The prospects of phosphorene as an anode material for high-performance lithium-ion batteries: a fundamental study

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Abstract
To completely understand lithium adsorption, diffusion, and capacity on the surface of phosphorene and, therefore, the prospects of phosphorene as an anode material for high-performance lithium-ion batteries (LIBs), we carried out density-functional-theory calculations and studied the lithium adsorption energy landscape, the lithium diffusion mobility, the lithium intercalation, and the lithium capacity of phosphorene. We also carried out, for the very first time, experimental measurement of the lithium capacity of phosphorene. Our calculations show that the lithium diffusion mobility along the zigzag direction in the valley of phosphorene was about 7 to 11 orders of magnitude faster than that along the other directions, indicating its ultrafast and anisotropic diffusivity. The lithium intercalation in phosphorene was studied by considering various Li$_n$P$_{16}$ configurations ($n = 1–16$) including single-side and double-side adsorptions. We found that phosphorene could accommodate up to a ratio of one Li per P atom (i.e. Li$_1$P$_{16}$). In particular, we found that, even at a high Li concentration (e.g. $x = 1$ in Li$_x$P), there was no lithium clustering, and the structure of phosphorene (when fractured) is reversible during lithium intercalation. The theoretical value of the lithium capacity for a monolayer phosphorene is predicted to be above 433 mAh g$^{-1}$, depending on whether Li atoms are adsorbed on the single side or the double side of phosphorene. Our experimental measurement of the lithium capacity for few-layer phosphorene networks shows a reversible stable value of $\sim$453 mAh g$^{-1}$ even after 50 cycles. Our results clearly show that phosphorene, compared to graphene and other two-dimensional materials, has great promise as a novel anode material for high-performance LIBs.

Keywords: phosphorene, lithium-ion battery, adsorption, diffusion, capacity, reversibility, cycling performance

(Some figures may appear in colour only in the online journal)

1. Introduction
One of the major challenges in developing anode materials for high-performance lithium-ion batteries (LIBs) is to find promising anode materials with high capacity, high-rate charging/discharging, large open-circuit voltage, and good reversibility in cycling performance [1, 2]. Graphite has conventionally been chosen as the anode in LIBs for commercial use because of its high energy stability, low cost, and good cycling performance [3–7]. But its low specific capacity of 372 mAh g$^{-1}$ (i.e. its most lithium-rich compound is LiC$_6$, with only one Li atom per six carbon atoms under ambient conditions [8, 9]) has limited its application as a promising anode for high-performance LIBs, and demands a search for better-performing anode materials beyond graphite. Silicon was found to be a very attractive anode with an
extremely high capacity of 4200 mAh g\(^{-1}\) [10–15]. However, the large volume expansion, due to the formation of the Li\(_2\)Si\(_3\) alloy during lithium intercalation, leads to an irreversibility of Li insertion/extraction [16] and, therefore, its stability in cycling performance is problematic. Intensive studies to nanostructured Si anode materials to enhance the cycling life have been performed [17–19]. Recently, black phosphorus has aroused much interest as a promising anode material in LIBs because of its weak van der Waals interlayer space and relatively high capacity of 2596 mAh g\(^{-1}\) [20–25]. Unfortunately, the cycling efficiency is limited due to the large volume expansion (~300% expansion [21]) when Li atoms are inserted into black phosphorus, causing the combined system to form an Li\(_2\)P alloy.

Quite recently, two-dimensional (2D) materials have been considered as potential anode materials for high-performance LIBs because of their high charge-carrier mobility [26], large surface-volume ratio [27], and broad electrochemical window [28], as compared to their bulk counterparts, which enable fast-ion diffusion and offer more ion insertion channels with the entire surface exposed. Two typical promising 2D anode materials in LIBs are graphene [29–47] and transition metal dichalcogenides (TMDCs), such as Molybdenum disulfide (MoS\(_2\)) [48–57]. The theoretical capacity of graphene was predicted to be 744 mAh g\(^{-1}\) with the hypothesis being that Li atoms could be adsorbed on the double side of graphene with the Li\(_2\)C\(_3\) configuration, and the separation of Li atoms could still keep at about 4.35 Å to avoid Li clustering, as found in graphite [42–44]. However, the experimental reports showed that at ambient temperature and pressure, Li metal invariably co-exists with the parallel layers of graphene [42], and only the crumpled or curved single-layered graphene nanosheet [44, 45] or carbonaceous arrangement such as a group of single-layered graphene in a ‘house of cards’ arrangement [43] could accommodate up to two Li atoms per six carbon atoms on both sides of graphene as well as on the edges. The reversible capacity of such curved graphene was found to strongly depend on the nanoporosity of graphene [42–45]. Similar results were also found in graphene-like MoS\(_2\) [58]. Furthermore, it was pointed out that the weak interactions between Li and graphene (e.g. the binding energy is about 1.04 eV [46]) might result in low open-circuit voltage and weaken the electrochemical performance [7, 28–31] in LIBs. Recently, another family of 2D materials [59], such as the 2D Ti\(_3\)C\(_2\) materials, was reported as promising host materials for LIBs. The calculated theoretical capacity for Li is 447.8 mAh g\(^{-1}\), higher than that of graphite, but the calculated open-circuit voltage is low. Searching for anode materials with strong interactions with Li atoms and large open-circuit voltage is, therefore, desirable [59].

Analogous to graphene and MoS\(_2\), phosphorene can be synthesized by mechanical exfoliation of black phosphorus [60, 61]. This newly discovered 2D material has quite unique properties. It exhibits a puckered honeycomb structure, and possesses semiconductor behavior with a direct band gap and anisotropic electronic properties. In addition to these properties, anisotropic mechanical, thermal, and optical properties, as well as related potential applications have been reported [62–69]. Based on the unique properties, a number of theoretical calculations of the diffusion and the capacity of phosphorene in Li-ion and Na-ion batteries have been carried out [70–78]. Two theoretical groups found that the diffusion energy barrier of Li in phosphorene is anisotropic [70, 71], and the diffusion mobility of Li atoms along the zigzag direction on phosphorene is about 10\(^{10}\) times faster than that along the armchair direction. The similar ultrafast diffusion mobility was also reported in a Na-ion battery [76, 77]. Noted that these calculations on the diffusion were carried out using the climbing image nudged elastic band method [79, 80] along specific orientations, and a comprehensive study on the diffusivity along various possible diffusion paths is desired so as to provide the entire picture about diffusivity on phosphorene surface. The theoretical capacity of Li on phosphorene monolayer was predicted to be about 433 mAh g\(^{-1}\) by Zhao et al using density-functional-theory (DFT) calculations [75]. Meanwhile, Kulish et al [77] predicted that the capacity for Na can be as high as 865 mAh g\(^{-1}\) using DFT calculations including the van der Waals interaction [81]. Therefore, a complete understanding of the capacity of Li in phosphorene is, indeed, necessary and experimental investigation along this orientation is indispensable.

In this work, we performed a systematically study of the Li adsorption energy landscape, the diffusion process, the ability of phosphorene to accommodate Li atoms, and the capacity of Li in phosphorene using the first-principles calculations. The interaction between Li and phosphorene was found to be much stronger than that in graphene implying the possible high open-circuit voltage and potential application in enhancing electrochemical performance. In particular, we found that the Li diffusion on phosphorene along the zigzag channel is about 10\(^4\) and 10\(^2\) times faster than on graphene and MoS\(_2\), which implies that phosphorene may exhibit outstanding rate charging/discharging. The estimated theoretical Li capacity can reach 433 mAh g\(^{-1}\) for the single-side adsorption and 865.5 mAh g\(^{-1}\) for the double-side adsorption, similar to the value predicted by Kulish et al for Na in phosphorene [77]. Interestingly, no Li clustering was found, and even if some of the phosphorous bonds broke at a high Li concentration (e.g. x = 1 in Li\(_x\)P), they could automatically reform after removal of the Li atoms, indicating good reversibility of phosphorene during the insertion/extraction process. Our experimental measurements on the Li capacity for few-layered phosphorene networks show a reversible and stable capacity of ~453 mAh g\(^{-1}\) after 30 cycles. Such value remained for over 50 cycles. Our current results clearly reveal the outstanding features of phosphorene as a promising host material for high-performance LIBs.

2. Computational details

Our first-principles calculations were performed using the DFT [82, 83] framework, as implemented in the Vienna ab initio Simulation Package (VASP) [84]. The electron-ion interactions were described by the projector augmented wave
and capacity of Li on the phosphorene monolayer. A vacuum space of 15 Å was set between adjacent layers to avoid any mirror interactions of Li atoms. The Brillouin zone is set using a Monkhorst–Pack grid of 16 × 12 × 1 in all calculations.

The adsorption energy per Li atom on monolayer phosphorene \( E_a \) is defined as

\[
E_a = \frac{(E_{Li,P_{16}} - E_{P_{16}} - nE_{Li})}{n},
\]

where \( E_{Li,P_{16}} \), \( E_{P_{16}} \), and \( E_{Li} \) are the total energy of the Li\(_{16}\)P\(_{16}\) system, the 2 × 2 pristine phosphorene (16 atoms), and the isolated Li atom, respectively, and \( n \) is the number of adsorbed Li atoms in the 2 × 2 supercell. From the energy adsorption defined in equation (1), we can calculate the adsorption energy landscape for a single Li atom loaded on the phosphorene surface and find the preferential positions for Li adsorbed on phosphorene.

Based on the adsorption energy landscape, the energy barrier along different diffusion paths was determined. Following the Arrhenius equation [89] for the temperature dependence of reaction rates, which can currently be used to model the temperature variation of diffusion coefficients, the diffusion constant (\( D \)) of Li can be estimated as

\[
D \sim \exp \left( -\frac{E_a}{k_B T} \right),
\]

where \( E_a \) is the activation energy (or diffusion barrier), \( k \) is the Boltzmann constant, and \( T \) is the environmental temperature (300 K was chosen in the calculation). Following equation (2), the diffusion constant of Li on phosphorene can be qualitatively evaluated, and the most preferential diffusion path for single Li atoms on phosphorene can be determined.

The theoretical capacity of an LIB was estimated by Faraday’s law through studying the formation energy involved in the intercalation process, which is defined by

\[
E_f(Li,P) = E_{Li,P} - E_p - xE_{Li},
\]

where \( E_{Li,P} \) is the total energy per formula unit of the Li\(_p\)P system, \( E_p \) the energy of the P atom in phosphorene, \( E_{Li} \) the energy of the Li atom in the BCC phase, and \( x \) the Li:P ratio. The capacity is then defined as

\[
C = \frac{x_{\text{max}} F}{M_p},
\]

where \( x_{\text{max}} \) is the highest atomic ratio of Li to P atoms in the combined Li\(_p\)P system with negative formation energy, or before the possible formation of the Li metal phase, \( F \) is the Faraday constant (26.8 Ah mol\(^{-1}\)), and \( M_p \) is the atomic mass of the P atom (31 g mol\(^{-1}\)).

3. Results and discussion

3.1. Adsorption energy landscape

The adsorption energy landscape of a Li atom adsorbed on phosphorene was obtained by performing the vertical relaxation of the Li\(_p\)P system with a single Li atom loading at

![Diagram of phosphorene with Li adsorption](image_url)
different sites above phosphorene. 40 possible Li adsorption positions were considered in the $1 \times 1$ unit cell of phosphorene, as shown in figure 1(a), in which the Li atom was placed either on top of P atoms (referred to as ‘TA’ sites and represented by red dots), or on top of the middle of P-P bonds (referred to as ‘TB’ and ‘VB’ sites and represented by blue dots), or at the center of the triangular region formed by P-P-P atoms (referred to as ‘TH’ and ‘VH’ sites and represented by green dots), or at other sites spread among these sites (represented by black dots). The characters ‘V’ and ‘T’ in the notations represent the positions of Li atom in the valley and on the top of ridge, respectively. The vertical relaxation was carried out by allowing the motion of Li and P atoms along the direction perpendicular to the phosphorene surface. The vertical distance ($d$) which is defined as the distance between the Li atom and the middle of the thickness of puckered phosphorene (as shown in figure 1(b)) was optimized at different adsorption sites. Figure 1(c) shows one example of the total energy as a function of the vertical distance $d$ for a Li atom loaded at the VH site. The optimized vertical distance at the VH site is 2.53 Å.

Based on the calculated adsorption energy at each site, the adsorption energy landscape was obtained (see figure 2). The colors in the right column in figure 2 indicate the adsorption energies ($E_a$) at different sites relative to that at site VH. The darker the color is, the lower the relative adsorption energy. Figure 2 clearly shows that the adsorption energy landscape possesses anisotropic behavior. The positions of the Li atom with relatively low adsorption energy are located in the valley along the zigzag direction with minimum energy at VH sites, while positions of the Li atom with relatively high energy are located on the top of the ridge along the zigzag direction with the maximum relative energy at TA sites. The adsorption energy difference between these two sites is about 0.78 eV/Li. The saddle points were found at the VB site and the TB site, as indicated by the white and blue boxes in figure 2(a). Their corresponding adsorption energies are lower than those of their neighbors along the bond direction, but higher than those of their neighbors along the direction perpendicular to the bond, as shown in detail in figures 2(b) and (c), respectively. The adsorption energy landscape reveals that Li prefers to stay at the most stable VH site, and also possibly to stay at the metastable VB and TB sites when the most stable VH sites are occupied. Furthermore, the energy difference along the zigzag direction in the valley is much smaller than that along the armchair direction, which indicates that the preferential diffusion path for a single Li atom will be along the zigzag direction in the valley.

3.2. Diffusion

Rate charging and discharging in the LIB relates to the mobility of Li ions in the anode/cathode. The faster the Li atom moves, the higher the charging/discharging rate and, therefore, the rate capacity in the LIB. To study how fast the Li atom moves/diffuses on phosphorene, we calculated the diffusion energy barrier $E_b$ (defined by the relative adsorption energy at the site along the diffusion pathway with respect to that at the corresponding initial site) along various diffusion paths between the preferential adsorption sites VH, VB, and TB. Figure 3 presents the four most possible diffusion paths: in path 1, the Li atom migrates along the zigzag direction, starting at a VH site, going through VB sites, and then ending up at another VH site (referred to as ‘VH → VB → VH’; see the black dots in figure 3(a)); in path 2, the Li atom migrates along the direction perpendicular to the zigzag direction, starting at a VB site, crossing over the ridge through the TB site, and then ending up at another VB site (referred as ‘VB → TB → VB’; see the green dots in figure 3(a)); in path 3, the Li atom migrates along the direction that starts at a VH site, crosses over the ridge through the TB site, and then ends up at another VH site (referred to as ‘VH → TB → VH’; see
the blue dots in figure 3(a)); and in path 4, the Li atom migrates along the armchair direction, crossing over the ridge through the highest adsorption energy site TA, and then ending up at another VH site (referred to as ‘VH → TA → VH’: see the red dots in figure 3(a)). The two different side views of these four paths are also shown in figures 3(b) and (c). Clearly, the Li atom migrates in the same valley along path 1, but it migrates from one valley over the ridge and to another valley along paths 2–4.

The corresponding energy barriers (E_d) with respect to the energy at the initial position for each path as a function of the relative distance are summarized in figure 4(a). The relative distance of a Li atom is defined by the ratio of the horizontal distance of the Li (with respect to the starting point) to the horizontal distance of the ending point (with respect to the starting point). It was found that the adsorption energy at the VB site is relatively higher than that at other sites along path 1, and the calculated corresponding diffusion energy barrier to the VH site is 0.09 eV. In path 2, the corresponding diffusion energy barrier is about 0.58 eV, which is about 0.49 eV higher than that in the path 1. It is found that there is a very shallow valley in the diffusion energy barrier around the TB site in path 2, which is attributed to the local minimum along the direction of the P-P bond at the TB site (see figure 2(b)). Similarly, Li moving along path 3 also crosses the TB site with the initial point at the VB site, but since path 3 is along the direction perpendicular to the P-P bond at site TB, there is no local minimum around the TB site. The calculated corresponding diffusion energy barrier in path 3 is about 0.69 eV, which is about 0.11 eV higher than that in path 2 and about 0.60 eV higher than that in path 1. In path 4, the Li atom migrates from the most preferential adsorption site VH along in the armchair direction, and crosses over the most unstable site TA; the calculated diffusion energy barrier is 0.78 eV, which is the highest among those diffusion paths. The Li diffusion constant can be quantitatively evaluated from equation (2). The evaluated value along path 1 is about $3.58 \times 10^7$ times faster than that along path 2, about $7.36 \times 10^9$ times faster than that along path 3, and about $1.89 \times 10^{11}$ times faster than that along path 4, respectively, indicating that the Li diffusion on phosphorene is ultrafast and anisotropic. In addition, a comparison of diffusion constants among these paths reveals that even though paths 2–4 all cross over the ridge, the mobility of Li is quite different. Such an anisotropic diffusion nature on phosphorene is quite different from the isotropic diffusion on graphene and MoS2 layer. Specifically, if Li diffuses on phosphorene along the zigzag channel in the valley, the diffusion energy barrier (0.09 eV) is much lower than that on graphene (0.327 eV) [47] and MoS2 (0.25 eV) [57].

The evaluated corresponding mobility of Li on phosphorene is then about 4 and 2 orders of magnitude faster than that on graphene and MoS2, respectively, indicating that the rate charging/discharging is much higher along the zigzag direction in phosphorene compared to graphene and MoS2. Such high Li diffusivity is important to satisfy the current-density requirements and is essential for the performance of the anode materials in LIBs. To utilize this ultrafast anisotropic diffusivity, high-quality phosphorene anodes that are highly orientated in the zigzag direction are required, which remains a huge challenge in terms of synthesis.

The ultrafast and anisotropic diffusion nature of a Li atom migrating on phosphorene comes from the unique puckered structure of phosphorene, which is crucial for the Li diffusion. Figure 4(b) shows the optimized vertical distances d as function of the relative distance along each path. It was found that the maximum vertical difference along path 1 is 0.09 Å, and such small height difference allows Li to migrate though the channel very easily. On the other hand, in paths 2–4, a Li atom has to climb from the valley up to the ridge by about 0.58–0.79 Å; hence much more energy is needed for Li to conquer the ridge. A comparison between the diffusion energy barrier (figure 4(a)) and the vertical distance (figure 4(b)) reveals that the lower the vertical distance d, the lower the diffusion energy barrier and the easier it is for Li to diffuse.

### 3.3. Lithium Intercalation

To study how much phosphorene can accommodate Li atoms and, therefore, to evaluate the capacity of Li on a phosphorene monolayer, several Li,P16 systems, including LiP16, LiI,P16, LiI,P16, LiI,P16, and LiI,P16 were studied. For each Li,P16 system, several configurations, including Li atoms loaded on single side and double sides of phosphorene were taken into consideration. In all configurations, Li atoms were initially placed in VH, VB, or TB sites and the
corresponding systems were fully relaxed to obtain the stable configurations with different Li concentrations. The results are discussed as follows.

### 3.3.1. LiP$_{16}$ system

The top and side views of the stable LiP$_{16}$ structures with a single Li atom adsorbed at VH, VB, and TB sites are shown in figure 5. The corresponding adsorption energy $E_a$ and the geometric properties are summarized in table 1. It is obvious from the 3rd column that the VH site is the most energetically stable adsorption site with an adsorption energy of $-2.086$ eV/Li. The next most stable adsorption site is the VB site ($-1.995$ eV/Li), followed by the TB site ($-1.427$ eV/Li). From the 4th and 5th columns in table 1, we found that the Li atom located at the VH site with a vertical distance ($d$) of 2.53 Å has three nearest P neighbors; the corresponding Li-P distances ($d_{Li-P}$) are 2.45, 2.54 and 2.54 Å, respectively. The Li atom at the VB site has two nearest P neighbors with an Li-P distance ($d_{Li-P}$) of 2.41 Å, and the vertical distance ($d$) is about 0.07 Å higher than that at the VH site. Meanwhile, at the TB site, the vertical distance ($d$) is about 0.7 Å higher than that at the VH site, and the two nearest Li-P distances ($d_{Li-P}$) are equal with the value of 2.58 Å. Since the Li-P distances in these configurations are within the Li-P bond length of 2.68 Å, this indicates that the Li atom is chemically bonded with P atoms. Such a chemical-bonding nature and low adsorption energy demonstrate that the interaction between Li and phosphorene is strong, compared to graphene and, therefore, could prevent Li clustering during Li insertion, which is desirable in the electrochemical performance.

### 3.3.2. Li$_2$P$_{16}$ system

We considered about 45 initial configurations for 2 Li atoms loaded on the single side of the phosphorene. These single-side configurations can be classified by six groups denoted by S-VH-VH, S-VH-VB, S-VH-TB, S-VB-VB, S-TB-TB, and S-VB-TB, respectively, where the first notation ‘S’ means the single-side adsorption, and the second and third notations indicate the locations of two Li atoms, respectively. We found that only 12 stable structures corresponding to groups of S-VH-VH, S-VH-VB, S-VH-TB, S-VB-VB, and S-TB-TB were obtained after full relaxation. In particular, initial configurations belonging to groups S-VH-TB and S-VB-TB were not stable and transferred to the configurations belonging to the group S-VH-VH after the full relaxation.

**Table 1.** Calculated adsorption energy ($E_a$), the distances between Li and the nearest-neighbor P atoms on phosphorene ($d_{Li-P}$), and the vertical distance ($d$) of the LiP$_{16}$ system with the Li atom at the preferential adsorption positions (VH, VB, and TB sites).

<table>
<thead>
<tr>
<th>System</th>
<th>Adsorption Site</th>
<th>$E_a$ (eV/Li)</th>
<th>$d_{Li-P}$ (Å)</th>
<th>$d$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiP$_{16}$</td>
<td>VH</td>
<td>$-2.086$</td>
<td>2.45, 2.54</td>
<td>2.53</td>
</tr>
<tr>
<td></td>
<td>VB</td>
<td>$-1.995$</td>
<td>2.41</td>
<td>2.61</td>
</tr>
<tr>
<td></td>
<td>TB</td>
<td>$-1.427$</td>
<td>2.58</td>
<td>3.23</td>
</tr>
</tbody>
</table>
distance (indicated in parentheses in columns 4 and 5. For example, in the configuration D-VH/VB, the distances between Li and the nearest-neighbor P atoms on phosphorene are 2.41 Å to 2.32 Å at the VB sites, and from 2.58 Å to 2.50 Å at the VH sites, respectively. The light and dark gray balls represent Li atoms above and below the phosphorene monolayer, respectively; while the light and dark purple colored balls denote phosphorus on the ridge and in the valley, respectively. For the notations corresponding to each configuration, please see their definitions in the text. Please also note that, in order to see the distribution of Li atoms on phosphorene clearly, Li-P bonds were not presented here (or in figures 7–10 for the same reason).

Figure 6. Top (up) and side (down) views of the stable Li2P16 system with single-side configurations (a) and double-side configurations (b), respectively. The light and dark gray balls represent Li atoms above and below the phosphorene monolayer, respectively; while the light and dark purple colored balls denote phosphorus on the ridge and in the valley, respectively. The light and dark gray balls represent Li atoms above and below the phosphorene monolayer, respectively; while the light and dark purple colored balls denote phosphorus on the ridge and in the valley, respectively.

Table 2. Calculated adsorption energy ($E_a$), distances between Li and the nearest-neighbor P atoms on phosphorene ($d_{i-P}$), the vertical distance ($d$), and the nearest Li-Li distance ($d_{i-Li}$) for the stable single-side (top panel) and double-side (bottom panel) configurations of the Li2P16 system. In cases where there are different types of configurations in the S-VH-VH, S-VH-VB, S-VB-VB, and S-TB-TB, the corresponding adsorption energies and geometric properties for these four configurations are listed in parentheses in columns 4 and 5. For example, in the configuration D-VH/VB, the $d_{i-P}$ and $d$ values at the VH and VB sites are indicated by ‘VH’ and ‘VB’ in the corresponding parentheses. Note that the large Li-Li distances (beyond 6.5 Å) in the double-side configurations in the Li2P16 system are not counted here.

<table>
<thead>
<tr>
<th>System</th>
<th>Configuration</th>
<th>$E_a$ (eV/Li)</th>
<th>$d_{i-P}$ (Å)</th>
<th>$d$ (Å)</th>
<th>$d_{i-Li}$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li2P16 (Single-side)</td>
<td>S-VH-VH</td>
<td>−2.045</td>
<td>2.35, 2.56</td>
<td>2.54</td>
<td>4.62</td>
</tr>
<tr>
<td></td>
<td>S-VH-VB</td>
<td>−2.000</td>
<td>2.38, 2.53 (VH)</td>
<td>2.54 (VH)</td>
<td>4.99</td>
</tr>
<tr>
<td></td>
<td>S-TB-TB</td>
<td>−1.957</td>
<td>2.31</td>
<td>2.63</td>
<td>4.62</td>
</tr>
<tr>
<td></td>
<td>S-VB-VB</td>
<td>−1.347</td>
<td>2.45</td>
<td>3.28</td>
<td>4.62</td>
</tr>
<tr>
<td>Li2P16 (Double-side)</td>
<td>D-VH/VH</td>
<td>−2.113</td>
<td>2.43, 2.53</td>
<td>2.51</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>D-VH/VB</td>
<td>−2.064</td>
<td>2.43, 2.53 (VH)</td>
<td>2.50 (VH)</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>D-VB/VB</td>
<td>−2.018</td>
<td>2.41 (VB)</td>
<td>2.58 (VB)</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>D-VH/TB</td>
<td>−1.755</td>
<td>2.34, 2.55 (VH)</td>
<td>2.53 (VH)</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>D-VB/TB</td>
<td>−1.718</td>
<td>2.40 (VB), 2.47 (TB)</td>
<td>2.59 (VB)</td>
<td>—</td>
</tr>
</tbody>
</table>

From the adsorption energy $E_a$ (the 3rd column in table 2), we found that the configuration in the S-VH-VH group (i.e. the first panel in figure 6(a)) is the most stable configuration compared with other single-side configurations (e.g. the 2nd–4th panels in figure 6(a)). There is no significant change in the vertical distance $d$ at sites VH, VB, and TB, compared with the LiP16 system when two Li atoms stay on the single side (see the 5th column in tables 1 and 2). But some of the Li-P distances ($d_{i-P}$) decrease in the Li2P16 system, for instance, from 2.45 Å to 2.35 Å at the VH sites, from 2.41 Å to 2.32 Å at the VB sites, and from 2.58 Å to 2.45 Å at the TB sites, respectively (see the 4th column in tables 1 and 2), indicating that the more the Li atoms are adsorbed, the stronger the Li-P attractive interactions, and the shorter the Li-P bonds. In addition, since the Li concentration is still low, the nearest Li-Li distance is larger (4.62–4.99 Å):
see the 6th column in table 2) than the Li-Li bond length (2.68 Å in our DFT calculation), indicating that the interaction between Li atoms is very weak.

By adding one more Li atom on the other side of the three stable configurations obtained in the LiP16 system, we constructed double-side configurations for the Li2P16 system. It should be noted that, on the other side of phosphorene, the corresponding stable adsorption sites (i.e. the VH, VB, or TB site) are those located below the TH, TB, and VB sites, if we see them from the top view of phosphorene (figure 1(a)). 48 initial double-side configurations were constructed following this consideration. They are classified by six groups, denoted by D-VH/VH, D-VH/VB, D-VH/TB, D-VB/VB, D-VB/TB, and D-TB/TB, respectively. The notation 'D' indicates the double-side adsorption; the notation before/after the slant indicates the Li atoms at the sites above/below the phosphorene monolayer. After full relaxation, only 15 stable double-side configurations corresponding to the first five groups were obtained, and the five most stable double-side configurations among them corresponding to each of the five groups are shown in figure 6(b). The corresponding adsorption energies and geometric properties are listed in table 2.

Comparing the adsorption energies $E_a$ of these stable single/double-side configurations (see the 3rd column in table 2) we found that the configuration D-VH/VH ($−2.113$ eV/Li) is the most stable structure in the Li2P16 system, followed by configuration D-VH/VB ($−2.064$ eV/Li), and then the single-side configuration S-VH-VH, which is about 0.02 eV higher than the configuration D-VH/VB. It was also found that, by adding one more Li atom on the other side of the stable LiP16 system, the nearest Li-P distance ($d_{L_i-P}$) (the 4th column in table 2) and the vertical distance $d$ (the 5th column in table 2) at sites VH, VB, and TB are similar to those in the stable LiP16 system (the 4th and 5th columns in table 1), since the separation of Li atoms on both sides are still the same as those in the stable LiP16 system.

3.3.3. Li$_4$P$_{16}$ system. In searching the stable configurations for the Li$_4$P$_{16}$ system with single-side adsorption, we mainly focused on the configurations in which four Li atoms were loaded at each of the four $1 \times 1$ unit cells above the phosphorene monolayer. The initial single-side configurations were classified into three groups, denoted by S-4VH, S-4VB, and S-4TB, respectively, where the number in the notations indicates the total number of Li atoms on the corresponding sites. These single-side configurations were fully relaxed and only five of them were stabilized to the structures denoted by S-4VHa, S-4VHb, S-2(VH-TH), S-4VB, and S-4TB, respectively (see figure 7(a)), in which the configurations S-4VHa and S-4VHb are distinguished by the distribution of the four Li atoms at the VH sites on the $2 \times 2$ supercell with different symmetry (see the two left panels in figure 7(a)). While, the configuration S-2(VH-TH) (i.e. the second right panel in figure 7(a)) was obtained from the initial configuration in the group S-4VH by distributing the four Li atoms at the VH sites with a Li-Li distance shorter than the Li-Li bond length. During the relaxation, these Li atoms push each other away, and two of them move to the TH sites, and the system is finally relaxed to a stable structure with an S-2 (VH-TH) configuration with Li-Li distances of 3.0 Å.

The corresponding adsorption energies and geometric properties are listed in table 3. It can be seen from the adsorption energy $E_a$ (the 3rd column) that configurations S-4VHa and S-4VHb are two relatively stable structures, as compared to the other three stable single-side configurations.

![Figure 7](image-url) Figure 7. Top (up) and side (down) views of the stable Li$_4$P$_{16}$ system with single-side configurations (a) and double-side configurations (b). The light and dark gray balls represent Li atoms above and below the phosphorene monolayer, respectively, while the light and dark purple colored balls denote phosphorus on the ridge and in the valley, respectively. For the notations corresponding to each configuration, please see their definitions in the text.
Comparing the values in the 4th and 5th columns in tables 1 and 3, we found that the nearest Li-P distances keep almost the same values in both LiP16 and Li4P16 systems, while the vertical distances \(d\) of the Li atom at the VH, VB, and TB sites in LiP16 are about 0.1–0.3 Å higher than those in LiP16, indicating a vertical increase of the phosphorene layer when more Li atoms are attracted by P atoms and, therefore, a slight expansion in volume. This phenomenon is also found when more Li atoms adsorbed to phosphorene (see the results and discussions for the Li6P16, Li8P16, and Li16P16 systems in the sections that follow).

Similar to our consideration in searching for stable double-side configurations for LiP16 structures, we added two more Li atoms on the other side of the four stable single-side configurations in the Li3P16 system (i.e. the four structures shown in figure 6(a)), and constructed 36 initial double-side configurations. Among them, only four stable structures are obtained after full relaxation. They are denoted by D-2(VH/VH)\(a/b\), D-2(VB/VB), and D-(VH-VB)/(VH-VB), respectively, where the subscripts \(a\) and \(b\) indicate the distribution of the four Li atoms in the same configuration with different symmetry. The top and side views of these stable structures are shown in figure 7(b) and the corresponding energetic and geometric properties are also listed in table 3. Comparing the adsorption energy \(E_a\) (the 3rd column in table 3) for all the obtained stable configurations in the LiP16 system, we found that all the double-side configurations have lower energy than those of single-side configurations, and the relatively more stable configurations are the double-side configurations D-2(VH/VH)\(a\) and D-2(VB/VB), followed by the double-side configuration D-(VH-VB)/(VH-VB). Furthermore, as shown in the last column in table 3, the Li-Li distance in these relatively stable structures is 4.62 Å in configurations D-2(VH/VH)\(a\) and D-2(VB/VB) and 4.40 Å in the configuration D-(VH-VB)/(VH-VB); therefore, the repulsive interactions between them are still weak.

3.3.4. \(Li_6P_{16}\) system. We added two more Li atoms on the same side of stable configurations S-4VH\(a\) and S-4VH\(b\) obtained in the LiP16 system (i.e. the structures shown in figure 7(a)) to search the stable configurations for the \(Li_6P_{16}\) system with single-side adsorption. The additional two Li atoms were loaded at the other two VH sites in two of the four \(1 \times 1\) unit cells, forming VH-VH pairs. Since some of the initial Li-Li distances (e.g. 1.72 Å) were shorter than the Li-Li bond length (2.68 Å), those Li atoms push each other away during the relaxation, leading to two Li atoms moving up to the TH sites, which is similar to the single-side adsorption of the LiP16 system. Two stable configurations S-4VH-2TH\(a/b\) were then obtained, where the subscripts \(a\) and \(b\) indicate the distribution of six Li atoms in the same configuration with

<table>
<thead>
<tr>
<th>System</th>
<th>Configuration</th>
<th>(E_a) (eV/Li)</th>
<th>(d_{Li-P}) (Å)</th>
<th>(d) (Å)</th>
<th>(d_{Li-Li}) (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiP16 (Single-side)</td>
<td>S-4VH(a)</td>
<td>-1.968</td>
<td>2.46, 2.53</td>
<td>2.64</td>
<td>3.31</td>
</tr>
<tr>
<td></td>
<td>S-4VH(b)</td>
<td>-1.949</td>
<td>2.42, 2.56</td>
<td>2.64</td>
<td>3.31</td>
</tr>
<tr>
<td></td>
<td>S-4VB</td>
<td>-1.885</td>
<td>2.41</td>
<td>2.74</td>
<td>3.31</td>
</tr>
<tr>
<td></td>
<td>S-2(VH-TH)</td>
<td>-1.769</td>
<td>2.44, 2.63 (VH)</td>
<td>2.75 (VH)</td>
<td>3.00</td>
</tr>
<tr>
<td>Li4P16 (Double-side)</td>
<td>S-4TB</td>
<td>-1.404</td>
<td>2.58</td>
<td>3.41</td>
<td>3.31</td>
</tr>
<tr>
<td></td>
<td>D-2(VH/VH)(a)</td>
<td>-2.090</td>
<td>2.41, 2.51</td>
<td>2.52</td>
<td>4.62</td>
</tr>
<tr>
<td></td>
<td>D-2(VB/VB)</td>
<td>-2.073</td>
<td>2.31</td>
<td>2.64</td>
<td>4.62</td>
</tr>
<tr>
<td></td>
<td>D-(VH-VB)/(VH-VB)</td>
<td>-2.048</td>
<td>2.41, 2.51 (VH)</td>
<td>2.51 (VH)</td>
<td>4.40</td>
</tr>
<tr>
<td></td>
<td>D-2(VH/VH)(b)</td>
<td>-1.978</td>
<td>2.41, 2.54</td>
<td>2.48</td>
<td>3.31</td>
</tr>
</tbody>
</table>
are indicated by distance to each 1
were constructed and denoted by $S-4$ TB pairs. The corresponding initial single-side configuration was found that the Li-P bond lengths at the VH and TH sites and energetic and geometric properties are also listed in table 4. It shows the top and side views of the stable single-side configuration with different symmetry. These structures were fully relaxed and only five of them were found to be stable. Figure 9(a) shows the Li-P bond lengths at the VH and TH sites are the same in both configurations (see the 4th column in table 4), while the vertical and the Li-Li distances (see the 5th and 6th columns in table 4) are slightly different. As discussed in section 3.3.3, the increase in the vertical distance implies slight volume expansion, and the shortness in the Li-Li distance will increase more repulsive interaction; therefore the adsorption energy in the configuration $S-4VH-2TH_a$ is about 0.044 eV higher than that in configuration $S-4VH-2TH_b$ (see the 3rd column in table 4).

When two more Li atoms were added on the other side of the stable single-side configurations of the Li$_8$P$_{16}$ system (i.e. the configurations shown in figure 7(a)), 12 initial double-side configurations were constructed. It should be noticed that the Li distribution in the Li$_8$P$_{16}$ system is asymmetric because the number of Li atoms on both sides is different, leading to difficulties in stabilizing the Li$_8$P$_{16}$ system. As a result, only three stable configurations are obtained after full relaxation. They are denoted by D-$4VH/2VH$, D-$4VB/2VB$, and D-$4TB/2VB$, respectively. The top and side views of these stable configurations are shown in figure 8(b) and the corresponding energetic and geometric properties are also listed in table 4. Similar to the Li$_2$P$_{16}$ and Li$_4$P$_{16}$ systems, the double-side configurations have lower adsorption energy (the 3rd column in table 4) than those of the single-side configurations, and the relatively more stable configurations are the double-side configuration D-$4VH/2VH$, followed by the double-side configurations D-$4VB/2VB$ and D-$4TB/2VB$.

### Table 4. Calculated adsorption energy ($E_d$), distances between Li and the nearest-neighbor P atoms on phosphorene ($d_{Li-P}$), the vertical distance ($d_v$) for the stable single-side (up panel) and double-side (bottom panel) configurations of the Li$_8$P$_{16}$ system. In the case where there are different types of $d_{Li-P}$ and $d_v$ values for a given configuration, notations corresponding to the sites are indicated in parentheses in columns 4 and 5. For example, in the configuration $S-4VH-2TH$, the $d_{Li-P}$ and $d_v$ values at the VH and TH sites are denoted by ‘VH’ and ‘TH’ in the corresponding parentheses.

<table>
<thead>
<tr>
<th>System</th>
<th>Configuration</th>
<th>$E_d$ (eV/Li)</th>
<th>$d_{Li-P}$ (Å)</th>
<th>$d_v$ (Å)</th>
<th>$d_{Li-Li}$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li$<em>8$P$</em>{16}$ (Single-side)</td>
<td>S-$4VH-2TH_a$</td>
<td>$-1.862$</td>
<td>$2.43$, $2.58$ (VH)</td>
<td>$2.54$ (VH)</td>
<td>$3.11$</td>
</tr>
<tr>
<td></td>
<td>S-$2VH-4TH_b$</td>
<td>$-1.818$</td>
<td>$2.43$, $2.58$ (VH)</td>
<td>$2.65$ (VH)</td>
<td>$2.96$</td>
</tr>
<tr>
<td>Li$<em>8$P$</em>{16}$ (Double-side)</td>
<td>D-$4VH/2VH$</td>
<td>$-2.034$</td>
<td>$2.41$, $2.52$</td>
<td>$2.58$</td>
<td>$3.36$</td>
</tr>
<tr>
<td></td>
<td>D-$4VB/2VB$</td>
<td>$-1.954$</td>
<td>$2.40$</td>
<td>$2.67$</td>
<td>$3.36$</td>
</tr>
<tr>
<td></td>
<td>D-$4TB/2VB$</td>
<td>$-1.657$</td>
<td>$2.40$ (VB)</td>
<td>$2.68$ (VB)</td>
<td>$3.36$</td>
</tr>
</tbody>
</table>

3.3.5. Li$_8$P$_{16}$ system. When two Li atoms were intercalated to each 1 $\times$ 1 unit cell at the VH, VB, and TB sites, they formed VH-VH, VH-VB, VH-TB, VB-VB, VB-TB, and TB-TB pairs. The corresponding initial single-side configurations were constructed and denoted by S-$4$(VH-VH), S-$4$(VH-VB)$_{a/b}$, S-$4$(VH-TB)$_{a/b}$, S-$4$(VB-VB), S-$4$(VB-TB)$_{a/b}$ and S-$4$(TB-TB)$_{a/b}$, respectively, where the subscripts a and b indicate the distribution of the eight Li atoms in the same configuration with different symmetry. These structures were fully relaxed and only five of them were found to be stable. Figure 9(a) shows the Li-P bond lengths at the VH and TH sites are the same in both configurations (see the 4th column in table 4), while the vertical and the Li-Li distances (see the 5th and 6th columns in table 4) are slightly different. As discussed in section 3.3.3, the increase in the vertical distance implies slight volume expansion, and the shortness in the Li-Li distance will increase more repulsive interaction; therefore the adsorption energy in the configuration $S-4VH-2TH_a$ is about 0.044 eV higher than that in configuration $S-4VH-2TH_b$ (see the 3rd column in table 4). When two more Li atoms were added on the other side of the stable single-side configurations of the Li$_8$P$_{16}$ system (i.e. the configurations shown in figure 7(a)), 12 initial double-side configurations were constructed. It should be noticed that the Li distribution in the Li$_8$P$_{16}$ system is asymmetric because the number of Li atoms on both sides is different, leading to difficulties in stabilizing the Li$_8$P$_{16}$ system. As a result, only three stable configurations are obtained after full relaxation. They are denoted by D-$4VH/2VH$, D-$4VB/2VB$, and D-$4TB/2VB$, respectively. The top and side views of these stable configurations are shown in figure 8(b) and the corresponding energetic and geometric properties are also listed in table 4. Similar to the Li$_2$P$_{16}$ and Li$_4$P$_{16}$ systems, the double-side configurations have lower adsorption energy (the 3rd column in table 4) than those of the single-side configurations, and the relatively more stable configurations are the double-side configuration D-$4VH/2VH$, followed by the double-side configurations D-$4VB/2VB$ and D-$4TB/2VB$.
Figure 9. Top (up) and side (down) views of the stable Li$_8$P$_{16}$ system with single-side configurations (a) and double-side configurations (b). The light and dark gray colored balls represent Li atoms above and below the phosphorene monolayer, respectively, while the light and dark purple colored balls denote phosphorus on the ridge and in the valley, respectively. For the notations corresponding to each configuration, please see their definitions in the text.

Table 5. Calculated adsorption energy ($E_a$), distances between Li and the nearest-neighbor P atoms on phosphorene ($d_{Li-P}$), the vertical distance ($d$), and the nearest Li–Li distance ($d_{Li-Li}$) for the stable single-side (up panel) and double-side (bottom panel) configurations of the Li$_8$P$_{16}$ system. In the case where there are different types of $d_{Li-P}$ and $d$ values for a given configuration, notations corresponding to the sites are indicated in parentheses in columns 4 and 5. For example, in the configuration S-4(VH/TH), the $d_{Li-P}$ and $d$ values at the VH and TH sites are indicated by ‘VH’ and ‘TH’ in the corresponding parentheses, and in the configuration S-4(VB-VB), the $d_{Li-P}$ and $d$ values at the VB sites in the up and down positions are indicated by ‘up’ and ‘down’ in the corresponding parentheses, respectively.

<table>
<thead>
<tr>
<th>System</th>
<th>Configuration</th>
<th>$E_a$ (eV/Li)</th>
<th>$d_{Li-P}$ (Å)</th>
<th>$d$ (Å)</th>
<th>$d_{Li-Li}$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li$<em>8$P$</em>{16}$ (Single-side)</td>
<td>S-4(VH-TH)</td>
<td>$-1.826$</td>
<td>2.43, 2.59 (VH)</td>
<td>2.69 (VH)</td>
<td>3.00</td>
</tr>
<tr>
<td></td>
<td>S-4(VB-TB)$_a$</td>
<td>$-1.805$</td>
<td>2.94 (TB)</td>
<td>3.08 (TB)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>S-4(VB-TB)$_b$</td>
<td>$-1.712$</td>
<td>2.94 (TB)</td>
<td>3.08 (TB)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>S-4(VB-VB)</td>
<td>$-1.658$</td>
<td>2.49</td>
<td>2.84 (down)</td>
<td>3.06</td>
</tr>
<tr>
<td></td>
<td>S-4(TB-TB)</td>
<td>$-1.481$</td>
<td>2.65</td>
<td>3.48 (down)</td>
<td>3.03</td>
</tr>
<tr>
<td>Li$<em>8$P$</em>{16}$ (Double-side)</td>
<td>D-4(VH/VH)</td>
<td>$-2.007$</td>
<td>2.40, 2.53</td>
<td>2.62</td>
<td>3.31</td>
</tr>
<tr>
<td></td>
<td>D-4(VH/VB)</td>
<td>$-1.965$</td>
<td>2.41, 2.54 (VH)</td>
<td>2.63 (VH)</td>
<td>3.31</td>
</tr>
<tr>
<td></td>
<td>D-4(VB-VB)$_a$</td>
<td>$-1.928$</td>
<td>2.40 (VH)</td>
<td>2.74 (VH)</td>
<td>3.31</td>
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<tr>
<td></td>
<td>D-4(VB-VB)$_b$</td>
<td>$-1.922$</td>
<td>2.40 (VH)</td>
<td>2.74 (VH)</td>
<td>3.31</td>
</tr>
<tr>
<td></td>
<td>D-4(VB/TB)$_a$</td>
<td>$-1.719$</td>
<td>2.53 (TB)</td>
<td>3.44 (TB)</td>
<td>3.31</td>
</tr>
<tr>
<td></td>
<td>D-4(VB/TB)$_b$</td>
<td>$-1.716$</td>
<td>2.53 (TB)</td>
<td>3.44 (TB)</td>
<td>3.31</td>
</tr>
<tr>
<td></td>
<td>D-4(TB/TB)$_a$</td>
<td>$-1.520$</td>
<td>2.53</td>
<td>3.43</td>
<td>3.31</td>
</tr>
<tr>
<td></td>
<td>D-4(TB/TB)$_b$</td>
<td>$-1.517$</td>
<td>2.53</td>
<td>3.43</td>
<td>3.31</td>
</tr>
</tbody>
</table>

at the VH, or the VB or TB site above the phosphorene layer and the other is located at the VH, or VB, or TB site below the phosphorene layer. The stable double-side configurations of the Li$_8$P$_{16}$ system are shown in figure 9(b), denoted by D-4(VH/VH), D-4(VH/VB), D-4(VB/VB)$_{a/b}$, D-4(VB/TB)$_{a/b}$, and D-4(TB/TB)$_{a/b}$, respectively, where subscripts a and b distinguish the different symmetry in the same configuration. The corresponding adsorption energies and geometric
properties are also listed in Table 5. As can be seen from Table 5, the most stable structure among the stable single/double-side configurations in the Li$_{16}$P$_{16}$ system is the one with the D-4(VH/VH) configuration ($E_a = -2.007$ eV/Li). Another three double-side configurations (i.e. D-4(VH/VB) and D-4(VB/VB)$_{ab}$) are about 0.042–0.085 eV higher than the D-4(VH/VH) configuration, but about 0.096–0.16 eV lower than the two single-side configurations (i.e. S-4(VH-TH) and S-4(VB-TB)$_b$). Furthermore, the single-side configuration (i.e. S-4(VB-TB)$_b$) with four Li atoms pulled up and away from the phosphorene layer is still competitive with the double-side configurations of D-4(VB/TB)$_a$ and D-4(VB/TB)$_b$. More interesting still, it is found that the single-side configuration S-4(VB/VB) is even more relatively stable than the double-side configuration D-4(TB/TB)$_{ab}$, indicating that when more Li atoms load on the phosphorene, some Li atoms prefer to stay at the single-side at the VB sites with higher vertical distance instead of staying at the double side at the TB sites with lower vertical distances. Comparing the nearest Li-P distance and vertical distance $d$ with the corresponding double-side Li$_{16}$P$_{16}$ configurations, we found that the Li-P distances did not change too much (see the 4th column in Table 5), but the vertical distances $d$ became higher (see the 5th column in Table 5), indicating a small vertical elongation of the phosphorene layer due to more Li-P attractions when more Li atoms were added on the phosphorene. Again, in all stabilized structures of the Li$_{16}$P$_{16}$ system, the repulsive force between the Li atoms drove them to occupy different sites with a Li–Li distance around 3.0 Å (see the 6th column in Table 5), and no Li clustering was found.

### 3.3.6. Li$_{16}$P$_{16}$ system

When more than eight Li atoms were intercalated in the 2 × 2 phosphorene, we found that there was no more stable configurations for single-side adsorption. Furthermore, as we found in the case of Li$_6$P$_{16}$, when the Li distribution is asymmetric on both sides, it is hard to find stable configurations for Li$_{16}$P$_{16}$ ($8 < n < 16$) systems with P-P bonds unbroken. Therefore, at such a high Li concentration, we focused on finding, for instance, the possible existence of double-side configurations in the Li$_{16}$P$_{16}$ system with symmetric Li distribution on both sides and no Li clustering. Following the same scheme that we used in constructing double-side configurations for the Li$_n$P$_{16}$ ($n = 2, 4, 8$) systems, we added eight Li atoms on the other side of the five stable single-side configurations obtained in the Li$_6$P$_{16}$ system (Figure 9(a)) to construct the double-side configurations for Li$_{16}$P$_{16}$, and five stable structures are obtained after full relaxation. They are denoted by D-4(VH-VH/VH-VH), D-4(VB-TB/VB-TB)$_{ab}$, D-4(VB-VB/VB-VB), D-4(TB-TB/TB-TB).
VH, initial and down zigzag chains case, due to the strong Li-P attractive interaction between Li atoms adsorbed on the phosphorene layer. In the properties. At this high Li concentration, we found two cases the top and side views of these stable structures, and table 6

Figure 11. The relative energy as function of molecular dynamics (MD) steps for (a) the relaxation procedure of 16 Li atoms inserted to both sides of the phosphorene layer with the initial configuration D-4(VH-VH/VH-VH) and (b) the relaxation procedure of the ‘fractured’ phosphorene layer which was obtained by removing the 16 Li atoms from the fully relaxed Li16P16 system with the configuration D-4(VH-VH/VH-VH) (i.e. the fully relaxed structure shown in case (a)). The relative energy is defined as the total energy difference between the initial and final stage of the system. The time step was set as 0.5 fs in the MD simulation. The top (up) and side (down) views of several intermediate configurations are illustrated in the insets with the stars representing the relative energy at corresponding MD steps. The bond reforming could be seen after 55 MD steps (see (b)). The light and dark gray colored balls represent Li atoms above and below the phosphorene monolayer, respectively, while the light and dark purple colored balls denote phosphorus on the ridge and in the valley, respectively.

VB, and D-4(TB-TB/TB-TB), respectively. Figure 10 shows the top and side views of these stable structures, and table 6 lists the corresponding adsorption energies and geometric properties. At this high Li concentration, we found two cases of Li atoms adsorbed on the phosphorene layer. In the first case, due to the strong Li-P attractive interaction between Li and P atoms on both sides, the puckered phosphorene layer was separated during the relaxation, forming buckled up and down zigzag chains (see configurations D-4(VH-VH/VH-VH), D-4(VB-TB/VB-TB), and D-4(VB-TB/VB-TB) in figure 10). In the second case, half of the Li atoms located at the zigzag valley move up/down from phosphorene layer (see configurations D-4(VB-VB/VB-VB), and D-4(TB-TB/TB-TB) in figure 10). Interestingly, it is found that the structures in the first case are more relatively stable than those in the second case (see the 3rd column in table 6); in particular, the structure with all Li atoms in the zigzag valley (i.e. the D-4 (VH-VH/VH-VH) configuration) is the most stable (i.e. EN = −2.046 eV/Li) in the Li10P16 system, and even more stable than the most stable structure in the Li8P16 system (i.e. the D-4(VH-VH) configuration). This indicates the ability of phosphorene to accommodate four Li atoms per 1 × 1 unit cell, but the cost is the volume expansion/bond broken between the P atoms. We found that, during the relaxation process, eight Li atoms on each side of the phosphorene, for example in the D-4(VH-VH/VH-VH) configuration (see figure 11(a)), strongly attract P atoms on both sides of the phosphorene layer, leading to the opposite motion of P atoms. As a result, the P-P bonds between P atoms at the valley and the ridge were broken, and the puckered phosphorene layer was separated into two buckled above/below zigzag chains with a separation of about 3.61 Å, similar to a volume expansion of ~56% during the charging process in the LIB. These kind of structures was also found in the Li10P16, Li12P16, and Li14P16 systems. The question, then, is whether such broken bonds can be self-reformed after Li atoms are removed from phosphorene. To unravel this puzzle, we examined the Li16P16 structures in the first case by relaxing the systems after removing Li atoms.

Figure 11(b) shows, for example, the relaxation process of the stable Li10P16 system with the configuration D-4(VH-VH/VH-VH) after removing the 16 Li atoms (mimicking the delithiation process). Since all Li atoms are removed, there is no Li-P attractive force to pull phosphorus atoms away from each other, and the buckled zigzag chains became flat (in about 17 fs) and then move close to each other, reforming the P-P bonds and, finally, the puckered phosphorene structure is recovered (in about 10 fs). The volume expansion of the phosphorene during Li insertion/discharging disappeared after the Li extraction, showing the reversibility of phosphorene as an anode material during the Li insertion/extraction process. This kind of reversibility has been observed in a very recent multi-cycle in situ TEM (transmission electron microscopy) electrochemical lithium/ delithiation experiment which showed that few-layer-thick phosphorene nanoflakes (less than 10 layers), after delithiation, can completely restore their original morphology and size without any visible structural decomposition (even after several cycles) [90]. Furthermore, we should point out that even though the Li atoms are close to each other at this high Li concentration, and the Li–Li distance is about 0.05–0.1 Å shorter than that in the other LinP16 systems (n = 2, 4, 8) (see the last column in
As discussed in sections 3.3.1–3.3.6, among all the obtained stable structures with the Li adsorption either at the single-side or at the double-side, the most stable configurations for each Li\(_n\)P\(_{16}\) system are those in which Li atoms always prefer to stay at the VH sites along the zigzag direction in the valley. This makes sense because these VH sites are the most preferential sites, as predicted from the adsorption energy landscape (as shown in figure 2(a)). On the other hand, in the Li\(_n\)P\(_{16}\) systems with higher adsorption energies more Li atoms have to stay at the VB and TB sites. It is also found that the adsorption energy in the most stable double-side configurations, for given \(n\) in Li\(_n\)P\(_{16}\) systems, is always lower than that in the most stable single-side configurations, as the repulsive Li–Li interaction is weaker in the former than in the latter.

### 3.4. Electronic properties

The electronic properties of phosphorene with various Li\(_n\)P\(_{16}\) configurations were studied from the total and projected density of states (i.e. DOS and PDOS). The DOS/PDOS for the four most stable single-side configurations in each Li\(_n\)P\(_{16}\) system (\(n = 1, 2, 4, 8\)) and the four stable double-side configurations in each Li\(_n\)P\(_{16}\) system (\(n = 2, 4, 8, 16\)) are presented in figures 12(a) and (b), respectively. The DOS of pristine phosphorene with a DFT band gap of 0.82 eV is also shown at the top of figures 12(a) and (b).

It can be seen from figures 12(a) and (b) that during the Li insertion, the tail at the bottom of the conduction band (CB) extends towards to the top of the valence band (VB) due to the orbital hybridization between Li 2s and P 2p orbitals. On the other hand, the Fermi level upshifts to the CB, due to the charge transfer from the Li atoms to phosphorene, indicating the ionic bonding between Li and P atoms. The PDOS of Li mainly appear in the CB near the Fermi energy, indicating that the 2s electron of Li contributes to the DOS near...
the Fermi level. With more Li atoms adsorbed, more active charge transfers from the Li atoms to phosphorene leading to the Fermi level to shift even further, more Li PDOS to appear close to the bottom of the CB, and the energy band gap gradually diminishes and eventually disappears. In particular, the semiconductor–metal transition was observed in both single-side and double-side adsorption, which is expected for the electron transport to be sufficiently fast in the phosphorene anode.

3.5. Specific capacity

To study the stability in forming the Li\(_x\)P system and, therefore, to predict the Li specific capacity, we calculated the formation energy of the Li\(_x\)P system using equation (3) and illustrated it, as a function of \(x\), in figure 13. The black open/red solid circles in the range of \(0 \leq x \leq 0.5\) represent the stable configurations of the Li\(_x\)P systems with the single-side adsorption (without/with the van der Waals correction), and the black open/red solid triangles in the range of \(0.125 < x \leq 1.0\) represent the stable configurations of the Li\(_x\)P system with the double-side adsorption (without/with the van der Waals correction), respectively. It is apparent that the van der Waals interactions lower the formation energy by about 0.2–0.4 eV. In contrast to the Li intercalation in graphene where the formation energy is always positive [91], all the formation energies of the Li\(_x\)P system are negative after van der Waals correction (see the solid circles and triangles in figure 13), showing the stability of forming the Li\(_x\)P system during the Li intercalation and no Li clustering or dendrite occurring. The lowest formation energies for the single- and double-side adsorptions (corresponding to the most stable configurations of Li\(_x\)P\(_{16}\) systems discussed in section 3.3), guided by the black dashed curves for the DFT calculations and red curves for the DFT-D2 calculations, decrease monotonically with increasing \(x\) (except the single-side adsorption without van der Waals correction). As we have pointed out in the discussion of Li intercalation (i.e. section 3.3), no more stable Li\(_x\)P systems with negative formation energy were found when \(x > 0.5\) for the single-side adsorption and \(x > 1.0\) for the double-side adsorption, respectively.

The achievable capacity limit is determined theoretically by the highest Li:P ratio \(x_{\text{max}}\) that can be achieved in the most stable configurations of the Li\(_x\)P system before Li clustering or the formation of Li dendrites. As can be seen from the formation energy (figure 13), in the case of the single-side adsorption, there are no more stable configurations with negative formation energy found for \(x \geq 0.5\), and in the case of the double-side adsorption, it was found that the fractured structure of phosphorene cannot be restored when more than 16 Li atoms (i.e. \(x > 1.0\)) were inserted. Therefore, the highest Li to P ratios \((x_{\text{max}})\) are around 0.5 for the single-side adsorption (corresponding to the LiP\(_2\) configuration), and 1.0 for the double-side adsorption (corresponding to the LiP configuration). The corresponding specific capacity is then predicted (from equation (4)) as \(\sim 433\) mAh g\(^{-1}\) for the single-side adsorption, and is expected to be \(\sim 865\) mAh g\(^{-1}\) for the double-side adsorption, respectively. The theoretically predicted values of specific Li capacity on monolayer phosphorene provide a fundamental guide for designing phosphorene as anode material for LIBs. Specifically, for a parallel layered phosphorene, the Li capacity could reach \(\sim 433\) mAh g\(^{-1}\) without the Li dendrite (corresponding to the single-side adsorption case), but it is a big challenge for synthesis to reach the theoretically predicted value of 865 mAh g\(^{-1}\) (corresponding to the double-side adsorption case) without the Li dendrite.

Currently, we have performed the very first experimental measurement of lithium’s storage capacity for few parallel-layer phosphorene networks with random orientations (see Supporting Information\(^1\) for a detailed description of the experiment). Figure 14 shows the galvanostatic charge–discharge curves of the phosphorene/TAB-2 electrode for rechargeable LIBs at the voltage range of 0.05–2.8 V at C/10 rate. It has an initial irreversible discharge capacity of 3065 mAh g\(^{-1}\) during the first cycle. The discharge potential

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\(^1\) See the Supplemental Material at [link] for a detailed description of the sample synthesis and characterizations.
plateau curve was large and flat at ~1 V and 0.4 V versus Li/Li+. Furthermore, the charge–discharge measurement of the phosphorene/TAB-2 (90/10) electrode shows the discharge capacities of 685, 477, and 453 mAh g⁻¹ during the 2nd, 10th, and 30th cycles, respectively. After 30 cycles, it retains a very stable discharge capacity of 453 mAh g⁻¹ (indicating the LiP₂ configuration). The first discharge capacity (Li insertion) gains a capacity of ~3065 mAh g⁻¹ due to the reaction of the electrolyte at the surface of phosphorene with transferred lithium atoms to form a passivating film, known as the ‘solid electrolyte interface’ (SEI). Once the SEI is formed, it prevents a further electrolyte reaction on the phosphorene surface. Thus, the first discharge profile is always different from the profiles of subsequent cycles (see detailed discussion in the Supporting Information see footnote 1). Nevertheless, the capacity is stabilized to 453 mAh g⁻¹ after the 30th cycle and remains highly reversible over 50 cycles. Such a value for few-layered phosphorene networks is close to the theoretically predicted value (433 mAh g⁻¹) for the single-side adsorption of monolayer phosphorene with the LiP₂ configuration. As already reported in the experimental results for the Li adsorption on parallel layers of graphene [42], the Li capacity could reach ~372 mAh g⁻¹ for graphite (corresponding to the single-side adsorption case), and Li metal might co-exist at a high Li concentration (corresponding to the double-side adsorption case). To reach the theoretically predicted value of 744 mAh g⁻¹ (corresponding to the double-side adsorption case), efforts must be made to enhance the space between graphene layers, such as the crumpled or curved single-layered graphene nanosheet [44, 45]. It is greatly expected that the reversible capacity of phosphorene could increase and reach the theoretically expected value of ~865 mAh g⁻¹ for the double-side adsorption if, for instance, the single-layered phosphorene can be arranged as ‘house of cards’, as found in the case of graphene [43], or capped with other 2D materials [92].

4. Conclusion

The novel features of phosphorene as an anode material for LIBs have been characterized based on first-principles calculations. When adsorbed on phosphorene, Li atoms prefer to reside at the most stable VH sites. The other two metastable sites (i.e. the VB and TB sites) can be occupied when there are more Li atoms loaded on phosphorene. The adsorption energy at the most stable VH site is ~2.086 eV/Li, indicating strong Coulomb interactions between Li and phosphorene, which are essential in the electrochemical performance for high-performance LIBs. The diffusion energy barrier of Li on phosphorene shows high anisotropic behavior and is extremely low when Li atoms migrate along the zigzag channel at the valley. The estimated diffusion constant also shows that ultrafast Li atom diffusion will occur directionally along the zigzag direction in the valley (e.g. about 10⁴ times faster than the diffusion across the ridge along the armchair direction). In particular, it was found that the Li directional diffusion on phosphorene is considerably faster than on graphene and MoS₂, which implies that phosphorene may exhibit an outstanding high-rate capacity.

The most stable structures for Li atoms adsorbed on the single/double-side of the phosphorene layer are those in which Li atoms occupy the VH sites along the zigzag direction in the valley. Importantly, the ability for phosphorene to accommodate Li atoms was found up to about 1:1 (i.e. the ratio of Li:P), demonstrating that the monolayer phosphorene could reach the predicted capacity with 865 mAh g⁻¹. The experimental measured specific capacity for a few-layered phosphorene network showed a very stable value of 453 after the 30th cycle and good cycling performance. A uniform single-layered phosphorene with nanoporosity is expected to increase the reversible capacity to the theoretically predicted value. More interesting still, it was found that phosphorene monolayer could self-recover when it was ‘distorted/fractured’ during Li intercalation at the high Li:P ratio, indicating its reversibility during the lithiation/delithiation (charging/discharging) process. Overall, our theoretical and experimental results show the beneficial properties of Li-adsorbed phosphorene including the high specific capacity, the ultrafast and anisotropic diffusivity, the reversibility in charging/discharging, stable cycling performance, and the good electrochemical performance following on from this, which make it an excellent candidate to be an anode material for high-performance LIBs.

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