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Layered Phosphorus-Like GeP$_5$: a Promising Anode Candidate with High Initial Coulombic Efficiency and Large Capacity for Lithium Ion Batteries

Wenwu Li,$^a$ Huiqiao Li,$^{a*}$ Zhijuan Lu,$^a$ Lin Gan,$^a$ Linbo Ke,$^a$ Tianyou Zhai$^{a*}$ and Haoshen Zhou$^b$

In this work, we for the first time investigate GeP$_5$ as an anode material for lithium ion batteries (LIB). By a facile high energy mechanical ball milling (HEMM) method, we successfully synthesize pure GeP$_5$ and GeP$_5$/C nanocomposite at ambient temperature and pressure. According to XRD Rietveld refinement and first principle calculation, GeP$_5$ holds a two-dimensional layered structure similar to black P and graphite, a high conductivity as 10000 and 10 times of black P and graphite, respectively. Serving as novel anode materials, both GeP$_5$ and its carbon composite deliver an unprecedented high reversible capacity of ca. 2300 mA h g$^{-1}$, combined with a high initial coulombic efficiency of ca. 95%. Ex-situ XRD and CV tests demonstrate GeP$_5$ undergoes conversion and alloying type lithium storage mechanism that its capacity is co-contributed by both Ge and P components. In addition, GeP$_5$/C exhibits superior cycle stability and excellent high-rate performance with a capacity of 2127 mA h g$^{-1}$ at 5 A g$^{-1}$, suggesting their promising application in next-generation high-energy and high-power LIB.

Introduction

Graphite has dominated the anode materials in commercial lithium ion batteries (LIB) due to its high reversibility and low potential. However, the specific capacity of graphite is limited to 372 mA h g$^{-1}$ corresponding to Li$_x$C$_6$ (x≈1). Moreover, graphite accommodates Li$^+$ at a low potential very close to that of Li plating, easily resulting in the safety problem of short circuit due to the formation of Li dendrite.$^{1,2}$ Therefore, many efforts have been devoted to exploring alternatives for graphite, with the hope of achieving simultaneously large capacities and proper potential to Li$^+$ intercalation.$^{3,4}$ Being the elements in same main group as carbon, silicon and germanium have been widely investigated as typical large capacity anode materials since they can store 4.4 and 4 unit Li per formula by forming Li$_x$Si and Li$_x$Ge alloys, corresponding to theoretical capacities of 4200 mA h g$^{-1}$ and 1600 mA h g$^{-1}$, respectively.$^{5,6}$ However, both of them suffers from quite a large irreversible capacity loss (usually 20-50%) during the initial discharge/charge cycle due to their irreversible phase transitions and side reactions with electrolyte. Such a low coulombic efficiency at the first cycle dramatically limits the practical application of Si and Ge as anodes in full LIB. Moreover, their discharge/charge processes usually undergo huge volume expansion/contraction during the formation/decomposition of Li$_x$M (M = Si, Ge) phases, which would severely degrade their cycle performances.

Apart from Si and Ge, elemental P, a low-cost abundant material locating in the fifth group of the periodic table, has attracted much attention in recent years for its high theoretical capacity of 2596 mA h g$^{-1}$ according to the formation of Li$_x$P.$^{12,21}$ As known, there are three main allotropes for element P, including white P, red P and black P. White P begins to burn at 34 $^\circ$C. Red P suffers a very low coulombic efficiency (< 5%) at the first cycle.$^{12,14}$ In contrast, black P especially its carbon composites, are found able to demonstrate a large capacity of -2000 mA h g$^{-1}$ with good cycle stability.$^{12,13,15}$ The much superior performance of black P than red P can be attributed to its graphite-like layered structure, which promises high electrical conductivity. Unfortunately, it is extremely difficult to fabricate black P because of the necessity of both high temperature and high pressure.$^{12,13}$ Worse, black P would be turned to red P at temperature above 125 $^\circ$C.$^{12}$ As alternatives to black P, several metal phosphides (MP$_x$, M = transition metal), like MnP$_4$, FeP$_2$, CoP$_2$, Ni$_2$P, Cu$_2$P, etc.$^{12-24}$ have been explored, which show attractive lithium storage properties via a conversion reaction as xLi$^+$ + xe$^- +$ MP = Li$_x$P + M, (M = Mn, Fe, Co, Ni, Cu et al).$^5$ Since these metals are inert for Li storage, the theoretical reversible capacities of these metal phosphides were usually less than 1200 mA h g$^{-1}$, much lower than that of black P. Besides, the reported metal phosphides usually show a very low first coulombic efficiency (<60%) and their cycle performances are

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still poor. Therefore, it is of great interest to explore new P-based compounds which is easy-obtained and more stable than black P, but can provide a high specific capacity as elemental P.

In this work, we for the first time investigated a metal phosphide GeP₅ as the anode material for LIB. It can be easily obtained in a large scale by simply mechanical milling of elemental Ge and low cost red P. According to XRD refinement and structural analysis, GeP₅ holds a layered structure similar to black P and graphite, which promises the bonding feasibility with graphic layer. Meanwhile, its conductivity is 10000 times higher than black P, and similar to that of graphite. Such high conductivity is considered very favourable for the lithium ion storage reaction. When served as an anode material, GeP₅ delivers a large specific capacity of 2266 mA h g⁻¹, much higher than those of metal phosphides mentioned above, due to its both reactive components of Ge and P for Li storage. Moreover, it can exhibit a first coulombic efficiency of 95%, to the best of our knowledge, which is the highest value among the reported anode materials up to now. By further compositing GeP₅ with conductive carbon in nanoscale, the cycle and rate performances of GeP₅ can be notably improved, which may profit from the homogeneous distribution of the active Ge and P components in the electrode, the good buffering to volume expansion by carbon matrix, and the existence of P-C bonds. In brief, as an anode material for LIB, GeP₅ exhibits excellent energy-storage properties comparable or surpass current reported results.

Results and discussion

Material synthesis, characterization and structural analysis

Figure 1. a) XRD patterns of as-synthesized powder products obtained at different ball milling time. b) Powder XRD patterns for Rietveld structure analysis of GeP₅. c) Crystal structure of orthorhombic black P, rhombohedral black P and rhombohedral GeP₅.

We fabricated GeP₅ with pure Ge powder and amorphous red P via high energy mechanical milling (HEMM). Simply, the mixture of Ge powder and red P, in a mole ratio of 1 to 5, was poured into HEMM vessel and after a certain milling time treatment, the GeP₅ powder can be collected in a large scale. The as-prepared GeP₅ is a crystalline powder. XRD tests in Figure 1a show that the diffraction peaks of GeP₅ phase can be clearly detected after 2 h ball milling, in spite of some residues of Ge peaks. Further, after 5 h milling, the peaks of Ge completely disappeared and all the observed peaks can be readily indexed to a pure GeP₅ phase (JCPDS Card No. 24-0455). Prolonging milling time to 10 h, the XRD pattern changes little but the intensity slightly decreased, suggesting degradation in GeP₅ crystal size or crystallization. As seen in SEM (Figure 3a, 3b) and TEM (Figure 3a) images, the GeP₅ sample obtained by 10 h milling is composed of large number of nanosized spherical particles which agglomerate into larger microsized secondary particles. HRTEM (in Figure 3b) on a typical GeP₅ particle shows its high crystalline nature, as ordered periodical lattice fringes with a d-spacing of 0.257 nm can be well observed, which evidences a crystalline GeP₅ particle with its (012) plane exposed to environment. The corresponding FFT pattern (Figure 3c) further confirms the single-crystalline nature of the particle.

XRD Rietveld refinement of GeP₅ was performed by using TOPAS. As shown in Figure 1b, all diffraction peaks can be well indexed by a rhombohedral cell in R-3m space group. Details of processing and refinement for GeP₅ including cell parameters, fractional atomic coordinates, and isotropic displacement parameters are given in Table S1-S2. The obtained parameters are highly close to the rhombohedral black P structure in which the unit cell contains six atoms in one identical atom site. Since the XRD pattern of GeP₅ doesn't show any ordered occupation of Ge and P, the atom site is randomly occupied by Ge and P in a fixed occupation of p=1/6 and p=5/6, respectively (Figure S2). The crystal structural relationship between GeP₅ and black P are shown by Figure 1c, in which the GeP₅ structure can be taken as a derivate of rhombohedral black P except for different atoms. Rhombohedral black P has been reported a transition form of orthorhombic black P under high pressure above 50K bars, the former holds a zigzag puckered structure while the latter holds an armchair ridge. In general, all of the three structures are of some similarities to that of graphite, e.g., a honeycomb-like lattice from the top view and a two-dimensional layered structure from the side view, although their puckered layers differ from the planar layer of graphite. Such a two dimensional layered structure is thought favorable to promise both high electrical conductivity and good structural flexibility for bonding with carbon. As reported, the electrical conductivity of GeP₅ is 1.0×10⁴ S m⁻¹, which is nearly 10000 and 10 times higher than that of black P and graphite, respectively (Table 1). The superior conductivity of GeP₅ to black P is consistent with the structural simulation results by first-principal calculations using density functional theory. As shown in Figure S3, the density of states (DOS) for GeP₅ at the Fermi level is much larger than that of orthorhombic black
P, implying its much higher conductivity than black P. In addition, all the three structures of GeP are rhombohedral black P and orthorhombic black P show non-zero DOS at their Fermi levels, indicating they are all of metallic conductivities. Other calculated results including electron density difference (Figure S4), bonding information (Table S3), and related discussion are given in Supporting Information. With the layered structural features and high conductivity, GeP$_5$ is expected to be a promising anode material for LIBs.

**Table 1.** Comparison of graphite, black P and GeP$_5$ in theoretical capacity, density, and conductivity.$^{12,37}$

<table>
<thead>
<tr>
<th>Material</th>
<th>$T_{cap}$ [mA h g$^{-1}$]</th>
<th>Density [g cm$^{-3}$]</th>
<th>Electrical conductivity [$\text{S m}^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphite</td>
<td>372</td>
<td>2.16</td>
<td>$3.3 \times 10^{-2} \times 10^5$</td>
</tr>
<tr>
<td>Black P</td>
<td>2596</td>
<td>2.69</td>
<td>$0.2 \times 3.3 \times 10^5$</td>
</tr>
<tr>
<td>GeP$_5$</td>
<td>2289</td>
<td>3.61</td>
<td>$1.0 \times 10^5$</td>
</tr>
</tbody>
</table>

As we know, large capacity anode materials generally suffer poor cycle performance; therefore, combination them with carbon has been adopted widely to improve their cyclability.$^{40-41}$ For black P, Cui’s groups$^{42}$ recently found that stable P-C bonds could be formed between P layers and graphitic layers in the composite of black P and carbon by high energy ball milling. And Wang’s group$^{18}$ also found the chemical bonding phenomena between red P and graphene. The existence of P-C bonds endows the composite with high electrical conductivity, rapid charge-transfer processes and good lithium ion diffusivity for lithium uptake and extraction. Inspired by the structural similarity of GeP$_5$ to black P, here we prepared GeP$_5$/C composite via high energy ball milling of GeP$_5$ and Super P in a mass ratio of 7:2, expecting to combine this two layered materials by forming P-C like bonds at the interface of their layers to improve the electrochemical performances. **Figure 2a** gives the XRD patterns of GeP$_5$/C composite obtained at different ball milling time. After 5 h milling, the diffraction peaks can still be observed but with lower peak intensity and broader width. When increasing the milling time to 10 h, most of the diffraction peaks except for (012) have almost disappeared, suggesting a much lowered crystallinity of GeP$_5$ in the composite. **Figure 3a and 3d** show the SEM images of GeP$_5$/C obtained by 10-10 h milling. They show similar morphology and comparable particle size as that of pure GeP$_5$. The microstructure of GeP$_5$/C nanocomposite is observed by HRTEM. As shown in **Figure 2b**, the composite seems to be almost amorphous. Meanwhile, it can still find some ultrafine nanocrystals (< 5 nm) embedded into carbon matrix (**Figure S5**). These observations are in good agreement with the selected area electron diffraction image (SAED): a halo-like ring pattern with some dispersed spots. Energy-dispersive spectroscopy (EDS) indicates no impurity elements in the sample and the atom ratio of Ge and P is around 1 : 5. Elemental mapping analysis in **Figure 2c-2f** shows highly homogeneous distribution of elemental Ge, P and C in the GeP$_5$/C composite, indicating GeP$_5$ and C are effectively combined with each other to form an ultranine nanocomposite during HEMM.

**Lithium-storage performance**

**Figure 4a and 4c** presents the discharge/charge profiles of GeP$_5$. At a current density of 200 mA g$^{-1}$, GeP$_5$ delivers a discharge and charge capacity of 2406 and 2266 mA h g$^{-1}$ at the first cycle respectively, corresponding to a high initial coulombic efficiency of 95%. In contrast, pure black P was reported to exhibit only a reversible capacity of 1354 mA h g$^{-1}$ with a much lower initial coulombic efficiency of 53.8%.$^{13}$ After 40 cycles, the capacity of pure GeP$_5$ gradually decreases to 250 mA h g$^{-1}$. And when the current density is increased from 0.1 A g$^{-1}$ to 5 A g$^{-5}$, the rate capacity also decays fast from 2250 mA h g$^{-1}$ to 200 mA h g$^{-1}$, as shown in **Figure 4c**. The dramatic capacity loss with cycle number and increased current densities suggests that pure GeP$_5$ undergoes large volume changes during Li$^+$ insertion/extraction processes. In comparison, the 10-10 h milled GeP$_5$/C nanocomposite (**Figure 4b and 4d**) shows much enhanced cycle stability and high-rate performance. The discharge/charge capacity of GeP$_5$/C...
maintains almost constant at ca. 2300 mA h g\(^{-1}\) during 40 cycles with a coulombic efficiency approaching to 100%. At a current density of 1 A g\(^{-1}\), the electrode can deliver over 1500 mA h g\(^{-1}\) after 150 cycles, as shown in Figure S6. Even at a high current density of 5 A g\(^{-1}\), a specific capacity of 2127 mA h g\(^{-1}\) can still be obtained, which is more than fivefold the theoretical capacity of graphite (372 mA h g\(^{-1}\)). When the current is back to 0.1 A g\(^{-1}\), the capacity recovers to 2361 mA h g\(^{-1}\) again. Besides, the 10-5 h milled GeP\(_5\)/C composite with medium crystallinity can also exhibit large capacity and superior cycle performance to pure GeP\(_5\) (Figure S7).

Figure 4. The discharge/charge profiles of a) Pure-phase GeP\(_5\); b) GeP\(_5\)/C nanocomposite during the initial 40 cycles at a current rate of 0.2 A g\(^{-1}\). The discharge/charge profiles of c) pure-phase GeP\(_5\); d) GeP\(_5\)/C nanocomposite at different current rates between 0.005-3 V vs. Li\(^+\)/Li.

The much enhanced cycle stability and high rate performances of GeP\(_5\)/C nanocomposite are profited from the good combination and homogenously distribution of GeP\(_5\) with carbon. According to Cui’s and Wang’s works,\(^{12,18}\) it is possible that P-C bonds are formed at the interface of GeP\(_5\) layers and carbon layers during HEMM, due to the similarity of their structures. As shown in Figure 5a, compared with pure GeP\(_5\), we can clearly see an extra broad Raman peak locating at 600-700 cm\(^{-1}\) in the GeP\(_5\)/C nanocomposite, which can be assigned to the P-C bonds between GeP\(_5\) layers and graphitic layers of carbon.\(^{12}\) In XPS spectra, an extra peak at 283.8 eV in the C 1s spectrum can be clearly found for GeP\(_5\)/C (Figure 5b). Besides, two extra peaks (Figure 5c) in GeP\(_5\)/C at 130.0 eV and 130.8 eV can also be found in the high-resolution spectra of P 2p\(_{1/2}\) and of P 2p\(_{3/2}\), respectively. The three extra peaks are thought also from the bonding between GeP\(_5\) and carbon, since similar extra XPS peaks have been identified for the P-C bonds by Cui et al in the composite of black P and carbon.\(^{12}\) As observed by TEM, ultrafine GeP\(_5\) nanoparticles are highly dispersed in the continuous three dimensional conductive carbon networks. On the one hand, the carbon network provides directional electron-transport paths and tight electronic contact between the active nanoparticles, so that electrons can be quickly transferred from the active sites to the electrode current collector along the carbon superhighway. On the other hand, the volume expansion and consequent local strain generated upon Li\(^+\) intercalation/extraction in active Ge and P components can be well buffered by flexible loose carbon matrix. Therefore, the GeP\(_5\)/C composite can well maintain the electrode integrity after cycling tests, as shown in Figure 6a and 6b. While for pure phase GeP\(_5\) electrode (Figure 6c and 6d), both the top and cross-section view of its SEM images show that the active material is seriously peeling off from the current collector due to the electrode pulverizations after cyclic discharge/charge.

Figure 5. Raman spectra of GeP\(_5\)/C (a\(_1\)) and pure GeP\(_5\) (the inset of a\(_1\)). XPS data of GeP\(_5\) and GeP\(_5\)/C: the high-resolution C 1s spectra of GeP\(_5\) (b\(_1\)) and GeP\(_5\)/C (b\(_2\)), respectively; the high-resolution P 2p spectra of GeP\(_5\) (c\(_1\)) and GeP\(_5\)/C (c\(_2\)), respectively.
As shown in Figure 7b, GeP$_5$/C sample exhibits two successive pronouncedable peaks at 0.70-0.50V, followed by a small peak at 0.18 V during the negative scan. The peaks at 0.70-0.50V can well refer to the wide reduction peak of P/C sample at 0.65 V, which means this peak region is related to the conversion reaction between Li and GeP$_5$ to form Li$_x$P denoted in Equation 1. While the peak at 0.18 V is observed well referred to the reduction peak of Ge/C sample at 0.1 V, which can be assigned to the further alloying of Li into Ge by forming Li$_x$Ge as Equation 2. By comparing the peak symmetry as well as peak areas between cathodic and anodic scans, the two broad peaks observed at about 0.5 V and 1.1 V in positive scan can be assigned to the extraction of lithium from Li$_x$Ge and Li$_x$P, respectively. These observations clearly show that GeP$_5$ undergoes synergistic Li-storage of both Ge and P. The potential differences between cathodic and anodic peaks in P/C and Ge/C are found larger than their counterparts in P/C and Ge/C, indicating the enhanced electrochemical kinetics of GeP$_5$ than elemental P and Ge. Figure S8 gives the CV curves of GeP$_5$/C at 1-30 cycles. During the initial two cycles, the reduction peak slightly shifts to higher potential and the oxidation peak becomes sharper, resulting in a smaller potential difference. This may be attributed to the decreased electrode polarization by initial activation of GeP$_5$/C in the first cycle of Li insertion/retraction. From the second cycle, the CV profiles show little changes in curve shape and peak area, confirming the high reversibility and good stability of GeP$_5$/C for Li storage.

Figure 6. The SEM images of the GeP$_5$/C electrode: a) before cycling; b) after cycling. The SEM images of GeP$_5$ electrode: c) before cycling; d) after cycling. The corresponding cross-section images are given as the insets.

Figure 7. a) The ex-situ XRD pattern of GeP$_5$ electrode after the first discharge. b) The typical cyclic voltammetry curves of Ge/C, P/C and GeP$_5$/C electrode.

In order to investigate the lithium storage mechanism of GeP$_5$, we performed ex-situ XRD tests on the discharged electrode. As shown in Figure 7a the GeP$_5$ electrode after discharging to 0.005 V clearly exhibits the XRD peaks of Li$_x$Ge$_5$ (Li$_x$Ge) and Li$_x$P phases, which evidences the large capacity of GeP$_5$ comes from the contribution of both Ge and P. According to this, the electrode reaction of GeP$_5$ can be described by the following equations:

$$\begin{align*}
15 \text{ Li}^+ + 15 \text{ e}^- + \text{GeP}_5 & \rightarrow \text{Ge} + 5 \text{ LiP} & (1) \\
4.4 \text{ Li}^+ + 4.4 \text{ e}^- + \text{Ge} & \rightarrow \text{Li}_{4.4}\text{Ge} & (2)
\end{align*}$$

In total: $$19.4 \text{ Li}^+ + 19.4 \text{ e}^- + \text{GeP}_5 \rightarrow \text{Li}_{4.4}\text{Ge} + 5 \text{ LiP} \quad (3)$$

By Equation 3, the theoretical capacity of GeP$_5$ can be calculated to be 2289 mA h g$^{-1}$ in which the five P atoms contribute 1770 mA h g$^{-1}$ based on Equation 1 and Ge atom donates the remaining capacity of 519 mA h g$^{-1}$ based on Equation 2. As obtained by discharge/charge tests, the first charge capacity for GeP$_5$ is 2266 mA h g$^{-1}$, very close to the theoretical value, which indicates the completely reaction of GeP$_5$ for lithium storage as Equation 3. Besides, the density (Table 1) of GeP$_5$ is 1.67 and 1.34 times of graphite and black P, respectively, which would promise a much higher volumetric energy density in application. CV measurements on GeP$_5$/C in comparison of Ge/C and P/C composites further confirm the above Li storage mechanism.

Figure 8. a) The first discharge/charge curves of GeP$_5$/C with graphite, Ge/C, and P/C anodes; b) comparison of initial coulombic efficiency of different anodes; c) cycling performances of GeP$_5$/C, Ge/C, and P/C at a current density of 0.2 A g$^{-1}$; d) rate capabilities of GeP$_5$/C, Ge/C, and P/C at current densities of 0.1, 0.2, 0.5, 1, 2, 5 A g$^{-1}$.

The coulombic efficiency especially at the first cycle of discharge/charge process is very important to an electrode material because it largely determines its practical application in a full battery. The bottle-neck of many large capacity anode materials for commercial utilization is their poor reversibility.
between the first charge and discharge process. For GeP$_5$ and GeP$_2$/C, they can both show a very high first coulombic efficiency, which may ascribe to their excellent conductivity. As shown in Table 1, the conductivity of GeP$_5$ is $1.0 \times 10^{-5}$ S m$^{-1}$, nearly 10 000 times and 10 times higher than black P and graphite, respectively. A similar case has been reported for RuO$_2$, who also is high conductive and can exhibit a high first coulombic efficiency.\(^{43}\) Figure 8a gives the first discharge/charge profiles of GeP$_5$/C in comparison of other anode materials. It can be seen that the capacity loss at the first cycle for P/C, Ge/C, nature graphite and GeP$_5$/C is 22.54%, 21.8%, 11.12% and 4.7%, respectively. Moreover, the obtained charge capacity of GeP$_5$/C is sixfold higher than graphite and 900 mA h g$^{-1}$ higher than P/C anode. To ensure reasonable comparisons, we prepared Ge/C and P/C nanocomposites using HEMM method at the same experimental conditions as GeP$_5$/C. Detailed structure informations of the Ge/C and P/C samples are also obtained by SEM, EDS, XRD and TEM (Figure S9–S13). It can be noted that the particle size, shape, crystallinity and elemental distribution of Ge/C and P/C are comparable to those of GeP$_5$/C. In terms of the curve shape, GeP$_5$/C anode has non-stepped smooth discharge and charge plateaus and the voltage gap between discharge and charge plateaus is much narrower than those of P/C and Ge/C anodes. The smaller gap is very beneficial to get high energy efficiency and high-power performance when used in practical full batteries. Besides, GeP$_5$/C anode gives a relatively high lithium intercalation voltage, which is much safer than graphite and Ge/C anodes. These superior electrochemical behaviours of GeP$_5$/C to Ge/C and P/C may result from the synergetic effects of its high conductivity and bi-active components. The coulombic efficiency of GeP$_5$/C composite is observed as 95% at the first cycle and rapidly up to 100% from the second cycle, which reaches the level of commercial graphite. In contrast, many metal oxides, metal phosphides and alloy-type anodes like Si and Ge usually exhibit a first coulombic efficiency among 30–70%,\(^{3-14, 16-17, 21-31, 40-41}\) much lower than that of commercial graphite (>85%), as illustrated in Figure 8b. The cycle performance and rate capability of GeP$_5$/C are presented in Figure 8c and 8d in comparison with those of Ge/C and P/C. Both GeP$_5$/C and P/C show very stable cycle performances while the capacity of Ge/C decays fast with ascending cycle number. When increasing the current, the capacities of P/C and Ge/C decay very fast to less than 40% of their initial capacities while GeP$_5$/C can well maintain 85% of its initial capacity at the current increasing from 0.1 to 5 A g$^{-1}$. Referring to Cui’s and Wang’s works,\(^{12, 18}\) P-C bonds are formed at the interface of GeP$_5$ layers and carbon layers during HEMM. The formation of P-C bonds would strengthen the structural resistance against the volume stress during Li$^+$ insertion/retraction, thus GeP$_5$/C and P/C can show much better cycle performances than Ge/C who cannot form P-C bonds. As for rate performances, the existence of P-C bonds together with the intermediate discharge/charge products of Ge and Li$_2$Ge, would guarantee an excellent conductive network for the active P component. Thus, GeP$_5$/C can exhibit much higher rate performance than P/C and Ge/C.

**Conclusion**

In summary, we for the first time investigated the electrochemical performances of GeP$_5$ as an anode of LIB. Through a simple method of HEMM at ambient temperature and pressure, pure phase GeP$_5$ can be prepared in a large scale and high quality, from commercially available amorphous red P and Ge powders. The crystal structure is simulated by XRD Rietveld refinement and first principle calculation, respectively. GeP$_5$ exhibits a good reversible capacity of 2266 mA h g$^{-1}$ with a first coulombic efficiency as high as 95%, much larger than those reported data for black P and other metal phosphides. The large capacity and high initial reversibility of GeP$_5$ are attributed to its high metallic conductivity and synergetic Li storage ability of its Ge and P components. Further, by forming an amorphous GeP$_5$/C nanocomposite, much enhanced rate performance and cycle stability can be achieved, e.g., a capacity of 2127 mA h g$^{-1}$ at a high current of 5 A g$^{-1}$ and a stable capacity of 2300 mA h g$^{-1}$ after 40 cycles. The enhanced performance of GeP$_5$/C composite may result from the effective combination between GeP$_5$ and C layers which provides not only an integrated continuous conductive network but also a good structural flexibility to buffer the volume changes and resist the structure stress during Li$^+$ insertion/retraction. Briefly, integration of high first coulombic efficiency, large capacity, safe voltage, and excellent rate performance, GeP$_5$ and its carbon nanocomposite offer great promise as a high power and high energy anode for next-generation high performance LIB.

**Experimental**

**Synthesis and Characterization of GeP$_5$ and GeP$_2$/C**

Pure phase GeP$_5$ was synthesized by high energy mechanical milling (HEMM, Fritsch Pulverisette-6) of stoichiometric amounts of Ge (20 mmol) and amorphous red P (100 mmol) powder with a rotation speed of 400 rpm/min under Ar atmosphere. GeP$_5$/C nanocomposite was also obtained by HEMM the above-synthesized GeP$_5$ and Super P in a mass ratio of 7:2 for 10 h at 400 rpm/min. For comparison, Ge/C and P/C samples were also prepared at the same condition in same weight ratio of Ge (or P): C = 7:2. The synthesized products were characterized by a X-ray diffraction (XRD, PANalytical X’pert PRO-DY2198), a scanning electron microscope (SEM, FEI Sirion 200), a transmission electron microscope (TEM, FEI Tecnai G2 F30), a confocal Raman spectrometer (Raman, JobinYvon HR800) with a 532 nm excitation laser and a X-ray photoelectron spectrometer (XPS, AXIS-ULTRA DLD-600W) using an Al Kα.

**Electrochemical Measurements**

Electrochemical characterization was performed, using 2032 coin cells. The GeP$_5$/C anodes were prepared by pasting the paste containing 90 wt% of GeP$_5$/C and 10 wt% of Li-PAA onto a Cu foil. For comparison, the bare GeP$_5$ anode was made up of 70 wt% pure GeP$_5$, 20 wt% Super P and 10 wt% Li-PAA. The
loading of the active material is ca. 1.5-2 mg cm$^{-2}$. The electrolyte was 1.0 mol L$^{-1}$ LiPF$_6$ dissolved in ethylene carbonate-diethyl carbonate (EC-DEC, 1:1 by vol.) solution. The lithium foil was performed as counter and reference electrodes. Cells were assembled in a glove-box with water-oxygen content below 1 ppm and tested at 25 °C. The galvanostatic discharge-charge tests were carried out on a LAND (Wuhan Kingnuo Electronic Co., China) cycler.

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Notes and references

Layered Phosphorus-Like GeP$_5$: a Promising Anode Candidate with High Initial Coulombic Efficiency and Large Capacity for Lithium Ion Batteries

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**Keywords**: GeP$_5$, layered structure, phosphorus-like, anode, lithium ion batteries

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Layer structured GeP$_5$ is firstly developed as an anode material for LIB, it delivers a reversible capacity of 2300 mA h g$^{-1}$ with a very high initial coulombic efficiency of 95%.
Broader context

Although great progresses had been made in last two decades, the performances of lithium-ion batteries are still far below the requirements of vehicle industry especially in comparison with the energy and power density of combustion engines. To make a breakthrough in energy and power density, new electrode materials must be searched to take place the current utilized LiCoO$_2$ cathode and graphite anode. For anode, various materials such as conversion-type metal oxides and alloy-type Si, Ge, Sn have been proposed as the alternatives of graphite. They are all capable to deliver a capacity several times that of graphite. However, none of them can behave a high reversibility as graphite. These large capacity materials usually suffer a very low initial coulombic efficiency (< 70%) and undergo a rapid capacity loss during cycling, which make them difficult to use in full batteries. Here, we for the first time develop GeP$_5$ as a new anode candidate. It holds a two-dimensional layered structure and a high electronic conductivity as graphite. It can deliver an unprecedented high capacity of ~2300 mA h g$^{-1}$ with a high initial coulombic efficiency of 95%, which is the highest value in reported anodes to our best knowledge.