

GeP₃/Ketjen Black Composite: Preparation via Ball Milling and Performance as Anode Material for Sodium-ion Batteries

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Abstract: Metal phosphides have been studied as prospective anode materials for sodium-ion batteries (SIBs) due to their higher specific capacity compared to other anode materials. However, rapid capacity decay and limited cycle life caused by volume expansion and low electrical conductivity of phosphides in SIBs remain still unsolved. To address these issues, GeP₃ was first prepared by high-energy ball milling, and then Ketjen black (KB) was introduced to synthesize composite GeP₃/KB anode materials under controlled milling speed and time by a secondary ball milling process. During the ball milling process, GeP₃ and KB form strong chemical bonds, resulting in a closely bonded composite. Consequently, the GeP₃/KB anodes was demonstrated excellent sodium storage performance, achieving a high reversible capacity of 933.41 mAh·g⁻¹ at a current density of 0.05 A·g⁻¹ for a special formula of GeP₃/KB-600-40 sample prepared at ball milling speed of 600 r/min for 40 h. Even at a high current density of 2 A·g⁻¹ over 200 cycles, the capacity remains 314.52 mAh·g⁻¹ with a retention rate of 66.6%. In conclusion, this work successfully prepares GeP₃/KB anode-carbon composite for electrodes by high-energy ball milling, which can restrict electrode volume expansion, enhance capacity, and improve cycle stability of SIBs.

Key words: sodium-ion battery; GeP₃/C composite; Ketjen black; ball milling

SIBs are gaining attention as an attractive alternative or supplement for lithium-ion batteries (LIBs) because of high abundance of raw materials, low cost, widespread global distribution, and similarity in physical and chemical properties of Li and Na^[1-5]. However, sodium has larger ionic radius, heavier atomic mass, and higher standard electrode potential than lithium, leading to unsatisfied electrochemical performance in SIBs^[6-8], which is mainly influenced by the structure and qualities of the electrodes. Therefore, researchers increasingly focus on seeking electrode materials with exceptional sodium storage properties^[9]. Phosphorus-based anodes achieve exceptionally high theoretical capacity (2596 mAh·g⁻¹) through the alloying reaction. However, low electrical conductivity (10⁻¹⁴ S·cm⁻¹) and large volume expansion during sodium storage resulted in poor cycling stability and rate capability^[10-13]. Recently, several studies demonstrated that the metal phosphides M_xP_y (M = Co, Ni, Ge) can enhance the reversibility, electrical conductivity, and stability of phosphorus-based anode^[14].

Metal phosphides M_xP_y (M = Co, Ni, Ge) have significant advantages including extra alloying reaction between metal and Na⁺, improved conductivity and appropriate redox potential (~0.3 V for Na/Na⁺)^[15-17], leading to enhanced electrochemical performance. Germanium phosphide (GeP_x) is germanium-phosphorus alloy and possesses different forms (GeP, GeP₃, GeP₅, etc.). Since Li *et al.*^[18] synthesized GeP₅ by high-energy ball milling and applied it in LIBs, it has been widely investigated for energy storage. Compared with GeP and GeP₅, GeP₃ has higher capacity and softer bonding properties, which can effectively adapt to the mechanical stress and deformation during sodiation/desodiation^[19]. However, similar to other metal phosphides, GeP₃ possesses the problem of capacity decay during cycling caused by volume expansion and poor conductivity as well^[6, 11, 20]. To solve this problem, general strategies including nanosizing of the metal phosphides and combining with carbonaceous materials have been applied^[21-22]. The incorporation of carbon materials, such as graphene,

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conductive carbon, and carbon nanotubes (CNTs), is able to buffer the volume change and further increase the conductivity of the phosphides^[23-28]. In addition, a carbon matrix is ideal to prevent the agglomeration of nanosized materials, maximizing the electrochemical performance.

High-energy ball milling is an efficient, economical and large-scale technique for preparing nanocomposites of carbon-based alloy-type anode materials. It has been widely used to enhance the capacity and improve the cycle stability of alloy-type anode materials to alleviate the huge volume changes. Ouyang *et al.*^[29] prepared Ge@FLG nanocomposite by plasma assisted ball milling. After 50 charge/discharge cycles at 0.4C, Ge@FLG nanocomposite retained a capacity of 846.3 mAh·g⁻¹, and the capacity retention rate was 86% of the initial value. Nam *et al.*^[30] synthesized layered GeP₃ and GeP₃/C nanocomposites by high-energy ball milling, and then studied their electrochemical properties and reaction mechanism as SIB anodes. The GeP₃/C anode showed a capacity of 984 mAh·g⁻¹ with a capacity retention rate of 95% after 30 cycles at 50 mA·g⁻¹, and a rate performance of 520 mAh·g⁻¹ after 30 cycles at a current density of 50 mA·g⁻¹. A germanium phosphide composite modified with two carbon species (GeP₃/C@rGO) was prepared by high-energy ball milling. The carbon layer effectively stabilized the internal GeP₃ nanoparticles, while the graphene network protected the outer surface from electrolyte erosion. The synergistic effect between two carbon matrices resulted in higher conductivity, provided the maximum surface area to ensure the rapid diffusion of Na⁺ and electrons, and effectively inhibited the volume change and loss of active materials during the cycle. As a result, GeP₃/C@rGO had a high reversible capacity of 1084 mAh·g⁻¹ at 0.05 A·g⁻¹ and 823 mAh·g⁻¹ after 400 cycles at 0.2 A·g⁻¹^[31]. The carbonaceous material in these composites not only improves the electrical conductivity, but also acts as a substrate to buffer the volume expansion of GeP₃.

GeP_x exhibits low conductivity and large volume expansion during charge and discharge, resulting in poor rate performance and cycle stability. Therefore, improving its structural stability and suppressing volume expansion are key to enhancing the electrochemical performance of GeP_x. This study used germanium powder and red phosphorus powder to synthesize GeP₃ by high-energy ball milling, and then followed by secondary ball milling to prepare GeP₃/C composite anode with KB.

1 Experimental

GeP₃/KB composites were prepared by a two-step

high-energy mechanical milling (HEMM) process. Germanium powder (99.999%, ≥200 mesh (74 μm), Aladdin Chemical Co., Ltd.) and red phosphorus (98.9%, Alfa Aesar) in a molar ratio of 1 : 3 were weighed in an argon-filled glove box and placed into a ball milling tank. The mixture was then subjected to planetary milling (QM-3SP4, Nanjing NanDa Instrument Plant) with a ball-to-powder mass ratio of 20 : 1 at a speed of 600 r/min for 48 h. GeP₃ was then mixed with KB (EC600JD, Suzhou Sinero Technology Co., Ltd.) in a mass ratio of 7 : 3, and the milling speed and time were adjusted in the same atmosphere. The mixture was ground at 300, 500, and 600 r/min for 10 and 40 h, respectively, to obtain the final GeP₃/KB nanocomposite product, labeled as GeP₃/KB-*x*-*y* (*x*: speed of ball milling, r/min; *y*: time of ball milling, h).

Characterization methods can be found in supporting materials.

2 Results and discussion

2.1 Structure and morphology characterizations

Fig. 1(a) shows the preparation process of GeP₃ and GeP₃/KB. GeP₃ was prepared by high-energy ball milling, and then KB was introduced at controlled milling speed and time, and the composite GeP₃/KB anode material was synthesized by a secondary ball milling process. The structures of bare GeP₃ and GeP₃/KB composites were examined by XRD (Fig. 1(b)) and Raman spectra (Fig. 1(c)). The bare GeP₃ prepared by mechanical alloying reaction using high-energy ball milling shows peaks at 2θ=34.5°, 47.2°, 51.8°, corresponding to (202), (024) and (220) crystal planes, respectively. The result is consistent with the previous report, indicating that bare GeP₃ was synthesized^[30]. The GeP₃/KB composites also present the characteristic peaks of bare GeP₃, albeit with decreased intensity, which indicates that hybridization with carbon does not affect the crystal structure of GeP₃^[32]. All GeP₃/KB composites show the characteristic peak of carbon material at 2θ=26°, corresponding to (002) crystal plane. The uniform mixing of GeP₃ and carbon matrix is also evidenced by weakened intensity of GeP₃ (202) peak. Higher rotation speeds and extended milling durations facilitate the formation of nanosized particles. As shown in Raman spectra (Fig. 1(c)), four characteristic peaks of bare GeP₃ in the range of 200–400 cm⁻¹ correspond to A_g¹, B_{2g}, B_{3g} and A_g² modes, respectively^[31]. After combined with carbon, D and G bands of carbon are near 1350 and 1590 cm⁻¹. D band is the defect of carbon atom lattice, and G band is caused by in-plane tensile vibration of carbon atom sp² hybridization, which indicates that the carbon in GeP₃/KB is amorphous^[33].

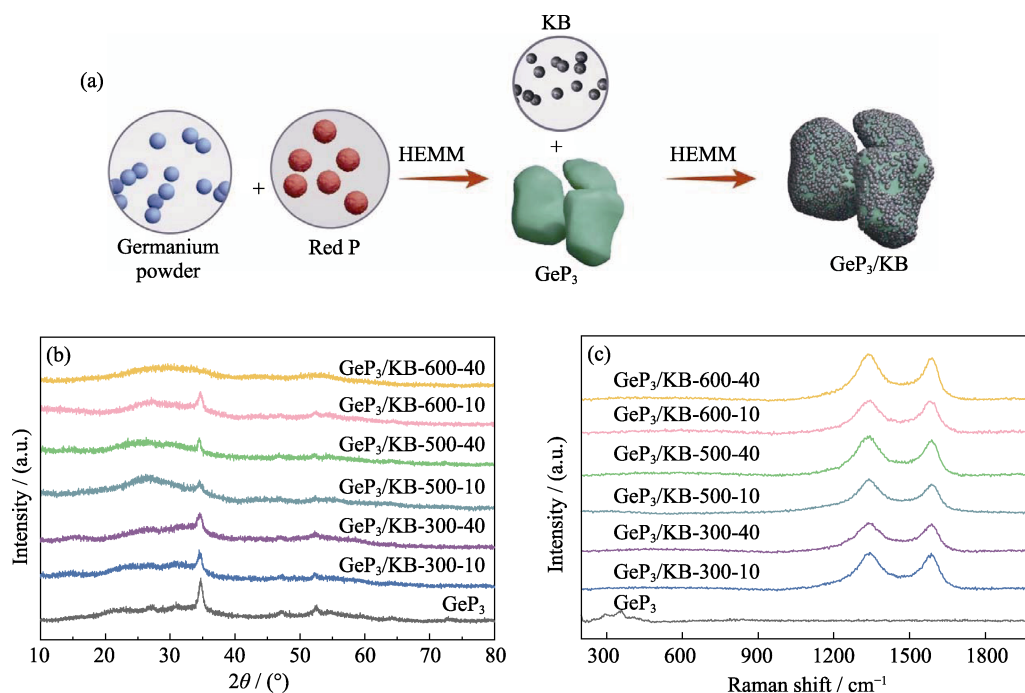


Fig. 1 Characterization of synthetic GeP₃/KB
(a) Schematic diagram of GeP₃/KB synthesis; (b) XRD patterns of GeP₃ and GeP₃/KB composites; (c) Raman spectra of GeP₃ and GeP₃/KB composites

In addition, the disorder and defect degree of GeP₃/KB structure can be reflected by I_D/I_G ^[34]. I_D/I_G of GeP₃/KB-300-10, GeP₃/KB-300-40, GeP₃/KB-500-10, GeP₃/KB-500-40, GeP₃/KB-600-10 and GeP₃/KB-600-40 were 1.00, 1.01, 1.03, 1.04, 1.01 and 1.05, respectively. GeP₃/KB-600-40 presents the highest I_D/I_G . It is shown that high rotation speed and long time of ball milling result in an increase in the disorder of C–C bonds and an increase in the sodium ion storage sites in GeP₃/KB.

The XPS survey spectra (Fig. S1) confirm the existence of P, C, O and Ge. In addition, the oxygen contents of the composites milled for 40 h are significantly higher than those of the composites milled for 10 h. GeP₃/KB-600-40 has the highest oxygen content of 38.92% (in atom) among composites. The oxygen content of GeP₃/KB samples increases with prolonged ball milling time. C1s XPS spectrum of GeP₃/KB-600-40 (Fig. 2(a)) can be deconvoluted into four different peaks: C–C, C–P, C–O and C=O. C–O and C=O bonds are formed due to the absorption of oxygen by exposure to air^[31]. The peak at ~129.2 eV in P2p XPS spectrum (Fig. 2(b)) is attributed to phosphide, and the peak at ~133.3 eV can be deconvoluted into P–O and P–O–C bonds. GeP₃, a black phosphorus analogue, forms P–O bonds due to inevitable surface oxidation, and strong P–O–C bonds between carbon materials and bare GeP₃ during ball milling^[35]. With the milling time of 40 h, P2p XPS spectra (Fig. 2(c, d)) of GeP₃/KB-300-40 and GeP₃/KB-500-40 show a significant increase in the strength of the P–O–C bonds. This indicates that the

combination of GeP₃ and KB, as well as the formation of P–O–C bonds, is more favorable at higher rotating speed with the same milling time, which is attributed to the high temperature and high pressure induced by high-energy mechanical milling, promoting the formation of P–C and P–O–C bonds between KB and GeP₃. As a result, the inherent conductive pathway and well-defined structure are ensured, leading to increased durability of the GeP₃/KB structure and consequently improved cycle stability and electrochemical reversibility of the electrode during electrochemical cycling^[25, 34].

From the SEM image and EDS mappings of GeP₃ (Fig. 3(a-c)), it can be observed that phosphorus and germanium are uniformly distributed in GeP₃, indicating that GeP₃ was synthesized. In addition, due to the further refinement of particles by secondary ball milling, the average particle size of GeP₃/KB-600-40 (Fig. 3(d)) is obviously smaller than that of GeP₃. Furthermore, during the ball milling process, the powder particles undergo repeated deformation, fracture, and cold welding, forming GeP₃-KB nanoparticle clusters. From EDS mappings of GeP₃/KB-600-40 (Fig. 3(e-i)), it can be observed that C, O, Ge, and P elements are uniformly distributed in the composites. The microcrystalline structure of GeP₃/KB-600-40 was further analyzed by TEM (Fig. 4(a)). Similar to SEM images, GeP₃/KB composite presents nanoparticle cluster structure. In the higher-resolution TEM image (Fig. 4(b)), GeP₃ particles are embedded in carbon matrix. The interlayer distance of GeP₃ is 0.26 nm, consistent with (202)

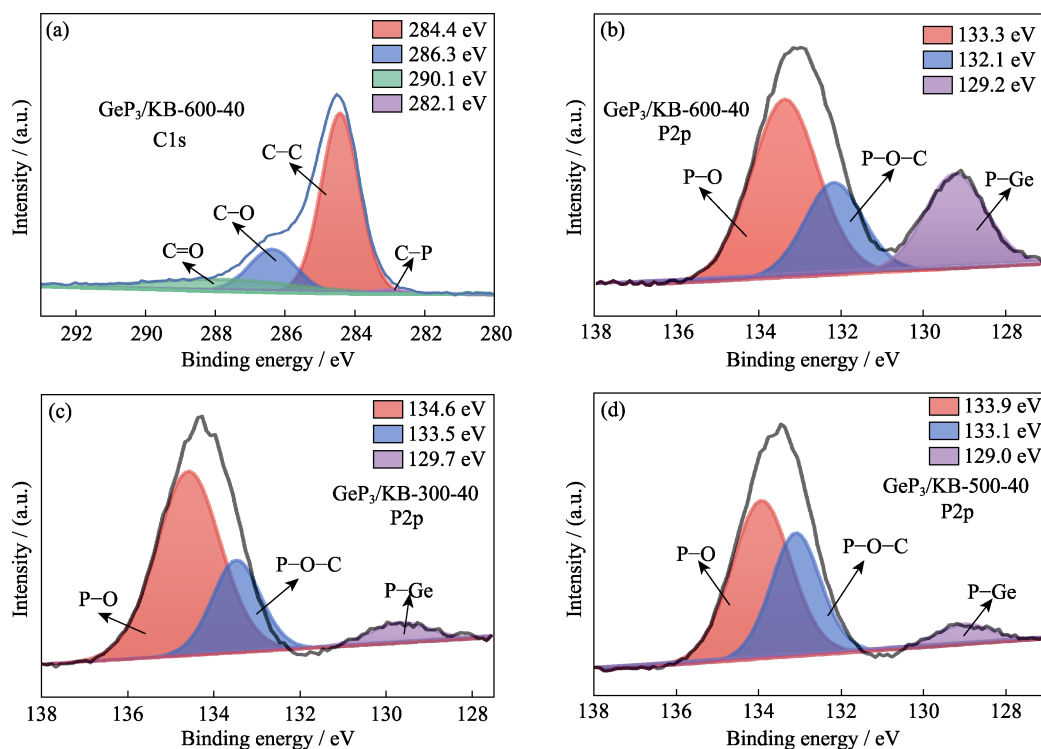


Fig. 2 High resolution XPS spectra of GeP_3/KB nanocomposites

(a) $\text{C}1\text{s}$ XPS spectrum of $\text{GeP}_3/\text{KB-600-40}$; (b-d) $\text{P}2\text{p}$ XPS spectra of (b) $\text{GeP}_3/\text{KB-600-40}$, (c) $\text{GeP}_3/\text{KB-300-40}$ and (d) $\text{GeP}_3/\text{KB-500-40}$. Colorful figures are available on website

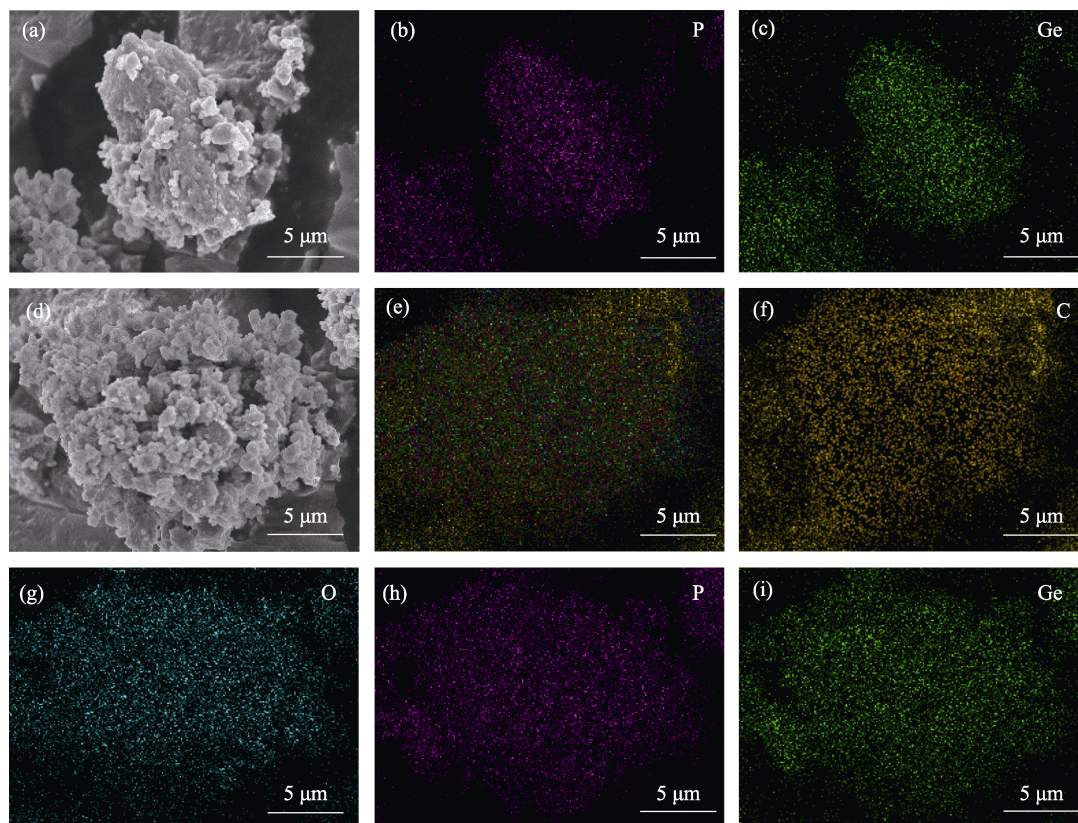


Fig. 3 SEM images and EDS mappings of (a-c) GeP_3 and (d-i) $\text{GeP}_3/\text{KB-600-40}$

(a) SEM image of GeP_3 ; (b, c) EDS mappings of P and Ge in GeP_3 ; (d) SEM image of $\text{GeP}_3/\text{KB-600-40}$; (e-i) EDS mappings of C, O, P and Ge in $\text{GeP}_3/\text{KB-600-40}$

lattice spacing of GeP_3 phase. These results further provide evidence for the existence of nanocrystalline

GeP_3 in GeP_3/KB composites. The SAED pattern of GeP_3 region in GeP_3/KB (Fig. 4(c)) shows a typical

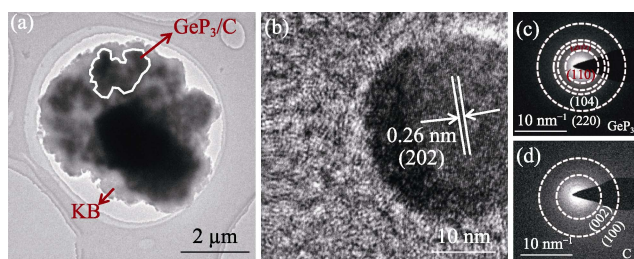


Fig. 4 (a, b) TEM images and (c, d) SAED patterns of GeP₃/KB-600-40

polycrystalline structure with clear diffraction rings, which are assigned to (110), (202), (104) and (220) planes of GeP₃ phase. The SAED pattern in the carbon region shows several wide and diffused diffraction rings (Fig. 4(d)), which are attributed to the fact that the carbon (002) and (100) planes are consistent with its amorphous feature.

2.2 Electrochemical performance

The charge-discharge curves of initial two cycles for all electrodes obtained at a current density of 50 mA·g⁻¹ and a voltage range of 0.1–2.5 V are presented (Fig. 5(a, b)). The bare GeP₃ electrode shows a high initial discharge capacity up to 1366.19 mAh·g⁻¹. A higher initial discharge capacity is demonstrated by GeP₃/KB composite electrodes, for instance, 1504.61 mAh·g⁻¹ by GeP₃/KB-600-40. The initial Coulombic efficiency (CE) of all electrodes is in the range from 45% to 60%. The

GeP₃/KB composite electrodes exhibit no significant improvement in the initial CE, which may be due to the nanosizing of the particles during secondary ball milling. Regarding CE of the second cycle, the GeP₃/KB electrodes demonstrate the clear advantage. CE of bare GeP₃ electrode is only 69.3% in the second cycle, which is due to the huge volume change of active materials. By sharp contrast, the second cycle CE is 87.7% for GeP₃/KB-300-10, and further improved to 93.8% for GeP₃/KB-600-40. The increased milling speed at the same milling time reduces the size of GeP₃ and strengthens the combination with KB to accommodate the volume expansion of GeP₃. The same effect can be achieved by appropriately prolonging the milling time at the same milling speed. CE of GeP₃/KB-600-40 is superior to other GeP₃/KB composite electrodes.

As shown in Fig. 5(c), the rate performance of GeP₃/KB composite electrode is significantly improved compared with that of bare GeP₃. The capacity of bare GeP₃ electrode decays rapidly after several cycles even at a low current density of 0.05 A·g⁻¹ and decreases to <10 mAh·g⁻¹ at 0.5 A·g⁻¹. It is caused by the rapid volume expansion and shedding of bare GeP₃ during sodium storage. With the milling time of 40 h, the difference in performance of GeP₃/KB composite electrodes with different rotation speeds is observed. With the increase of rotation speed, the rate performance

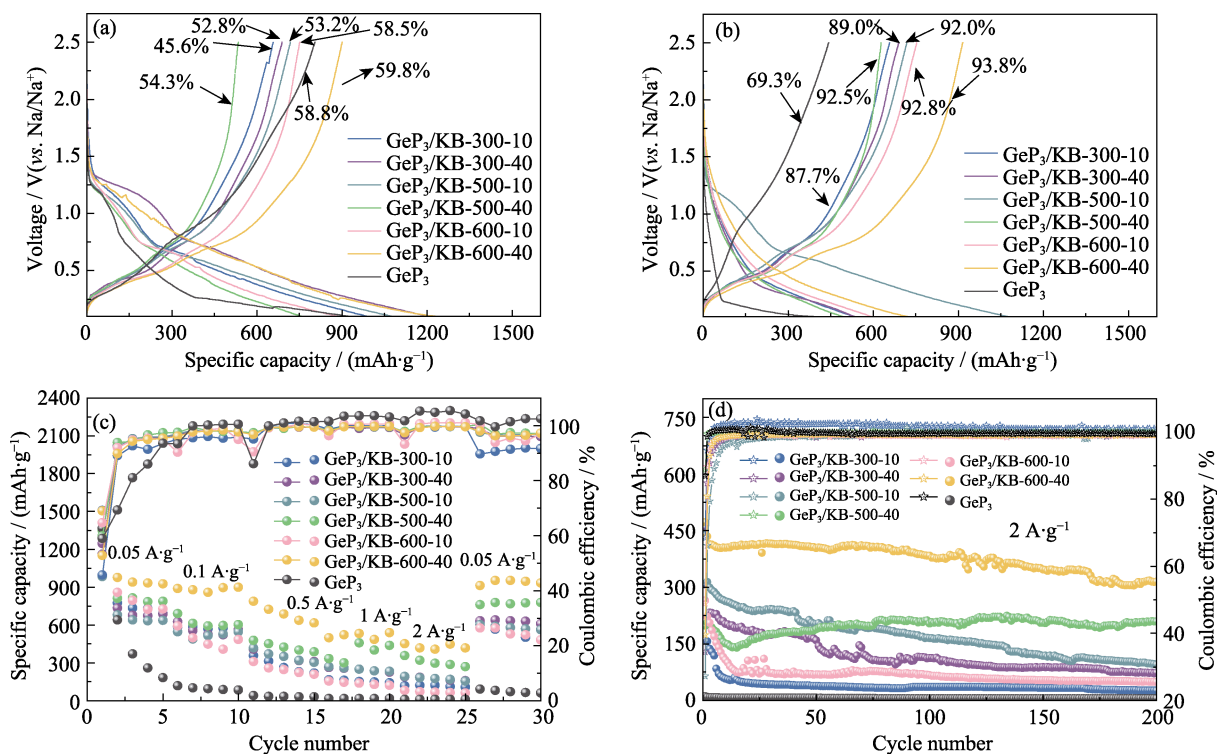


Fig. 5 Electrochemical performance of GeP₃ and GeP₃/KB composites
(a) Initial and (b) second charge-discharge curves of bare GeP₃ and GeP₃/KB electrodes; (c) Rate performance of bare GeP₃ and GeP₃/KB electrodes at 0.05, 0.1, 0.5, 1 and 2 A·g⁻¹; (d) Cycling performance of all electrodes at 2 A·g⁻¹

Colorful figures are available on website

of GeP₃/KB composite electrode improved. GeP₃/KB-600-40 composite electrode delivers reversible capacities of 926.12, 898.91, 616.85, 538.49 and 418.16 mAh·g⁻¹ at current densities of 0.05, 0.1, 0.5, 1 and 2 A·g⁻¹, respectively. When the current density decreases to 0.05 A·g⁻¹, it recovers a reversible capacity of 933.41 mAh·g⁻¹, which exhibits excellent rate performance. The improvement of rate performance is due to the increased sodium storage sites and the formation of P–O–C bonds in the GeP₃/KB-600-40 electrode, which effectively inhibit volume expansion and refine particles during high-energy ball milling^[36]. As XPS spectra revealed, GeP₃/KB-600-40 possesses higher oxygen content compared with other composite electrodes, which is beneficial to the formation of P–O–C bonds, resulting in excellent rate performance. In a long-term cycling test at a higher current density of 2 A·g⁻¹ (Fig. 5(d)), the GeP₃/KB-600-40 composite electrode maintains a capacity of 314.52 mAh·g⁻¹ after 200 cycles with a capacity retention rate of 66.6% of the initial value. In contrast, the capacity retention rates of other GeP₃/KB composite electrodes range from 22.59% (GeP₃/KB-500-40) to 8.58% (GeP₃/KB-300-10). The bare GeP₃ electrode exhibits a capacity of only 9.18 mAh·g⁻¹ after 25 cycles, indicating severe capacity decay. The unique structure of GeP₃/KB significantly enhances the cycling performance of the electrode.

As shown in Fig. 6(a, b), the irreversible broad peak at 0.5 V during the first cycle of the CV curve is attributed to the formation of the solid electrolyte interface (SEI) film^[37], which disappears in the second cycle. The two reduction peaks at 0.25 and 0.15 V in GeP₃/KB electrode are attributed to the formation of Na₃P and NaGe in the alloying process, while the two oxidation peaks on the forward scanning curves correspond to the dealloying process. The CV curves of GeP₃/KB composite electrodes show much improved reversibility compared to GeP₃.

To further investigate the electrochemical mechanism of GeP₃/KB-600-40 electrode, CV tests were performed at different scan rates (Fig. S2). Furthermore, b is calculated using Eq. (1) to characterize the specific electron/ion transfer behavior.

$$i = av^b \quad (1)$$

Where i is the peak current (mA); v is the scan rate (mV/s); a and b are variable parameters. The electron/ion transfer is associated with the diffusion-controlled “battery behavior” mechanism with b close to 0.5 and the surface-controlled “pseudocapacitive behavior” mechanism with b close to 1. In Fig. S3(a), b of GeP₃/KB-600-40 is 1.15, exhibiting partial pseudocapacitive behavior. Generally, the contribution of Faraday reaction to capacity gradually decreases with the increase of current

density, whereas the contribution of pseudo capacitance remains unchanged, which is one of the reasons for the superior rate capacity of GeP₃/KB-600-40^[31].

To quantitatively analyze the contribution proportion of the sodium-ion storage behavior, the CV curve was further calculated by the following formula:

$$i(v) = k_1v + k_2v^{1/2} \quad (2)$$

where $i(v)$ is the current at a specific voltage (mA); k_1v and $k_2v^{1/2}$ refer to the surface control capacity and diffusion control capacity, respectively^[38]. The capacitance contribution of sodium storage in GeP₃/KB-600-40 increases from 47% to 82% as the CV scan rate increases (Fig. S3(b)). The enhancement of capacitance storage can accelerate the diffusion of Na⁺ and prevent excessive volume expansion of active materials during high-rate charge and discharge, thus obtaining good rate performance.

The Nyquist plots of bare GeP₃ and GeP₃/KB composite electrodes, obtained in the frequency range from 0.01 Hz to 100 kHz, are shown in Fig. 6(c). The charge transfer impedance (R_{ct}) is indicated by the diameter of the semicircle in the intermediate frequency region. Among the GeP₃/KB composite electrodes, GeP₃/KB-600-40 exhibits the smallest semicircle diameter with R_{ct} of 41.1 Ω . R_{ct} values of other GeP₃/KB composite electrodes are relatively higher, ranging from 57.5 Ω (GeP₃/KB-500-10) to 44.8 Ω (GeP₃/KB-500-40). In contrast, the bare GeP₃ electrode has the largest semicircle diameter with R_{ct} of 447.6 Ω . The lower charge transfer resistance of GeP₃/KB-600-40 accounts for its excellent electrochemical performance. These results indicate that the GeP₃/KB electrode synthesized by the high-energy ball milling method enhances ion exchange between the electrode and electrolyte, providing faster and more efficient transport channels for the sodium insertion/extraction process.

The morphological changes of GeP₃ and GeP₃/KB electrodes before and after 100 cycles at 2 A·g⁻¹ were investigated by SEM. The formation of dense structure on the surface of the GeP₃ electrode after 100 cycles is related to the volume expansion of the active material during Na⁺ intercalation/deintercalation, thus hindering the diffusion of Na⁺, resulting in poor rate and cycling performance (Fig. S4(a, b)). In contrast, the GeP₃/KB-600-40 electrode can maintain structural integrity to a large extent after 100 cycles compared to the original electrode^[39] (Fig. S4(c, d)). Therefore, compared with the bare GeP₃ electrode, the electrochemical performance of the GeP₃/KB-600-40 electrode is greatly improved.

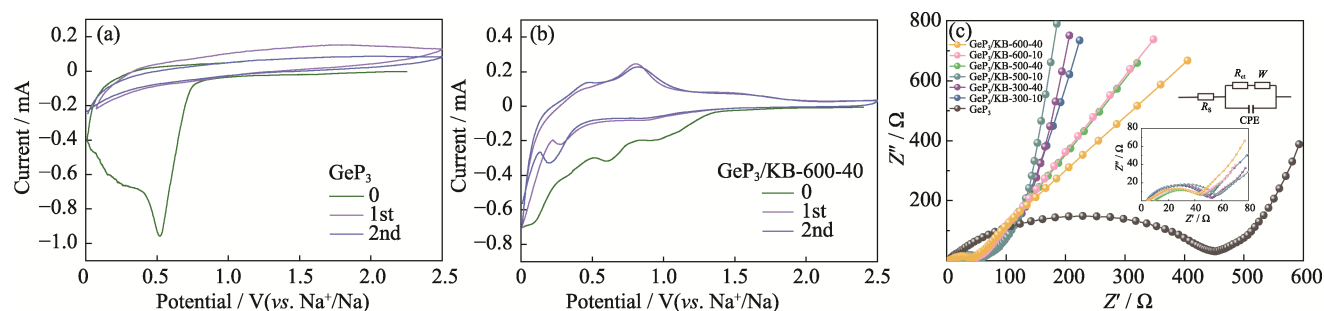


Fig. 6 CV curves of (a) GeP₃ and (b) GeP₃/KB-600-40, and (c) Nyquist plots of all electrodes with inset showing equivalent circuit

Colorful figures are available on website

3 Conclusions

In summary, the GeP₃/KB anode material was prepared using a simple two-step high-energy ball milling process with germanium powder, red phosphorus, and KB as raw materials. The effects of ball milling time and rotation speed on the properties of the GeP₃/KB composite anode material were studied. The introduced conductive carbon KB effectively combines with GeP₃ during high-energy ball milling, which inhibits the volume expansion of the anode materials and improves structural stability, thus endowing the GeP₃/KB composites with good cycle stability. A high reversible capacity of 933.41 mAh·g⁻¹ for GeP₃/KB composites obtained by milling at 600 r/min for 40 h was achieved at a current density of 0.05 A·g⁻¹. After 200 cycles at a current density of 2 A·g⁻¹, a capacity of 314.52 mAh·g⁻¹ was maintained with a capacity retention rate of 66.6%. This work demonstrates that prolonging the milling time and increasing the milling speed are beneficial for improving the electrochemical performance of the GeP₃/KB composite electrode.

Supporting Materials

Supporting materials related to this article can be found at <https://doi.org/10.15541/jim20240360>.

References:

- [1] ZHANG H, HASA I, PASSERINI S. Beyond insertion for Na-ion batteries: nanostructured alloying and conversion anode materials. *Advanced Energy Materials*, 2018, **8**(17): 1702582.
- [2] ZHOU J H, SHI Q T, ULLAH S, et al. Phosphorus-based composites as anode materials for advanced alkali metal ion batteries. *Advanced Functional Materials*, 2020, **30**(49): 2004648.
- [3] GUO J Z, GU Z Y, DU M, et al. Emerging characterization techniques for delving polyanion-type cathode materials of sodium-ion batteries. *Materials Today*, 2023, **66**: 221.
- [4] DU M, DU K D, GUO J Z, et al. Direct reuse of oxide scrap from retired lithium-ion batteries: advanced cathode materials for sodium-ion batteries. *Rare Metals*, 2023, **42**(5): 1603.
- [5] DING C S, CHEN Z, CAO C X, et al. Advances in Mn-based electrode materials for aqueous sodium-ion batteries. *Nano-Micro Letters*, 2023, **15**(1): 192.
- [6] CHEN F Z, XU J, WANG S Y, et al. Phosphorus/phosphide-based materials for alkali metal-ion batteries. *Advanced Science*, 2022, **9**(17): 2200740.
- [7] FU Y Q, WEI Q L, ZHANG G X, et al. Advanced phosphorus-based materials for lithium/sodium-ion batteries: recent developments and future perspectives. *Advanced Energy Materials*, 2018, **8**(13): 1703058.
- [8] WU S M, YANG W, LIU Z T, et al. Organic polymer coating induced multiple heteroatom-doped carbon framework confined Co_{1-x}S@NPSC core-shell hexapod for advanced sodium/potassium ion batteries. *Journal of Colloid and Interface Science*, 2024, **660**: 97.
- [9] HWANG J Y, MYUNG S T, SUN Y K. Sodium-ion batteries: present and future. *Chemical Society Reviews*, 2017, **46**(12): 3529.
- [10] NAYAK P K, YANG L T, BREHM W, et al. From lithium-ion to sodium-ion batteries: advantages, challenges, and surprises. *Angewandte Chemie International Edition*, 2018, **57**(1): 102.
- [11] ZENG L C, HUANG L C, ZHU J H, et al. Phosphorus-based materials for high-performance alkaline metal ion batteries: progress and prospect. *Small*, 2022, **18**(39): 2201808.
- [12] CHEN L T, LIU Z T, YANG W, et al. Micro-mesoporous cobalt phosphosulfide (Co₃S₄/CoP/NC) nanowires for ultrahigh rate capacity and ultrastable sodium ion battery. *Journal of Colloid and Interface Science*, 2024, **666**: 416.
- [13] LIU R, YU L, HE X, et al. Constructing heterointerface of Bi/Bi₂S₃ with built-in electric field realizes superior sodium-ion storage capability. *eScience*, 2023, **3**(4): 100138.
- [14] WANG L Z, LI Q M, CHEN Z Y, et al. Metal phosphide anodes in sodium-ion batteries: latest applications and progress. *Small*, 2024, **20**(26): 2310426.
- [15] LIU J F, WANG S T, KRAVCHYK K, et al. SnP nanocrystals as anode materials for Na-ion batteries. *Journal of Materials Chemistry A*, 2018, **6**(23): 10958.
- [16] LI Q F, YANG D, CHEN H L, et al. Advances in metal phosphides for sodium-ion batteries. *SusMat*, 2021, **1**(3): 359.
- [17] SONG H, EOM K. Overcoming the unfavorable kinetics of Na₃V₂(PO₄)₂F₃/SnP_x full-cell sodium-ion batteries for high specific energy and energy efficiency. *Advanced Functional Materials*, 2020, **30**(31): 2003086.
- [18] LI W W, LI H Q, LU Z J, et al. Layered phosphorus-like GeP₃: a promising anode candidate with high initial Coulombic efficiency and large capacity for lithium ion batteries. *Energy & Environmental Science*, 2015, **8**(12): 3629.
- [19] KIM D, ZHANG K, LIM J M, et al. GeP₃ with soft and tunable bonding nature enabling highly reversible alloying with Na ions. *Materials Today Energy*, 2018, **9**: 126.

- [20] YANG F H, HONG J, HAO J N, *et al.* Ultrathin few-layer GeP nanosheets *via* lithiation-assisted chemical exfoliation and their application in sodium storage. *Advanced Energy Materials*, 2020, **10**(14): 1903826.
- [21] GU Z Y, WANG X T, HENG Y L, *et al.* Prospects and perspectives on advanced materials for sodium-ion batteries. *Science Bulletin*, 2023, **68**(20): 2302.
- [22] SUI S M, XIE H, CHEN B, *et al.* Highly reversible sodium-ion storage in a bifunctional nanoreactor based on single-atom Mn supported on N-doped carbon over MoS₂ nanosheets. *Angewandte Chemie International Edition*, 2024, **63**(43): e202411255.
- [23] CHANG Q Q, JIN Y H, JIA M, *et al.* Sulfur-doped CoP@nitrogen-doped porous carbon hollow tube as an advanced anode with excellent cycling stability for sodium-ion batteries. *Journal of Colloid and Interface Science*, 2020, **575**: 61.
- [24] SHI S S, SUN C L, YIN X P, *et al.* FeP quantum dots confined in carbon-nanotube-grafted P-doped carbon octahedra for high-rate sodium storage and full-cell applications. *Advanced Functional Materials*, 2020, **30**(10): 1909283.
- [25] QI W, ZHAO H H, WU Y, *et al.* Facile synthesis of layer structured GeP₃/C with stable chemical bonding for enhanced lithium-ion storage. *Scientific Reports*, 2017, **7**: 43582.
- [26] ZHAO W X, MA X Q, WANG G Z, *et al.* Carbon-coated CoP₃ nanocomposites as anode materials for high-performance sodium-ion batteries. *Applied Surface Science*, 2018, **445**: 167.
- [27] LIU J, YAO M, WU A M, *et al.* Inverse capacity growth and progressive lithiation of SnP-semifilled carbon nanotubes anodes. *Applied Surface Science*, 2021, **568**: 1580844.
- [28] ZHANG C F, PARK G, LEE B J, *et al.* Self-templated formation of fluffy graphene-wrapped Ni₃P₄ hollow spheres for Li-ion battery anodes with high cycling stability. *ACS Applied Materials & Interfaces*, 2021, **13**(20): 23714.
- [29] OUYANG L Z, GUO L N, CAI W H, *et al.* Facile synthesis of Ge@FLG composites by plasma assisted ball milling for lithium ion battery anodes. *Journal of Materials Chemistry A*, 2014, **2**(29): 11280.
- [30] NAM K H, JEON K J, PARK C M. Layered germanium phosphide-based anodes for high-performance lithium- and sodium-ion batteries. *Energy Storage Materials*, 2019, **17**: 78.
- [31] WANG T, ZHANG K, PARK M, *et al.* Highly reversible and rapid sodium storage in GeP₃ with synergistic effect from outside-in optimization. *ACS Nano*, 2020, **14**(4): 4352.
- [32] WANG R, MO H X, LI S, *et al.* Influence of conductive additives on the stability of red phosphorus-carbon anodes for sodium-ion batteries. *Scientific Reports*, 2019, **9**: 946.
- [33] ZHANG Z X, LI S Q, GAO S L, *et al.* Sn/P@G-CNTs composites as high-performance anode materials for sodium-ion batteries. *Electrochimica Acta*, 2021, **388**: 138532.
- [34] LEE J, KIM K H, KIM H H, *et al.* NiP₂/C nanocomposite as a high performance anode for sodium ion batteries. *Electrochimica Acta*, 2022, **403**: 139686.
- [35] WU X, ZHAO W, WANG H, *et al.* Enhanced capacity of chemically bonded phosphorus/carbon composite as an anode material for potassium-ion batteries. *Journal of Power Sources*, 2018, **378**: 460.
- [36] HAGHIGHAT-SHISHAVAN S, NAZARIAN-SAMANI M, NAZARIAN-SAMANI M, *et al.* Strong, persistent superficial oxidation-assisted chemical bonding of black phosphorus with multiwall carbon nanotubes for high-capacity ultradurable storage of lithium and sodium. *Journal of Materials Chemistry A*, 2018, **6**(21): 10121.
- [37] BOMMIER C, JI X L. Electrolytes, SEI formation, and binders: a review of nonelectrode factors for sodium-ion battery anodes. *Small*, 2018, **14**(16): 1703576.
- [38] LIANG M, XIE H N, CHEN B, *et al.* High-pressure-field induced synthesis of ultrafine-sized high-entropy compounds with excellent sodium-ion storage. *Angewandte Chemie International Edition*, 2024, **63**(27): e202401238.
- [39] ZENG T B A, FENG D, LIU Q, *et al.* Boosting cyclability performance of GeP anode *via in-situ* generation of free expansion volume. *Journal of Alloys and Compounds*, 2021, **883**: 160857.

GeP₃/科琴黑复合材料作为钠离子电池高性能负极材料

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摘 要: 金属磷化物因具有比其他阳极材料更高的比容量而作为潜在的钠离子电池(SIBs)阳极材料。然而, 其体积膨胀和导电性差, 导致 SIBs 的容量衰减快, 循环寿命短。因此, 本研究采用高能球磨法制备 GeP₃, 然后进行二次球磨, 通过引入科琴黑(KB), 合成 GeP₃/KB 复合阳极材料。球磨过程使得 GeP₃ 和 KB 紧密结合, 形成强有力的化学键, 因此 GeP₃/KB 阳极表现出优异的储钠性能。GeP₃/KB-600-40 样品(第二次球磨速度 600 r/min, 球磨时间 40 h)在 0.05 A·g⁻¹ 的电流密度下获得了 933.41 mAh·g⁻¹ 的高可逆容量; 在 2 A·g⁻¹ 的高电流密度下循环 200 次后容量仍保持在 314.52 mAh·g⁻¹, 容量保持率为 66.6%。研究表明, 通过高能球磨法制备的合金-碳复合阳极材料, 可以缓解阳极在循环过程中产生的体积膨胀, 增大 SIBs 容量和改善循环稳定性。

关 键 词: 钠离子电池; GeP₃/C 复合材料; 科琴黑; 高能球磨法

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Supporting information:**GeP₃/Ketjen Black Composite: Preparation via Ball Milling and Performance as Anode Material for Sodium-ion Batteries**

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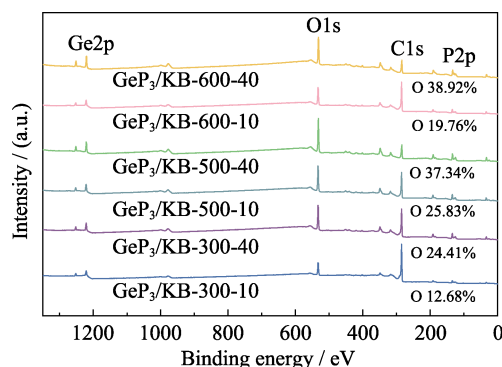
Structure characterization

The purity and crystal structure of the samples were analyzed using an X-ray diffraction (XRD) spectrometer (Bruker D8 Advance). Diffraction data in the range of $2\theta=10^{\circ}$ – 80° were recorded using CuK α radiation ($\lambda=1.5418$ Å) with a step size of $2\theta=0.05^{\circ}$ and analyzed using MDI Jade software. Raman spectroscopy (THEM DXRxi) was performed with a 532 nm laser. The sample morphology was examined using high-resolution field emission scanning electron microscopy (SEM, FEI Verios 460, USA) equipped with energy-dispersive spectroscopy (EDS) module. Microcrystalline structure images and selected area electron diffraction (SAED) patterns were collected using a transmission electron microscope (TEM, FEI Tecnai G2 F20). X-ray photoelectron spectroscopy (XPS) measurements were conducted using a PerkinElmer PHI 1600 ESCA system to analyze the bonding state and elemental composition of the material.

Electrochemical measurement

The active material, conductive carbon, and polyvinylidene fluoride (PVDF) binder were mixed in a mass ratio of 8 : 1 : 1. After thorough grinding, *N*-methyl-2-pyrrolidone (NMP) solvent was added to form a slurry. The slurry was coated onto copper foil, dried in a vacuum oven at 60 °C for 12 h, and then cut into circles with a diameter of 14 mm. The mass of the active material was maintained at 1–1.5 mg·cm⁻².

1 mol/L NaClO₄ electrolyte was prepared with a solvent mixture of dimethyl carbonate (DMC) and ethylene carbonate (EC) in a volume ratio of 1 : 1. CR2032 coin cells were assembled in an argon-filled glove box, using sodium foil as the counter electrode and glass fiber filter paper as the separator. Constant current charge and discharge tests were conducted in a voltage range of 0.01–2.5 V at different current densities using a battery test system (Neware CT-4008, China). Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) studies were performed using a potentiostat (CHI660E). The EIS tests covered a frequency range of 0.01–100000 Hz with an amplitude voltage of 5.0 mV. CV curves were recorded at a scan rate of 0.1 mV·s⁻¹ within a voltage range of 0–2.5 V.

Fig. S1 XPS survey spectra of GeP₃/KB

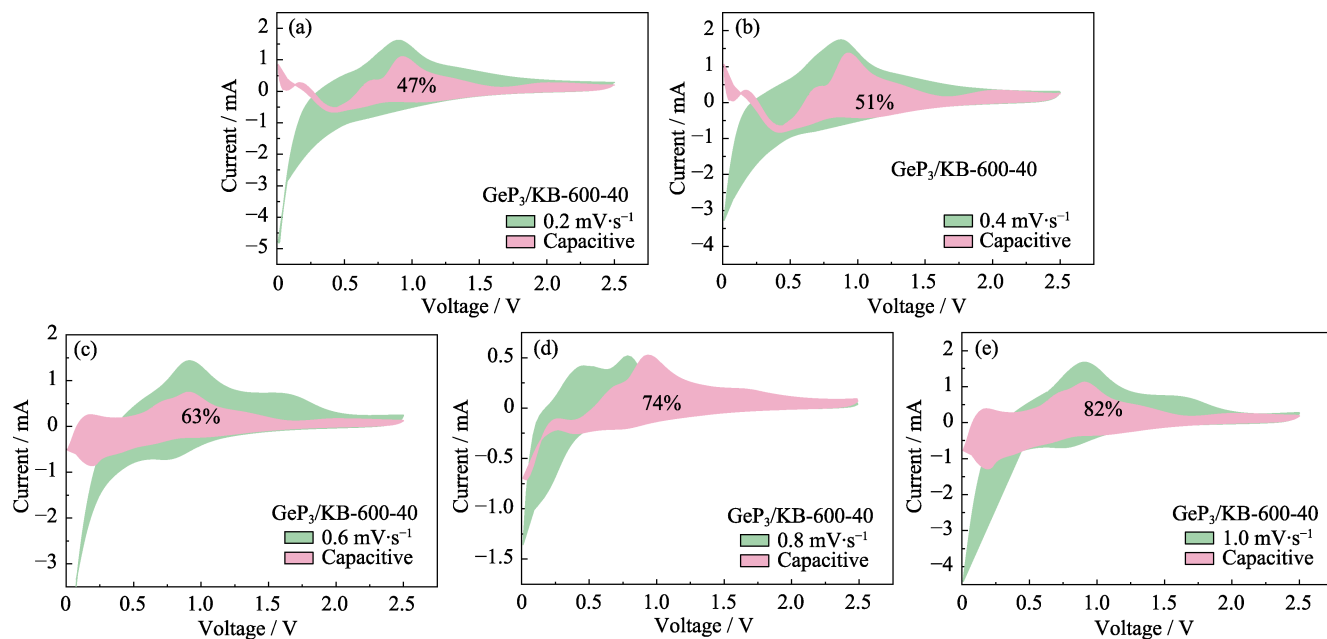


Fig. S2 CV curves with calculated capacitive contribution of $\text{GeP}_3/\text{KB-600-40}$
Scan rates of (a) 0.2, (b) 0.4, (c) 0.6 (d) 0.8 and (e) 1.0 $\text{mV}\cdot\text{s}^{-1}$

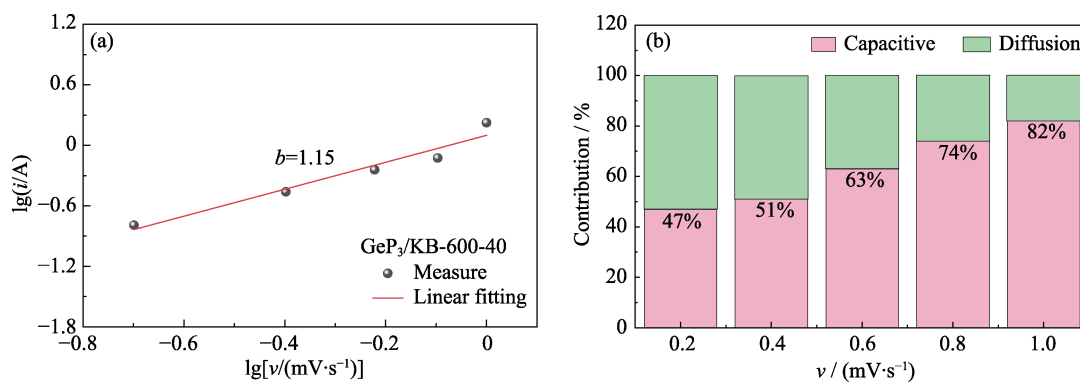


Fig. S3 (a) Relationship between peak current and scan rate in logarithmic format and (b) capacitance contribution at different scan rates of $\text{GeP}_3/\text{KB-600-40}$

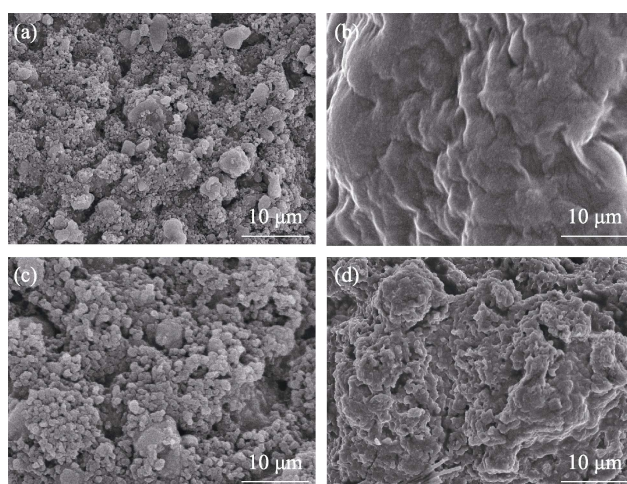


Fig. S4 SEM images of (a, b) bare GeP_3 and (c, d) $\text{GeP}_3/\text{KB-600-40}$ (a, c) before and (b, d) after 100 cycles