Article

Boron-Doped Graphene as a Promising Anode Material for Potassium-Ion Batteries with a Large Capacity, High Rate Performance, and Good Cycling Stability

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Supporting Information

ABSTRACT: Potassium-ion batteries (KIBs), as alternatives to lithium-ion batteries (LIBs), have attracted increasing attention due to the abundance of K in the Earth's crust. Here, using first-principles calculations, we have found that boron (B)-doped graphene is a promising anode material for KIBs. The studied B_4C_{28} structure has a large specific capacity of 546 mAh/g, a small migration barrier of 0.07 eV, and a moderate potassiation voltage of 0.82 V to suppress the formation of a SEI layer. Moreover, B-doped graphene with a doping concentration of 12.5 at. % is metallic with good electron conductivity that can improve rate performance. Also, B doping makes the substrate electron-deficient and results in significant charge transfer from K to the substrate, thus preventing K atoms from clustering, inhibiting dendrite growth, and leading to a good cycling stability.



INTRODUCTION

Lithium-ion batteries (LIBs), as a leading energy storage technology, have achieved tremendous success in electronic devices, electric vehicles, and energy storage systems for the electric grid.¹ Since the usage of LIBs is ever increasing, it may suffer from unsustainability in the future because of the rarity of lithium, as shown in Table 1.² In searching for the alternatives to LIBs, sodium-ion batteries (NIBs) and potassium-ion batteries (KIBs) have been proposed as two competitive candidates due to their abundance and similarities to LIBs.³ Although it is natural to assume that the closest neighboring element (Na) is the best choice for the replacement due to its larger similarity with Li, K is indeed a competitive candidate with its own advantages, such as less complicated interfacial reactions⁴ and higher ionic conductivity in solution.^{3,5} Hence it is worthy to further investigate KIBs and search for promising electrodes.

Recently, anode materials for KIBs have been hotly explored including carbon materials,^{3,6} MoN₂,⁷ YN₂,⁸ GeS₂,⁹ Nb₂C,¹⁰ and tin-based composite.¹¹ As alternatives to LIBs, the anode materials for KIBs should also be mainly composed of abundant and cheap elements. Therefore, it is not practical to primarily use rare Nb, Y, Sn, Mo, and Ge to design future anodes for KIBs. As for carbon materials, several structures have been proposed as anode materials for KIBs, including graphite,¹² reduced graphene oxide,⁶ and amorphous carbon.¹³ However, they all suffer from poor cycling stability and limited specific capacity, mainly resulting from the huge volume change caused by large K-ion intercalation. It was suggested that using loosely packed nanosheets with enlarged interlayer spacing can

accommodate large volume variation and alleviate the structural instability confronted by bulk structures.¹⁴ Furthermore, nanosheets have several additional advantages, such as large surface area for better accommodation of metal ions¹⁵ and shortened path for fast diffusion of alkali metal ions.9,14 Graphene sheets¹⁶ have been extensively studied as an anode¹⁷ due to their excellent electronic conductivity and good structural integrity with all sp²-hybridized bonds.¹⁸ However, pristine graphene is not a good choice for anode materials due to its poor adsorption ability.¹ Thus, point defects,¹⁹ edges,²⁰ grain boundaries,²¹ and doping,²² are introduced to enhance the electrochemical performance of graphene. Among them, controllable doping of graphene has been achieved in atomic precision²³ with good thermodynamics.²² Because boron and carbon have similar atomic size and boron doping can feature electron-deficiency, both 3D B-doped carbon structures²⁴⁻² and B-doped graphene^{22,28-31} have been widely explored for anode materials for LIBs and NIBs, displaying large capacity and good cycling stability. These advances encourage us to study whether B-doped graphene can also serve as an anode material for KIBs.

In this work, first-principles calculations based on density functional theory (DFT) are performed to evaluate the performance of B-doped graphene as an anode material for KIBs and for the first time known to the authors, a comprehensive DFT study on the cycling stability and safety

 Received:
 July 31, 2017

 Revised:
 October 14, 2017

 Published:
 October 16, 2017

Table 1. Element Concentrations (in ppm) in the Upper Continental Crust²



Figure 1. (a and b) Optimized structures of B-doped graphene with doping concentrations of 3.125% (BC₃₁) and 12.5% (B₄C₂₈), respectively. Color coding: B, green; C, brown. (c) Adsorption energy curve for B₄C₂₈. The points drawn are those minimum adsorption energies under different K concentrations.

is carried out. The results show that the B-doped graphene sheet simultaneously possesses a large capacity (564 mAh/g), good rate performance, and cycling stability. In addition, BG performs better for KIBs than for NIBs with a larger capacity, smaller diffusion barrier, and slighter structural deformation. These findings all suggest that B-doped graphene is a promising anode material for KIBs.

COMPUTATIONAL METHODS

All the calculations, including structure optimization, total energy and electronic structure calculations, are conducted using density functional theory (DFT) implemented in Vienna ab initio simulation package (VASP).³² The projector augmented wave (PAW) method³³ is used with a kinetic energy cutoff of 500 eV, and the exchange-correlation interactions are treated using a Perdew-Burke-Ernzerhof (PBE) functional.³⁴ A 4 \times 4 \times 1 supercell is employed in most cases, 30,35 while an 8 × 8 × 1 supercell is used for calculating the cluster formation energy.^{36,37} To avoid the interactions between periodic images a large vacuum space of 20 Å in the perpendicular direction is used. The first Brillouin zone is sampled by the Monkhorst-Pack scheme³⁸ with a grid density of $2\pi \times 0.03$ Å⁻¹, and the convergence criteria of 10^{-4} eV for total energy and 10^{-2} eV/Å for atomic forces are used. Bader charge analysis³⁹ is carried out to study the charge transfer. The minimum energy pathways of Na and K diffusion on B-doped graphene and corresponding energy barriers are determined using the nudged elastic band (NEB) method.⁴⁰

In order to derive the maximum specific capacity, the adsorption energy (E_{ad}) is defined as

$$E_{\rm ad} = E_{\rm K+BG} - E_{\rm BG} - x\mu_{\rm K} \tag{1}$$

where $E_{\rm BG}$ and $E_{\rm K+BG}$ are the total energies of the system before and after introducing potassium atoms, respectively, $\mu_{\rm K}$ is the chemical potential of potassium bulk, and x is the number of K atoms adsorbed on the BG substrate. In the experiment, K would be continuously adsorbed on BG until the chemical potential of K on BG ($\mu_{\rm K,BG}$) equals that of the K metal, which implies:

$$\mu_{\rm K+BG} \le \mu_{\rm K} \tag{2}$$

The chemical potential of K on BG equals

$$\mu_{\rm K+BG} = (\partial G/\partial x)_{T,P} \tag{3}$$

$$G = E_{\rm K+BG} + PV - TS \tag{4}$$

where $P\partial V$ is on the order of 10^{-5} eV and $T\partial S$ is comparable to 0.026 eV at 300 K;^{30,35} thus, these two terms are negligible. Combining eqs 2–4, the potassiation process requires:

$$\left(\frac{\partial E_{\mathrm{K+BG}}}{\partial x}\right)_{\mathrm{T},\mathrm{P}} \le \mu_{\mathrm{K+metal}} \tag{5}$$

Finally, eq 1 and eq 5 gives

$$\left(\frac{\partial E_{\rm ad}}{\partial x}\right)_{T,P} \le 0 \tag{6}$$

Therefore, the adsorption of K atoms becomes energetically unfavorable when the newly added K atom elevates the adsorption energy. Correspondingly, the maximum specific capacity $(C_{\rm M})^7$ can be obtained as

$$C_{\rm M} = x_{\rm m} F / M_{\rm BG} \tag{7}$$

where $x_{\rm m}$ is the maximum number of K atoms absorbed on the BG substrate, *F* is the Faraday constant with the value of 26.8 Ah/mol, and $M_{\rm BG}$ is the mass of the BG substrate.

RESULTS AND DISCUSSION

Geometries of BG and K Adsorption at Dilute Concentration. First of all, it is necessary to examine the effect of boron doping on K adsorption at a low doping concentration. In a $4 \times 4 \times 1$ supercell of graphene with 32 atoms, one carbon atom is replaced by one boron atom (BC_{31}) , corresponding to a doping concentration of 3.125 at. % (atom percent), as shown in Figure 1a. Three K adsorption sites are considered, where the hollow site (H) is the site of the center of the six-membered ring, the on-top site (O) is the one on the top of the boron atom, and the bridge site (B) is the one above the middle of the B-C bond. Geometry optimizations indicate that the H site is the most favorable adsorption position for K, because a K atom would migrate there upon geometrical optimization when introduced on an O site or B site, similar to the cases for Li and Na.^{29,30} The adsorption of the second K atom is an exothermic reaction, while it is an endothermic one for the second Na atom adsorption on the same BC31 substrate,^{30,31} suggesting that BG has a better ability to adsorb K than Na. However, the adsorption of the third K atom is energetically unstable. Thus, the specific capacity of BC_{31} is limited to K_2BC_{31} , or about 140 mAh/g.

In order to achieve a larger specific capacity, a higher doping concentration is required.³⁰ Three facts are considered to select the doping level and design the structure: (1) B-doped graphene remains in the planar structure.⁴¹ (2) Even in heavily doped graphene, boron atoms are evenly distributed and do not form clusters.^{28,41} (3) Although widely used in industry and applied as dopant, boron is actually not so abundant on earth.² If the doping concentration is selected to be too high, like 25 at. % (BC_3) ,³⁰ the intention of designing anodes for KIBs using abundant carbon materials is contradicted. Therefore, the modest and experimental achievable 42,43 doping level of 12.5 at. % (BC₇) is chosen for both previously mentioned reasons and its metallic feature,^{29,30} in which boron atoms are uniformly distributed as shown in Figure 1b. Following the same procedure above, the hollow site is again determined to be the most energetically favorable K adsorption position, and Bader charge analysis shows that the adsorbed K atom transfers 0.89 e⁻ to the BG substrate, indicating the cationic state and chemical adsorption of K.

K Adsorption at High Concentration. In this case, there are many possible adsorption sites for K atoms in a supercell, which makes manually determining the favorable adsorption configurations under different K concentrations difficult. Here, 20 different K adsorption patterns for a given concentration are randomly generated using our in-house code and then fully relaxed using the DFT calculations.²² A flowchart about the code is shown in the Supporting Information. After calculating 100 different patterns, the adsorption energy curve is plotted, as shown in Figure 1c. We note that, after eight potassium atoms are adsorbed onto the BG substrate, the slope of the adsorption energy curve becomes positive when additional K atoms are introduced, suggesting that the maximum number of K that can be adsorbed is eight in the supercell $(K_8B_4C_{28})$, and the corresponding specific capacity is 564 mAh/g, which is larger than 423 mAh/g, the maximum capacity of BG anode for NIBs.³⁰

The average open circuit voltage (OCV) is defined by^{35,44}

$$OCV = E_{ad,x_m} / x_m \tag{8}$$

where x_m is the maximum number of K atoms adsorbed on the BG substrate and E_{ad,x_m} is the corresponding adsorption energy. Based on the data in Figure 1*c*, x_m equals 8, and then the open circuit voltage is calculated to be 0.82 V.

For further analysis, the adsorption patterns of $K_8B_4C_{28}$ are carefully checked. Two configurations with the lowest adsorption energies are given in Figure 2, labeled as C_I and C_{II} , respectively, where K atoms are all located on the hollow sites and evenly distributed on each side of the BG substrate. The energy difference between the two configurations is only 0.03 eV. To further confirm the reliability of the results regarding the adsorption configuration of $K_8B_4C_{28}$, adsorption energies of 40 new K adsorption patterns generated by our code are calculated. Once again C_I and C_{II} are found to be the structures with the lowest energies. In the rest of the paper, configuration C_I , the most energetically favorable K adsorption pattern, is further studied as an example of the $K_8B_4C_{28}$ structure.

After the adsorption behaviors of K atoms on the BG substrate at both dilute and high concentrations are studied, the underlying adsorption mechanism needs to be discussed. As



Figure 2. (a) Top and (b) side views of the adsorption configuration C_{I} . (c) Top and (d) side views of the adsorption configuration C_{II} .

shown in Figure 3, the hollow sites are the most electrondeficient positions in all cases, indicating that charge transfer of



Figure 3. (a–d) Charge density (in Bohr/Å3) in the plane 1 Å above the sheet for pristine graphene (C_{32}), B-doped graphene (B_4C_{28}), $K_1B_4C_{28}$, and $K_8B_4C_{28}$ substrates, respectively.

electrons into these sites occurs more easily than into any other sites. This is consistent with the fact that alkali metal atom adsorption is energetically preferable on these sites.⁴⁵ However, Figure 3a shows that electrons in the π orbitals of pristine graphene form a passivated layer around the hollow sites resulting in ineffective adsorption, which was also observed in a previous study.46 While when graphene is doped with B, the electron distribution changes significantly, as shown in Figure 3b, and the adsorption at B-doped sites is greatly improved. At high K concentration, the chemical bonding effect is balanced by the repulsion between the ionized K cations. Figures 2a,c and 3d illustrate that each side of $K_8B_4C_{28}$ features four hollow sites that are occupied by K atoms and filled with electrons. In order to minimize the repulsion between K cations, occupation of those hollow sites is uniformly distributed. Meanwhile, the same BG substrate adsorbs fewer Na atoms than K³⁰ due to the large ionization potential of Na and corresponding weak chemical bonding effect.

Electronic Conductivity. In addition to specific capacity, rate performance is another key parameter to evaluate an electrode. Because the rate performance of anode materials is often controlled by the kinetics of electronic and ionic transport, electronic conductivity is studied. Figure 4a-c



Figure 4. (a-c) PDOS of B₄C₂₈, K₄B₄C₂₈, and K₈B₄C₂₈, respectively. (d-f) The corresponding band structures.



Figure 5. (a) Three diffusion paths of K on B_4C_{28} substrate. (b) Corresponding diffusion energy barrier profiles. (c) Height (h) profiles of Na and K on path 3.

Table 2. Comparison of Specific Capacity (in mAh/g), Open Circuit Voltage (OCV; in V), Diffusion Barrier (det E_d ; in eV), and Electronic Conductivity of Candidate Anode Materials for KIBs

| materials | B4C28 | MoN ₂ ⁷ | YN ₂ ⁸ | GeS ₂ ⁹ | Nb_2C^{10} | graphite (LIBs) ¹ | B_4C_{28} (NIBs) ³⁰ |
|--------------|----------|-------------------------------|------------------------------|-------------------------------|--------------|------------------------------|----------------------------------|
| capacity | 564 | 432 | 229 | 256 | 136 | 372 | 423 |
| OCV | 0.82 | 1.11 | 0.48 | 0.36 | 0.29 | 0.2 | 0.61 |
| $detE_d$ | 0.074 | 0.49 | 0.27 | 0.050 | 0.004 | 0.4 | 0.17 |
| conductivity | metallic | metallic | metallic | semiconducting | metallic | metallic | metallic |

gives the partial density of states (PDOS) of the selected B₄C₂₈ substrate with 0, 4 and 8 K atoms adsorbed, showing that the studied BG anode would keep the metallic feature with good electronic conductivity before and after K atom adsorption. The analysis of PDOS also provides another perspective to understand the adsorption behavior. As an electron deficient system, there are many empty states right above the Fermi level in BG to accommodate electrons from K atoms. As a result, after K atoms donate electrons to the states above the Fermi level, they become K cations. The band structures of B₄C₂₈, $K_4B_4C_{28}$, and $K_8B_4C_{28}$ are drawn in Figure 4d-f for further understanding the mechanisms, where Figure 4d shows the metallic features of the BG sheet. One can see a downward shift of Fermi level due to the B doping induced deficiency of electrons,47-49 and an upward shift of Fermi level happens in K-absorbed B₄C₂₈ because of the injected electrons from K atoms.

lonic Conductivity. The diffusion constant (D) can be evaluated by the Arrhenius equation:⁵⁰

$$D \propto \exp(-\det E_{\rm d}/K_{\rm B}T)$$
 (9)

where det E_d is the diffusion energy barrier magnitude, K_B is the Boltzmann's constant, and T is the temperature. For a given temperature, the magnitude of the K diffusion barrier determines the K diffusion rate using the expression above. Three K diffusion paths with high symmetry are considered and their diffusion energy barriers are calculated using the NEB method, as illustrated in Figure 5a,b. Although path 3 is found to have the lowest diffusion barrier of 0.074 eV, the others are also found to possess diffusion barriers a little bit larger than that of path 3, indicating that all three paths might be possible routes for K ion diffusion with small energy barriers, ensuring good ionic conductivity.⁵¹ For comparison, diffusion barriers of Na are also calculated, and path 3 is again found to have the

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lowest diffusion barrier of 0.16 eV, which is in good agreement with that in a previous work.³⁰ The smaller energetic barriers observed in studied K diffusion systems than corresponding Na systems can be ascribed to the larger ionic radius of K. As is shown in Figure 5c, the larger cation–substrate distance (height) and lower interstate height variation of studied K diffusion paths also contribute to these energetic barrier differences, similar to trends observed in the cases of MA-ALGr,⁵² VS₂,⁵³ and MoN₂.⁷

The overall performance of the BG sheet as an anode material for KIBs is then compared to that of other candidates over several different parameters. Table 2 summarizes the parameters for the comparison. The BG anode for KIBs simultaneously possesses a large specific capacity, excellent ionic and electronic conductivity, and a modest open circuit voltage, and among all of the listed candidates in the table, the BG anode for KIBs is the only one without notable disadvantages found in other materials (e.g., MoN₂ has a large OCV and diffusion barrier; YN2 has a small specific capacity; GeS₂ exhibits a poor electronic conductivity; Nb₂C has a quite small specific capacity). Meanwhile, the BG anode for KIBs outperforms the commercial graphite anode for LIBs and the BG anode for NIBs with respect to specific capacity and ionic conductivity, which indicates a great potential for KIBs based on BG anodes to replace LIBs based on graphite anodes in the future.

Cycling Stability. When evaluating cycling stability the degree of structural deformation is crucial as enormous distortion would result in a great loss of capacity in a few cycles.^{54,55} Thus, the changes of bond lengths (bonds around the occupied hollow site) are measured to evaluate the degree of deformation.^{30,56} As shown in Table 3, the B–C bond length

Table 3. Bond Length d (in Å) of the B₄C₂₈ Substrate before and after Na or K Adsorption

| | B_4C_{28} | $Na_1B_4C_{28}$ | $K_1B_4C_{28}$ | $K_8B_4C_{28}$ |
|--------------|-------------|-----------------|----------------|----------------|
| $d_{(B-C)}$ | 1.50 | 1.50 | 1.50 | 1.50 |
| $d_{(C-C)1}$ | 1.43 | 1.44 | 1.44 | 1.44 |
| $d_{(C-C)2}$ | 1.47 | 1.48 | 1.47 | 1.48 |

remains almost unchanged in all studied cases, and the C–C bonds vary by 0.01 Å at both dilute and saturated K concentrations, indicating a good cycling stability. Meanwhile, the bond length change of $K_1B_4C_{28}$ is smaller than that of Na₁B₄C₂₈, which suggests that the adsorption of K atoms would not cause larger structural deformation than that of Na in the case of the B₄C₂₈ substrate.

Another concern is the formation of the solid-electrolyteinterface (SEI) layer. If the potassiation voltage of the anode lies outside of the electrochemical window of the electrolyte, electrons from the external circuit would transfer to the conduction band of the electrolyte, reducing the electrolyte to form a SEI layer.⁵⁷ For better cycling performance and safety, suppression of the SEI layer is necessary for two primary reasons. First, SEI layers could potentially block the adsorption and transportation of K atoms.³⁰ Second, in order to form a stable SEI layer to protect the electrolytes from further decomposition, organic molecules such as EC and VC, which are highly flammable and pose safety concerns, must currently be included in electrolytes.^{58,59} To mitigate this effect, it was proposed that the OCVs of anodes should be higher than the conduction band minima of electrolytes.^{30,57} Electrochemical windows for different pertinent electrolytes are generally 0.79-1.19 V vs K⁺/K.⁵⁷ Thus, the potassiation voltage of BG substrate used for KIBs (0.82 V) would be located within the window of some ionic liquids,⁶⁰ ensuring good cycling stability when using these ionic liquids as electrolytes. For comparison, the sodiation voltage of 0.44 V^{30} for the same BG substrate is far below the conduction band minima of electrolytes (0.57-0.97 V vs Na^+/Na ,^{30,57} which would result in remarkable formation of SEI layers.

At high current densities, the transport in the anode is too slow for the charge redistribution to reach equilibrium, which lowers capacity with increasing current density^{57,61} and degrades the cycling stability.^{7,37,56,57} Such an effect, however, should be not too prominent in the studied system, as both the electronic and ionic conductivity of the BG anode for KIBs has been proved to be excellent. Meanwhile, the ionic conductivity of BG anodes for KIBs are better than those for NIBs, suggesting that the BG anodes for KIBs would loss less capacity at the same current density than those for NIBs.

Finally, whether the high mobility of K atoms on the BG surface would lead to K clustering is examined, for clustering may result in dendrite growth,³⁷ which is extremely harmful to the cycling performance and safety.⁶² Simply considering the voltage criterion,^{9,30} the average potassiation voltage of 0.82 V is large enough to avoid the formation of metal dendrites. More specifically, the formation energy of a K–K cluster is defined as^{36,37}

$$E_{c} = E(K_{2}B_{16}C_{112}) + E(B_{16}C_{112}) - E_{1}(K_{1}B_{16}C_{112}) - E_{2}(K_{1}B_{16}C_{112})$$
(10)

where $E(B_{16}C_{112})$, $E_1(K_1B_{16}C_{112})$, $E_2(K_1B_{16}C_{112})$, and $E(K_2B_{16}C_{112})$ denote the total energies of the BG substrate,



Figure 6. (a) Profile of the cluster formation energy. (b) Electron localization functions of the (001) section of adsorption configuration C₁.

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the two adsorption patterns with one K atom, and the pattern with two K atoms, respectively. The calculated results are plotted in Figure 6a, and larger positive energies at higher K–K separation clearly show that K atoms favorably separate from each other on the BG substrate. For comparison, the formation energy of an isolated K_2 dimer is calculated. The negative energies at higher K–K distances, in conjunction with the positive values at lower distances, indicate that freestanding K atoms tend to attract each other and cluster. After studying the clustering behavior at dilute K concentration, the electron localization functions (ELF) are calculated to evaluate the state of K atoms at high concentration. As shown in Figure 6b, no electrons localize between the K ions, suggesting that those K atoms do not form clusters.^{7,8}

CONCLUSIONS

In summary, B-doped graphene (BG) is proposed as a promising anode material for KIBs. The maximum specific capacity of the selected B_4C_{28} anode can reach 564 mAh/g, larger than that of most anodes for KIBs. The metallic band structure of B_4C_{28} favoring the fast K ions diffusion can enhance the rate performance. Moreover, to study the cycling stability, four harmful effects are considered, namely structural deformation, the formation of the SEI layer, capacity loss with increasing current density, and metal dendrite growth. We find that B-doped graphene is robust against these factors and performs better as an anode material for KIBs than for NIBs. We hope that this theoretical study can stimulate experimental efforts on this subject to further promote the research and development of KIBs.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.7b07583.

Flowchart of the code generating K adsorption patterns under different K concentrations. (PDF)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work is supported by grants from the National Key Research and Development Program of China (2016YFE0127300 and 2017YFA0205003), the National Natural Science Foundation of China (NSFC-51471004), and the National Training Program of Innovation for Undergraduates of China (201611001008). The calculations were carried out at the High Performance Computing Platform of CAPT at Peking University, China.

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