Exploring the Superior Anchoring Performance of the Two-Dimensional Nanosheets B$_2$C$_4$P$_2$ and B$_3$C$_2$P$_3$ for Lithium–Sulfur Batteries

Hiba Al-Jayyousi, Mathan Kumar Eswaran, Avijeet Ray, Muhammad Sajjad, J. Andreas Larsson, and Nirpendra Singh

ABSTRACT: Potential anchoring materials in lithium–sulfur batteries help overcome the shuttle effect and achieve long-term cycling stability and high-rate efficiency. The present study investigates the two-dimensional nanosheets B$_2$C$_4$P$_2$ and B$_3$C$_2$P$_3$ by employing density functional theory calculations for their promise as anchoring materials. The nanosheets B$_2$C$_4$P$_2$ and B$_3$C$_2$P$_3$ bind polysulfides with adsorption energies in the range from −2.22 to −0.75 and −2.43 to −0.74 eV, respectively. A significant charge transfer occurs from the polysulfides, varying from −0.74 to −0.02e and −0.55 to −0.02e for B$_2$C$_4$P$_2$ and B$_3$C$_2$P$_3$, respectively. Upon anchoring the polysulfides, the band gap of B$_2$C$_4$P$_2$ reduces, leading to enhanced electrical conductivity of the sulfur cathode. Finally, the calculated barrier energies of B$_2$C$_4$P$_2$ and B$_3$C$_2$P$_3$ for Li$_x$S indicate fast diffusion of Li when recharged. These enthralling characteristics propose that the nanosheets B$_2$C$_4$P$_2$ and B$_3$C$_2$P$_3$ could reduce the shuttle effect in Li–S batteries and significantly improve their cycle performance, suggesting their promise as anchoring materials.

INTRODUCTION

Due to high efficiency, high capacity, and environment-friendly characteristics, lithium–sulfur (Li–S) batteries continue to develop as the most promising rechargeable energy source for the near future.\(^1,2\) Compared to commercial lithium-ion batteries, Li–S batteries show a higher theoretical capacity of 1675 mAh g$^{-1}$ and specific energy of 2600 Wh kg$^{-1}$\(^3,4\). In addition to the higher energy content, a lower cost is associated with Li–S batteries since sulfur cathodes are cheap and have many merits including abundant resources.\(^5,6\) However, several challenges that limit the commercial implementation of Li–S batteries need to be addressed. These limitations include low active material utilization, high volume changes in the charge/discharge process, and formation of lithium dendrites, which may lead to short circuits during cycling, termed as the shuttle effect.\(^7,8\) This notorious and intractable effect is due to the migration of sulfur intermediates between the positive and negative electrodes in the charging and discharging process.\(^9,10\) In this process, lithium polysulfides (LiPSs) Li$_2$S$_n$ $2 < x \leq 8$, are formed because sulfur atoms react with the transferred lithium ions that risk transportation back to the Li electrode upon recharging, which leads to depletion of S in the S electrode and low Coulombic efficiency along with fast capacity fading.\(^11,12\) Over the past few years, considerable efforts to suppress the shuttle issue have been reported, including electrode tuning\(^13,16\), cathode functionalization\(^17–19\), and introducing anchoring materials that block the diffusion pathway of the polysulfides.\(^20–24\) As a result, promising anchoring materials, which can activate strong interactions with the Li$_2$S$_x$ species, have been noticed as an adequate way to overcome these problems and achieve long-term cycling stability and high-rate performance. The anchoring materials are classified as weak (chlorides), moderate (sulfides), and strong (oxides) anchoring materials. Therefore, the entrapment effect is related to the chemical architecture of the anchoring materials. Ideal anchoring materials should have the following criteria: (a) display moderate binding energies for the Li$_2$S$_x$ species, (b) have sufficiently active regions, and (c) be lightweight; these would lead to sufficiently confined polysulfides and prevent their dissolution into the electrolyte. In addition, it would be advantageous for the anchoring material to improve the electrical conductivity of the S electrode since it is relatively low.
Due to their unique and remarkable properties that meet the above-mentioned criteria, two-dimensional (2D) materials have been recognized to play an increasingly important role in developing efficient anchoring materials.\textsuperscript{25−27} Several 2D materials have been proposed as anchoring materials to suppress the shuttling effect, such as graphene, Ti\textsubscript{2}C MXene terminated with OH, F, and S,\textsuperscript{28} porous vanadium nitride nanoribbon with graphene,\textsuperscript{29,30} and borophosphorene.\textsuperscript{31} In this regard, two new members of hybrid 2D graphene-like nanosheets, B\textsubscript{2}C\textsubscript{4}P\textsubscript{2} and B\textsubscript{3}C\textsubscript{2}P\textsubscript{3}, predicted recently based on density functional theory (DFT) calculations, are greatly interesting.\textsuperscript{32} These nanosheets have structural and thermodynamic stability and could be fabricated through carbon doping of boron phosphide. B\textsubscript{2}C\textsubscript{4}P\textsubscript{2} is metallic, while B\textsubscript{3}C\textsubscript{2}P\textsubscript{3} is a moderate band gap semiconductor (0.35 eV), suggesting good conductivity and high carrier mobility. It also has a planar lattice, a critical feature in constructing batteries with a fast charge/discharge rate, proposing its potential as an anchoring material. Therefore, comprehensive first-principles calculations are employed to reveal the promise of the nanosheets B\textsubscript{2}C\textsubscript{4}P\textsubscript{2} and B\textsubscript{3}C\textsubscript{2}P\textsubscript{3} as anchoring materials for Li\textsubscript{2}S batteries.

### COMPUTATIONAL METHODS

All the density functional theory (DFT) calculations are performed using the Vienna Ab initio Simulation Package.\textsuperscript{33,34} The plane-wave cutoff energy is set to 500 eV combined with an exchange−correlation functional of the generalized gradient approximation (Perdew−Burke−Ernzerhof flavor). The change

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**Figure 1.** (a, b) Optimized 3 × 3 × 1 supercell of nanosheets B\textsubscript{2}C\textsubscript{4}P\textsubscript{2} and B\textsubscript{3}C\textsubscript{2}P\textsubscript{3}. (c, d) Calculated DOS at the PBE level. The brown, green, and purple spheres represent carbon, boron, and phosphorous atoms, respectively. The red hollow circle defines the possible sites tested for the adsorption of Li\textsubscript{2}S\textsubscript{x}.

**Figure 2.** Optimized structures of (a) Li\textsubscript{2}S\textsubscript{2}, (b) Li\textsubscript{2}S\textsubscript{4}, (c) Li\textsubscript{2}S\textsubscript{6}, (d) Li\textsubscript{2}S\textsubscript{8}, (e) Li\textsubscript{2}S\textsubscript{10} and (f) S\textsubscript{8} adsorbed on the nanosheet B\textsubscript{2}C\textsubscript{4}P\textsubscript{2}. The yellow, light green, brown, green, and purple solid spheres represent the sulfur, lithium, carbon, boron, and phosphorus atoms, respectively.
Figure 3. Optimized structures of (a) Li$_2$S, (b) Li$_2$S$_2$, (c) Li$_2$S$_8$, (d) Li$_2$S$_{10}$, (e) Li$_2$S$_{14}$ and (f) S$_8$ adsorbed on the nanosheet B$_3$C$_2$P$_3$. The yellow, light green, brown, green, and purple solid spheres represent the sulfur, lithium, carbon, boron, and phosphorus atoms, respectively.

Table 1. Binding Energies (eV) of LiPSs and S$_8$ over B$_2$C$_2$P$_2$, B$_3$C$_2$P$_3$, Graphene, and Blue Phosphorene$^{a}$

|       | B$_2$C$_2$P$_2$ | B$_3$C$_2$P$_3$ | graphene$^{20}$ | blue phosphorene$^{26}$ |
|-------|-----------------|-----------------|-----------------|------------------------|
| Li$_2$S | 2.22 (2.13)     | 2.43 (1.89)     | -0.50           | -2.50                  |
| Li$_2$S$_2$ | -1.31 (2.53)   | -1.71 (2.31)     | -0.50           | -1.50                  |
| Li$_2$S$_4$ | -0.76 (3.04)    | -0.83 (2.90)     | -0.60           | -1.10                  |
| Li$_2$S$_6$ | -0.93 (2.78)    | -0.93 (2.81)     | -0.70           | -0.90                  |
| Li$_2$S$_8$ | -1.03 (2.60)    | -1.09 (2.64)     | -0.90           | -1.00                  |
| S$_8$  | -0.75 (3.2)     | -0.74 (3.2)      | -0.70           | -0.50                  |

$^{a}$The separation distances (Å) of LiPSs and S$_8$ over B$_2$C$_2$P$_2$ and B$_3$C$_2$P$_3$ are given in parenthesis.

Table 2. Charge Transferred (in e) from LiPSs and S$_8$ Clusters to the Nanosheets after Adsorption

|       | Li$_2$S | Li$_2$S$_2$ | Li$_2$S$_4$ | Li$_2$S$_6$ | Li$_2$S$_8$ | S$_8$ |
|-------|--------|------------|------------|------------|------------|------|
| B$_2$C$_2$P$_2$ | -0.74 | -0.60 | -0.05 | -0.04 | -0.01 | 0.03 |
| B$_3$C$_2$P$_3$ | -0.55 | -0.45 | -0.12 | -0.02 | -0.02 | 0.04 |

in total energy and maximum atomic force converged to $10^{-6}$ and 0.01 eV Å$^{-1}$, respectively. A $3 \times 3 \times 1$ supercell and $5 \times 5 \times 1$ Monkhorst–Pack grid of $k$-points were used for geometry relaxation. 6 $\times$ 6 $\times$ 1 and 9 $\times$ 9 $\times$ 1 $k$-meshes were employed for self-consistent and density of states (DOS) calculations, respectively. The DFT-D3 approach$^{33}$ accurately accounts for the van der Waals forces. A vacuum of 18 Å eliminates spurious interlayer interactions due to periodicity in the out-of-plane direction. Bader charge analysis is used to quantify the charge transfer during the LiPS interaction with the sheets. The binding energy ($E_b$) and charge density difference ($\rho_{total}$) are determined using

$$E_b = E_{total} - (E_{sheet} + E_{LiPS/S})$$

(1)

$$\rho_{total} = \rho_{sheet} + \rho_{LiPS/S}$$

(2)

where $E_{total}$, $E_{sheet}$, and $E_{LiPS/S}$ correspond to the total energies of B$_2$C$_2$P$_2$/B$_3$C$_2$P$_3$ sheets with adsorbed LiPS/S$_8$ pristine B$_2$C$_2$P$_2$/B$_3$C$_2$P$_3$ sheets, and isolated LiPS/S$_8$ species, respectively. Similarly, $\rho_{total}$, $\rho_{sheet}$, and $\rho_{LiPS/S}$ represent the charge densities of B$_2$C$_2$P$_2$/B$_3$C$_2$P$_3$ sheets with adsorbed LiPS/S$_8$ pristine B$_2$C$_2$P$_2$/B$_3$C$_2$P$_3$ sheets, and isolated LiPS/S$_8$ species, respectively.

RESULTS AND DISCUSSION

The optimized lattice parameters of the honeycomb nanosheets B$_2$C$_2$P$_2$ and B$_3$C$_2$P$_3$ are $a = 5.63$ Å and $b = 4.94$ Å for B$_2$C$_2$P$_2$ and $a = 6.06$ Å and $b = 5.20$ Å for B$_3$C$_2$P$_3$, in agreement with those reported in previous work.$^{32}$ Both dynamic stability and thermal stability of B$_2$C$_2$P$_2$ and B$_3$C$_2$P$_3$ were confirmed before in the literature.$^{33}$ The optimized $3 \times 3 \times 1$ supercells of B$_2$C$_2$P$_2$ and B$_3$C$_2$P$_3$ are presented in Figure 1a,b. The partial density of states (DOS) of B$_2$C$_2$P$_2$ (Figure 1c) demonstrates a strong hybridization between the states of phosphorus, boron, and carbon atoms, giving an aggregate contribution in the vicinity of the Fermi level. On the other hand, the partial DOS of B$_3$C$_2$P$_3$ (Figure 1d) shows that phosphorus mainly contributes to the valence band maximum constitution, while the conduction band...
minimum is formed as a consequence of the hybridization of states from boron, carbon, and phosphorus atoms.

Polysulfides considerably impair the capacity and cycling stability of Li–S batteries. Through geometry optimization, we obtained the most stable structures of the Li$_x$S$_y$ ($x = 1, 2, 4, 6, 8$) and S$_8$ clusters formed at the S electrode. As the number of sulfur atoms increases, high-order LiPSs can be ionized and risk transportation back to the Li electrode in the recharging process, resulting in the shuttle effect. As evident from Figure 1a,b, the nanosheets possess multiple possible adsorption sites, as shown in Figure 1a,b. All rotational and translational configurations of LiPSs and S$_8$ are considered on these sites, whereas the most stable configurations and the corresponding binding energies are presented in Figures 2 and 3 and Table 1, respectively. We have found that the nanosheet B$_x$C$_y$P$_z$ and B$_x$C$_y$P$_z$ strongly bind Li$_x$S and Li$_x$S$_y$, whereas for higher ordered LiPSs and S$_8$, the binding energies are lower but above 0.74 eV. The noticeable trend in the binding energy values is directly reflected in the distance between the polysulfides and the nanosheets. Li$_x$S$_y$ binds at 2.13 Å from B$_x$C$_y$P$_z$ and 1.89 Å from B$_x$C$_y$P$_z$$_y$, indicating chemical bonding. Such distances are shorter than those obtained for the other LiPSs and S$_8$ that are physiosorbed; therefore, the binding energies are higher for Li$_x$S. The calculated binding energies (see Table 1) are larger than those of graphene and comparable to those of blue phosphorene. Compared to graphene, the noticeable increase in binding energies for B$_x$C$_y$P$_z$ and B$_x$C$_y$P$_z$ can be understood by examining the bonding within the nanosheets. In the case of graphene, all the polysulfide physiosorbed through dispersion van der Waals interactions, while in B$_x$C$_y$P$_z$ and B$_x$C$_y$P$_z$$_y$, the electronegativity difference between C, P, and B causes electrons in the C–P, C–B, and B–P bonds to be unequally shared, and binding through bond dipoles is also possible, which makes the van der Waals interactions stronger. Together, these findings suggest the better performance of the studied nanosheets to counter the shuttle effect.

Moreover, also, the S$_8$ cluster binds with the surface with binding energies of 0.75 and 0.74 eV for B$_x$C$_y$P$_z$ and B$_x$C$_y$P$_z$$_y$, respectively. The interaction is weak due to the absence of Li atoms (in all LiPSs, the Li atoms interact with the surfaces). The S$_8$ cluster orients parallel to the surface with a distance of 3.20 Å, which is also captured in the previous studies for similar 2D materials. An increase in binding energy with decreasing S content makes the discharge process over the surface possible. Also, we calculated the Li–S bond length of all LiPSs after adsorption on the nanosheets. In the case of B$_x$C$_y$P$_z$, the average Li–S bond lengths increase compared to those of the free clusters, 0.24, 0.09, 0.13, 0.14, and 0.05 Å for Li$_x$S, Li$_2$S$_2$, Li$_3$S$_4$, Li$_4$S$_6$, and Li$_5$S$_8$, respectively. Similarly, for the nanosheet B$_x$C$_y$P$_z$$_y$, the changes in the Li–S bond lengths are 0.20, 0.21, 0.01, 0.14, and 0.04 Å, respectively. In the case of a higher S content, the change in bond lengths is smaller than that for the Li$_x$S and Li$_x$S$_y$ clusters. An increased Li–S bond length reflects the weakening of the bond, governed by the strength of the cluster–surface interaction, and could help facilitate the discharge process.

We performed a Bader charge analysis to better understand the nanosheets’ binding mechanisms. The results show that the LiPSs donate charge to the nanosheets B$_x$C$_y$P$_z$ and B$_x$C$_y$P$_z$$_y$ (see Table 2). The charge is mainly accumulated (depleted) on S

![Figure 4](https://doi.org/10.1021/acsomega.2c03898) Charge density difference after (a) Li$_4$S, (b) Li$_4$S$_2$, (c) Li$_4$S$_4$, (d) Li$_5$S$_8$, (e) Li$_5$S$_6$, and (f) S$_8$ adsorption on the nanosheet B$_x$C$_y$P$_z$. The cyan and yellow regions indicate charge depletion and accumulation, respectively (isosurface value 4 × 10$^{-1}$ e Å$^{-3}$).
Li) before adsorption and substantially transferred to the sheet after adsorption. The Bader charge values indicate that Li$_2$S, Li$_2$S$_2$, and Li$_2$S$_4$ donate considerable charge to the surface, agreeing with their high binding strength and chemical bonding nature. The charge donation from the higher LiPSs is negligible. The charge distribution between the LiPSs and B$_2$C$_2$P$_2$/B$_3$C$_2$P$_3$...
Figures 4 and 5. Electrons are mainly accumulated between Li atoms, and the promise of 2D nanosheets in LiS batteries has been systematically explored using DFT calculations. Both nanosheets show significant adsorption energies of LiPSs due to the charge transfer from LiPSs to the nanosheets, favoring counter the shuttle effect in Li–S batteries. B$_2$C$_2$P$_2$ possesses a metallic character, whereas B$_2$C$_2$P$_3$ upon LiPS adsorption, undergoes band gap reduction, which enhances the electrical conductivity of the sulfur electrode as necessary in Li–S batteries. Moreover, the calculated barrier energy of Li$^+$ detachment is found to be 0.92 and 1.20 eV for B$_2$C$_2$P$_2$ and B$_2$C$_2$P$_3$, respectively, indicating fast diffusion as compared to blue phosphorene and metal sulfides. These findings would encourage developing and synthesizing the nanosheets B$_2$C$_4$P$_2$ and B$_2$C$_2$P$_3$ as high-performance anchoring materials.

## CONCLUSIONS

In summary, the promise of 2D nanosheets B$_2$C$_4$P$_2$ and B$_2$C$_2$P$_3$ as anchoring materials has been systematically explored using DFT calculations. Both nanosheets show significant adsorption energies of LiPSs due to the charge transfer from LiPSs to the nanosheets, favoring counter the shuttle effect in Li–S batteries. B$_2$C$_2$P$_2$ possesses a metallic character, whereas B$_2$C$_2$P$_3$ upon LiPS adsorption, undergoes band gap reduction, which enhances the electrical conductivity of the sulfur electrode as necessary in Li–S batteries. Moreover, the calculated barrier energy of Li$^+$ detachment is found to be 0.92 and 1.20 eV for B$_2$C$_2$P$_2$ and B$_2$C$_2$P$_3$, respectively, indicating fast diffusion as compared to blue phosphorene and metal sulfides. These findings would encourage developing and synthesizing the nanosheets B$_2$C$_4$P$_2$ and B$_2$C$_2$P$_3$ as high-performance anchoring materials.

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### Notes

The authors declare no competing financial interest.

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