyquist plots of the SnP_3 -CNTs, SnP_3 -CNTs/KB, and SnP_3 -KB composites before and after 200 cycles.

SnP_3 -CNTs/KB, and SnP_3 -KB composites are 45.20%, 64.05%, and 64.07%, respectively. EIS Nyquist plots of the composites before and after 200 cycles are shown in Fig. 7e. The R_{ct} values of SnP_3 -CNTs/KB both before and after cycling are significantly lower than those of the other two electrodes. As displayed in Table 2, the reversible capacity of SnP_3 -CNTs/KB after long cycling at a high current density is higher than those of most previously reported tin phosphide-based anodes for PIBs.^{15,16,31–38}

Table 2 Summary of cycling performances of some tin phosphides for PIBs

Materials	Current density (mA g^{-1})	Cycle number	Capacity (mA h g^{-1})	Ref.
$\text{Sn}_4\text{P}_3/\text{C}$	50	50	307.2	31
$\text{Sn}_4\text{P}_3/\text{carbon fiber}$	500	1000	160.7	32
$\text{Sn}_4\text{P}_3/\text{RGO}$	600	60	156	33
$\text{Sn}_4\text{P}_3/\text{C}$	500	800	181.5	34
$\text{SnP}_{0.94}/\text{GO}$	200	100	106	15
SnP_3/C	500	80	225	35
r- SnP/C	1000	200	235.9	36
T- SnP	500	180	298.2	37
$\text{SnP}_3/\text{CNTs-20}$	1000	150	190	16
SnP_3 -CNTs/KB	1000	200	200.2	This work

Based on all the above-mentioned results, the SnP_3 -CNTs/KB composite used as anodes displayed better lithium/potassium storage performance than the SnP_3 -KB and SnP_3 -CNTs composites, which mainly depends on the multi-geometric design of the composite carbon support. The high surface area of KB could enable a uniform distribution and tight encapsulation of SnP_3 particles, while the high conductivity of KB and CNTs yielded a dual conductive network in the SnP_3 -CNTs/KB composite. Such a unique structure could greatly enhance the electronic conductivity and increase the mechanical strength of the composite, and hence improve its rate performance and prolong its cycle life. The attractive lithium/potassium storage properties of the SnP_3 -CNTs/KB composite demonstrate its wide range of applications.

Conclusions

The SnP_3 -CNTs/KB composite with a SnP_3 content as high as 90 wt% was successfully synthesized by a two-step HEBM method, which delivered a high reversible capacity of $998.6 \text{ mA h g}^{-1}$ over 100 cycles at 50 mA g^{-1} and $810.4 \text{ mA h g}^{-1}$ even after 500 cycles at 1000 mA g^{-1} for LIBs. Moreover, the achieved capacities of SnP_3 -CNTs/KB for PIBs, especially at high current densities, are better than those of most other reported tin phosphide anodes. These results might be attributed to the multi-geometric structure of the carbon support in the composite, which is not only beneficial for reducing the transfer distance of ions and electrons, but also can relieve large volume expansion during the charging/discharging process. This study affords a new insight for enhancing the performance of tin phosphide-based anodes.

Author contributions

Zhongliang Hu: data curation, formal analysis, and writing – original draft; Xixia Zhao: conceptualization, funding acquisition, methodology, supervision, and writing – review & editing; Yanqing Zhao: data curation and investigation; Qian Zhao: funding acquisition and supervision; Xin Zhao: funding acquisition and supervision; Guijuan Wei: funding acquisition, supervision, and writing – review & editing; Honglei Chen: funding acquisition, supervision, and writing – review & editing.

Data availability

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Conflicts of interest

The authors declare no conflict of interest associated with this article.

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