Barrier Reduction of LithiumIon Tunneling through Graphene with Hybrid Defects: First-Principles Calculations


Atomically thin 2D materials such as graphene and hexagonal boron nitride are increasingly explored as a possible platform for atomic diffusion barriers and novel separation technologies. However, a perfectly dense networked lattice structure is impermeable to nearly all ions thereby limiting their application as atomically thin barriers. In this work, climbing image nudged elastic band simulation is applied to identify meaningful strategies to reduce the energy barrier height of Li ions tunneling through monolayer (ML) graphene sheets. Our results reveal that defects such as pore defects, ripples, and some atomic substitutions can effectively reduce the Li ion tunneling barrier and the defects can alter the Li ion adsorption energy to influence the deintercalation process. Furthermore, hybrid defects can balance the energy barrier and potential well to increase the permeability of Li ions through graphene sheets.

1. Introduction

Two dimensional films such as graphene have attracted much research interest as a possible platform for atomic diffusion barriers and separation technologies. Previous literature has demonstrated that the perfect lattice in the monolayer (ML) 2D materials is nearly impermeable to most molecules, atoms, and even ions. In this respect, there are many potential applications, such as particle sieves and ion battery electrode materials. Owing to the large specific surface area, graphene provides a large amount of adsorption points for Li ions leading to superior storage performance and graphene extensively explored as promising electrode materials for Li-ion battery. However, this superior storage behavior can only occur in very thin films or materials reduced to nanoscale dimensions since it is difficult to fully charge when graphene sheets are introduced in the electrode materials. The Li ions with a certain direction driving force cannot avoid penetrating the monolayer graphene walls stood in front of them in the bulk electrode materials. In order to promote the application of graphene in electrode material for superior storage performance, reduction the lithium ion tunneling barrier in monolayer graphene is an effective way to full charge electrode materials by enhanced ions migration. As an important factor impacting the battery performance, Li ions migration process on the graphene film can be modulated by defects. Artificial defects with the desirable tunneling barrier may help to lower the diffusion barriers for some specific ions. Thus a good understanding of the influence between Li ions and graphene defects is indispensable to the application of graphene to Li-ion batteries.

In this work, first-principles calculations are implemented to investigate the mechanism of Li ion tunneling process. Single defects in graphene enhance the permeability of Li ions whereas hybrid defects obtained by different single defects affect the Li ion tunneling barrier and adsorption energy in the graphene sheets. Atomic substitution and pore defects play an important role in balancing the barrier and potential well and the two processes cannot be avoided when Li ions pass over the graphene sheets. Strategies to reduce the barrier height for Li ion tunneling by introducing graphene defects are proposed. The results provide insights into the Li ions tunneling process and a direction to realize rapid loading of Li ions in graphene electrodes by defect engineering to improve the performance of Li-ion batteries.

2. Computational Methods

The calculation is performed with the Vienna Ab initio Simulation Package using the projector augmented wave potentials of Perdew–Burke–Ernzerhof. The climbing-image nudged elastic band method is adopted to identify the reaction pathways for Li Ions with a cutoff energy of 400 eV and spin polarization is considered in the computation. The electron energies are...
Figure 1. Li ion tunneling through monolayer graphene sheets with different sizes: A) Barrier height and B) diameter of center benzene ring for various supercells. The brown balls represent carbon atoms and red balls represent lithium atoms.

Table 1. Li ion tunneling through monolayer various graphene sheets. The energy barrier represents the energy tunneling barrier and the relative change in the energy represents the barrier of the supercell compared to the smaller one. The diameter of the benzene ring represents the diameter of the nearest-neighbor benzene ring and the relative change in the diameter represents the diameter of the nearest-neighbor benzene ring compared to the experimental data (2.845 Å).[21,22]

<table>
<thead>
<tr>
<th>Super cell structure</th>
<th>Graphene (C_{12})</th>
<th>Graphene (C_{50})</th>
<th>Graphene (C_{72})</th>
<th>Graphene (C_{98})</th>
<th>Graphene (C_{128})</th>
<th>Graphene (C_{162})</th>
<th>Graphene (C_{200})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Relative change in energy barrier [%]</td>
<td>−</td>
<td>4.8</td>
<td>1.2</td>
<td>0.6</td>
<td>0.7</td>
<td>1.5</td>
<td>0.5</td>
</tr>
<tr>
<td>Relative change in diameter [%]</td>
<td>7.9</td>
<td>8.3</td>
<td>8.6</td>
<td>8.6</td>
<td>8.7</td>
<td>8.8</td>
<td>8.8</td>
</tr>
</tbody>
</table>

Note: Diameter of benzene ring is 2.845 Å experimentally.[21,22]

Table 2. Li ion adsorption sites and adsorption energy on both sides of the primary monolayer graphene (C_{128}). The initial and final states represent the adsorption sites under and above the graphene sheets, respectively.

<table>
<thead>
<tr>
<th>Distance of Li-ion adsorption [Å]</th>
<th>Initial</th>
<th>Final</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adsortion energy [eV]</td>
<td>−2.960</td>
<td>−2.959</td>
</tr>
</tbody>
</table>

Considerable efforts are made to choose a proper size for the supercell. The theoretical equilibrium graphene lattice parameters are a = b = 2.466 Å, c = 6.802 Å and 1.424 Å, and the optimized C–C bond length is 1.424 Å in good agreement with experimental values.[21,22] We set the supercell with the periodic boundary conditions and a vacuum layer is added to avoid the interaction between the graphene layers, in the c directions. Unit cell of graphene extended in a direction and b direction for supercell with monolayer carbon atoms. As shown in Figure 1A, the energy barrier and diameter of the nearest-neighbor benzene ring tend to converge as the size increases “C_{12}, C_{50}, C_{72}, C_{98}, C_{128}, C_{162}, C_{200}”.

We sample the Brillouin zone with a 1 × 1 × 1 k-point mesh and 8 × 8 × 1 sampling in a supercell (128 C atoms) is employed for graphene.

3. Results and Discussion

3.1. Li Ion Tunneling in Primary Graphene

3.1.1. Adsorption of Li Ions on Graphene Surface

When Li ions are close to graphene, they attach to the graphene surface with a relatively strong bond. In order to reveal the interaction between Li ions and graphene sheets, different relative positions and possible adsorption sites in the graphene are investigated and calculated. To characterize the interaction between Li ions and graphene sheets, we define the adsorption energy as

\[ E_{\text{ads}} = E_{\text{tot}} - E_{\text{gra}} - E_{\text{ion}} \]  

where \( E_{\text{tot}} \) is the total energy of the Li-ion/graphene superstructure and \( E_{\text{gra}} \) and \( E_{\text{ion}} \) are the energies of the isolated graphene sheets and Li ions, respectively. Prior to structure optimization, different sites above/below graphene are explored and the Li ions tend to adsorb on the same hollow sites. As shown in Table 2, Li ion adsorption on graphene at distances of 1.746 Å (below the graphene sheets) and 1.756 Å (above the graphene sheets) from the graphene sheet with adsorption energy −2.960 eV and −2.959 eV, respectively, is shown in the images of the initial and final states. The distance between the Li ion and the carbon center of a hexagonal carbon ring is about 2.280 Å which guarantees strong binding between the carbon and Li ions.
3.1.2. Tunneling Process through Primary Graphene

To study the initial and final states, climbing-image nudged elastic band simulation is performed to identify the transport pathway of the Li ion. As shown in Figures 2A,B, the tunneling barrier as obtained from the potential energy carve of the Li ions approaching the center of the benzene ring of graphene is found to be 7.791 eV. Compared to diffusion along the graphene surface, the energy barrier is much high for Li ion tunneling.[20,23,24] At the transition state, the Li ion is in the center of the benzene ring at a distance of 1.546 Å from each carbon atom and the diameter of the nearest-neighbor benzene ring extends to 3.092 Å from 2.845 Å at the initial or final state.

According to the spatial distribution of the charge difference in Figure 2C, the electron cloud around the center of the benzene ring is redistributed in the absence of the Li atom, whereas the electron cloud around Li adds to the nearby carbon atom. Electron transfer from the Li atom to carbon produces strong binding between the carbon and Li atoms. As shown in Figure 2D, the Li atom in the supercell possesses a positive charge with an extra-nuclear 0.765 electron loss and the system towards the \( \text{ML}^+ + \text{Li}^+ \) system instead of the \( \text{ML}^+ + \text{Li} \) system. The fact that primary monolayer graphene has the great energy barrier for Li ion tunneling can be explained by electron cloud density distribution. The 2s orbit of carbon interacts with the two p orbits forming strong sp\(^2\) covalent bonds with the nearest three atoms. The strong orbital overlap at 6.704 eV between the Li ion and carbon atom generates a large repulsive force leading to lattice expansion and the dense electron cloud generates the large tunneling energy barrier as shown in Figure 2E.

3.2. Li Ion Tunneling in Graphene with Defects

3.2.1. Pore Defects

During the preparation of graphene, pore defects are unavoidably produced and have a great impact on the electron cloud distribution of the graphene sheets as Li ions can enter the nanotubes through pore defects.[7,8,20,23] To reveal the impact on the Li ion tunneling process in monolayer graphene, as shown in the insets in Figure 3A, we consider two configurations with two and four carbon atoms removed in the NEB calculation in comparison with primary graphene. The results reveal that the energy barrier decreases to 1.377 eV with two carbon atoms removed and 0.095 eV with four carbon atoms removed compared to the energy barrier of 7.791 eV for perfect graphene, as shown in Figure 3A. Meanwhile, a larger defect size gives rise to a smaller penetration barrier which increases the permeability of Li ions through graphene. At the transition state, carbon atoms close to the pore defects relax to the stable state and a 2D metastable carbon allotrope are formed as shown in Figures 3C,D. Nine-carbon ring and eight-carbon ring are established which are easier to tunnel for Li ion compared with hex atomic ring. Li ion tends to tunnel through the graphene at the larger rings. The Li ion adsorption site is nearer on graphene with defects than primary graphene. Owing to the pore defects in graphene, the electron cloud is thinner than those of the other sides affecting Li ion tunneling.

The influence of pore defects extends to nearby sites. As shown in the Figure 3B, the tunneling barrier of some sites increases while that of other sites may decrease for the same scale of pore defects (two carbon atoms removed) and different places may decrease to different extent. On account of the pore defects, the electron cloud in the system is redistributed and the local charge density (purple sites) becomes sparse, as shown in Figures 3C,D. The tunneling barrier decreases at sites with sparse and dense electron clouds.

3.2.2. Ripples Defects

Owing to the interaction with the supporting substrates and thermal fluctuations induced by ripples existing intrinsically in graphene, ripple defects have a large impact on the graphene...
properties.\textsuperscript{[25–27]} To investigate the influence of ripples on the tunneling process, we constructed flat graphene sheet and graphene sheet with ripples. By controlling the degree of compression,\textsuperscript{[28,29]} ripples with different period-to-amplitude ratios (ripple 1: 6, ripple 1: 7, ripple 1: 9 and ripple 1: 12) are obtained as shown in Figure 4.

Similar to flat graphene sheets, Li ions tunnel through the center of a hexagonal carbon ring (hollow site). Li ion tunneling through the flat graphene, ripple 1: 12, ripple 1: 9, ripple 1: 7 and ripple 1: 6 have energy barriers of 7.791, 7.665, 7.645 and 7.627 eV, respectively, as shown in Figure 4. The height of the tunneling energy barrier decreases with increasing period-to-amplitude ratios. At the transition state, the diameter of nearest-neighbor benzene ring increases to 3.092, 3.120, 3.134, 3.176 Å for flat graphene, ripple 1: 12, ripple 1: 9, ripple 1: 7 and ripple 1: 6, respectively. The diameter of nearest-neighbor benzene rings increases with period-to-amplitude ratios decreasing the energy barrier. Furthermore, ripples introduce more space for the Li ions to reduce the energy by changing the lattice curvature. Consequently, Li ions prefer to tunnel through graphene ripples rather than flat sheets.

3.2.3. Atomic Substitution

The effects of atomic substitution on the interaction between Li and graphene are studied. Edge-doping of B, C, N, and O into zigzag graphene nanoribbons can maximize loading of charges.\textsuperscript{[16,30–33]} As shown in Figure 5, compared to primary graphene, boron and nitrogen substitution is taken into consideration to analyze the influence on the tunneling barrier. The results reveal that the energy barrier diminishes to 7.036 eV for one boron atom substitution and 5.094 eV for three boron atom substitution compared to the primary graphene sheet. On the contrary, the energy barrier increases to 8.425 eV for three nitrogen atom substitution and 7.899 eV for one nitrogen atom substitution. The tunneling energy barrier height decreases with increasing number of boron atoms and increases with increasing number of nitrogen atoms.

Li ion adsorption on graphene with defects is investigated. Nitrogen has one electron more than carbon atom and two more than boron, thus contributing a sparser electron cloud after boron atom substitution and a denser electron cloud after nitrogen atom substitution compared to primary graphene sheets at the...
Figure 4. Li ion tunneling through monolayer graphene with ripples with different period-to-amplitude ratios (h:d). The inset shows the supercells in various processes and the brown balls represent carbon atoms.

Figure 5. Li ion tunneling through monolayer graphene with boron/nitrogen atoms substitution with the inset showing the supercells in various processes. The brown balls represent carbon atoms, red balls represent lithium atoms, silver balls represent nitrogen atoms, and green balls represent boron atoms.

Table 3. Li ion adsorption sites and adsorption energy on both sides of the monolayer graphene supercells. The initial and final states represent the adsorption sides under and above the graphene sheets, respectively.

<table>
<thead>
<tr>
<th></th>
<th>Energy barrier [eV]</th>
<th>Initial adsorption energy [eV]</th>
<th>Final adsorption energy [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>C_{125}B_3</td>
<td>5.904</td>
<td>-4.119</td>
<td>-4.103</td>
</tr>
<tr>
<td>C_{127}B_1</td>
<td>7.036</td>
<td>-3.490</td>
<td>-3.490</td>
</tr>
<tr>
<td>C_{128}</td>
<td>7.791</td>
<td>-2.960</td>
<td>-2.959</td>
</tr>
<tr>
<td>C_{125}N_3</td>
<td>7.899</td>
<td>-2.552</td>
<td>-2.552</td>
</tr>
<tr>
<td>C_{125}N_3</td>
<td>8.425</td>
<td>-2.044</td>
<td>-2.073</td>
</tr>
</tbody>
</table>

The sparse electron cloud decreases the tunneling energy barrier. In the transition state, the Li ion is in the center of the benzene ring at a distance of 1.546 Å from each carbon atom and the diameter of the nearest-neighbor benzene ring extends to 3.092 Å from 2.845 Å in the initial or final state. When there is no pore defect, nitrogen atom substitution reduces the adsorption energy of the Li ion and boron atom substitution reduces the adsorption energy as illustrated in Table 3.

3.3. Li Ion Tunneling in Graphene with Hybrid Defects

The influence of various types of single defects is discussed in the previous section and there are also hybrid defects in 2D materials. Owing to the roughness of the substrates, pore defects and ripples are quite common in 2D materials,[34,35] in addition to other defects such as line defects and atomic substitution. To assess the tunneling process, various hybrid systems are chosen as shown in Figure 6A,B. Pore defects hybrid with atomic substitution are taken into consideration in the graphene supercells with or without ripples (h:d = 1:7). The supercell of C_{x}B_{y}/C_{x}N_{y} represents that the number of lacking atoms is 128-x and the number of boron/nitrogen atom substituted is y.

As shown in Figure 6A, the tunneling barrier drops to 6.730, 1.519, 1.666, 1.212, 0.116, and 0.008 eV for the supercells of defect sites. The sparse electron cloud decreases the tunneling energy barrier. In the transition state, the Li ion is in the center of the benzene ring at a distance of 1.546 Å from each carbon atom and the diameter of the nearest-neighbor benzene ring extends to 3.092 Å from 2.845 Å in the initial or final state. When there is no pore defect, nitrogen atom substitution reduces the adsorption energy of the Li ion and boron atom substitution reduces the adsorption energy as illustrated in Table 3.

Figure 6. Li ion tunneling through monolayer graphene with hybrid defects: A) Tunneling barrier of Li ions in various supercells and B) lattice structure of different supercells. The brown balls represent carbon atoms, red balls represent lithium atoms, silver balls represent nitrogen atoms, and green balls represent boron atoms.
Illustrated in Table 4, Li ion tunneling through monolayer graphene with hybrid defects. The energy barrier represents the energy tunneling barrier. The initial and final states represent the adsorption sides under and above the graphene sheets, respectively.

<table>
<thead>
<tr>
<th>Defects</th>
<th>Energy barrier [eV]</th>
<th>Initial adsorption energy [eV]</th>
<th>Final adsorption energy [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>C_{124}</td>
<td>7.791</td>
<td>−2.960</td>
<td>−2.960</td>
</tr>
<tr>
<td>C_{124}B_{2}</td>
<td>6.730</td>
<td>−3.012</td>
<td>−3.012</td>
</tr>
<tr>
<td>C_{124}B_{2}</td>
<td>1.519</td>
<td>−3.458</td>
<td>−3.458</td>
</tr>
<tr>
<td>C_{124}B_{2} with ripples</td>
<td>1.666</td>
<td>−3.502</td>
<td>−3.360</td>
</tr>
<tr>
<td>C_{124}N_{3}</td>
<td>1.212</td>
<td>−5.645</td>
<td>−5.645</td>
</tr>
<tr>
<td>C_{124}N_{2}</td>
<td>0.116</td>
<td>−4.600</td>
<td>−4.600</td>
</tr>
<tr>
<td>C_{124}N_{2} with ripples</td>
<td>0.008</td>
<td>−4.600</td>
<td>−4.601</td>
</tr>
</tbody>
</table>

C_{124}B_{2}, C_{124}B_{2}, C_{124}B_{2} with ripples, C_{124}N_{2}, C_{124}N_{2}, and C_{124}N_{2} with ripples (h x d = 1.7), respectively. For the C_{124}B_{2} and C_{124}B_{2} supercells, four carbon atoms are substituted by three boron atoms or double boron atoms. There are one atom pore defect and two atom pore defect similar to C_{124}N_{1} and C_{124}N_{1}. All the defect terminations are energetically favorable compared to primary graphene and the Li ion tends to tunnel through the graphene sheets at the hybrid defects. Lowering of the barrier of sheets with nitrogen in the pore defects is more effective than boron. In comparison, supercells with nitrogen in the pore defects possess larger adsorption energy of 4.6–5.6 and 3.0–3.5 eV for boron supercell, which is not beneficial to Li ions de-intercalation as illustrated in Table 4.

To tunnel through the graphene sheets, the Li ions have to pass over the barrier and potential well. Li ions easily adsorb on one site of the graphene because of the interaction between Li ions and carbon atoms. Blocking of Li ion comes from crossing graphene and de-intercalation from graphene sheets. Although there is a small increase in the adsorption energy, the tunneling barrier is greatly reduced for graphene with hybrid defects compared to a perfect one. Therefore, hybrid defects in 2D materials can balance the energy barrier and potential well thereby increasing the permeability of Li ions through the graphene sheets. The observed phenomenon can be utilized for Li ion separation in Li-ion batteries.

4. Conclusion

Tunneling of Li ions through monolayer graphene is investigated to explore the permeability of monolayer graphene sheets. The effects of the charge and adsorption site in the initial, translational, and final states are explored and discussed. The electron clouds outside the dense network lattice structure lead to a large Li ion tunneling barrier. The tunneling energy barrier decreases to 1.377 eV after removing two carbon atoms and 0.095 eV after removing four carbon atoms. Li ions tend to tunnel through the electron cloud pores where the electron density is sparse. The permeability of Li ions through graphene can be increased by introducing ripples and the tunneling energy barrier height decreases with increasing period-to-amplitude ratios. The tunneling barriers increases for carbon atoms in a central aromatic ring in the flat graphene layer substituted by nitrogen atoms, but decreases for boron atom substitution. Our results indicate that defects in the graphene sheets have a large influence on the permeability and the described strategies can be combined to adjust the energy barrier and potential well to cater to different practical requirements. This study provides insights into the role of defects in tunneling barrier and diffusion dynamics which can be a useful guideline for tailoring the energy barrier of graphene in battery and separation applications.

Abbreviation
ML, monolayer

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Conflict of Interest
The authors declare no conflict of interest.

Keywords
defects, first-principles calculations, graphene, lithium ion tunneling

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