Enhanced lithiation in defective graphene

Dibakar Datta a, Junwen Li b, Nikhil Koratker c,d,* , Vivek B. Shenoy b,e,*

a School of Engineering, Brown University, Providence, RI 02912, United States
b Department of Materials Science and Engineering, University of Pennsylvania, Philadelphia, PA 19104, United States
c Department of Mechanical, Aerospace and Nuclear Engineering, Rensselaer Polytechnic Institute, Troy, NY 12180, United States
d Department of Materials Science and Engineering, Rensselaer Polytechnic Institute, Troy, NY 12180, United States
e Department of Mechanical Engineering and Applied Mechanics, University of Pennsylvania, Philadelphia, PA 19104, United States

ABSTRACT
We performed first-principle calculations based on density functional theory (DFT) to investigate adsorption of lithium (Li) on graphene with divacancy and Stone–Wales defects. Our results confirm that lithiation is not possible in pristine graphene. However, enhanced Li adsorption is observed on defective graphene because of the increased charge transfer between adatom and underlying defective sheet. Because of increased adsorption, the specific capacity is also increased with the increase in defect densities. For the maximum possible divacancy defect density, Li storage capacities of up to $1675 \text{mAh/g}$ can be achieved. While for Stone–Wales defects, we find that a maximum capacity of up to $1100 \text{mAh/g}$ is possible. Our results provide deeper understanding of Li-defect interactions and will help to create better high-capacity anode materials for Li-ion batteries.

1. Introduction
Rechargeable lithium ion batteries (LIBs) are driving a renaissance in electric-vehicle development, portable electronics, light vehicles, advanced energy storage systems and miscellaneous power devices [1]. The seemingly ubiquitous LIBs are the systems of choice, offering high energy density, flexible and lightweight design, and longer lifespan than comparable battery technologies [2,3]. However, as the global energy demand increases, developing new materials with higher charge capacity and better cycling performance for LIBs are of extreme importance [4]. Among the most intensively studied anode materials in LIBs are silicon and graphite [5]. Graphite is the widely used anode material in LIBs due to its high coulombic efficiency (the ratio of the number of charges that enter the battery during charging compared to the number that can be extracted from the battery during discharging) and excellent electrochemical stability [2]. However, its gravimetric capacity is relatively low (theoretical value of $372 \text{mAh/g}$) leading to its limited performance in LIBs [2,6]. Compared to graphite, silicon offers ~10 times higher gravimetric energy densities as LIB anodes. However, this extremely high capacity of silicon is associated with massive structural changes and volume expansion on the order of 300%, resulting in electrode particle fracture, disconnection between the particles, capacity loss, and thus very limited cycle life [7]. Recent experimental studies show that low dimensional materials like graphene [8,9] and its oxide [10],
carbon nanotubes [11,12], fullerenes [13], and silicon nanowires [14,15] offer higher specific capacities and could serve as a potential anode materials in LIBs.

Among the low dimensional materials, graphene, an atomic layer of carbon atoms arranged in a honeycomb lattice, is actively being pursued as a materials for next generation power devices since its discovery in 2004 [16]. Because of its superior electrical conductivity, high charge carrier mobility (20 m$^2$ V$^{-1}$ s$^{-1}$), high surface area (2600 m$^2$ g$^{-1}$) and a broad electrochemical window [17,18], graphene can be particularly advantageous for its applications in energy storage devices [19], for example in LIBs [20,21]. However, impurities and defects (both vacancy and Stone–Wales) in graphene cannot be avoided [22,23] either because of the production process being used or because of the conditions under which the graphene device operates [24]. Recently, transmission electron microscopy (TEM) [25,26] and scanning tunneling microscopy (STM) [27,24] have been used to obtain images of defective graphene with atomic resolution [22]. Topological defects significantly influence the electronic, optical, mechanical, and thermal properties of graphene [22]. DFT studies [28] suggest that the intentional creation of point defects before absorbing Li would enhance adsorption significantly. In our recent paper [29], we have demonstrated this in terms of gravimetric capacity and investigated defect-induced plating of lithium metal within porous graphene networks. Despite studies on Li adsorption in defective graphene, several important questions remain unclear: What will be the lithiation and corresponding capacities for different percentages of divacancy (DV) and Stone–Wales (SW) defects? For different defect densities, what will be the maximum possible capacities? How exactly do lithium adatoms cluster on and around the defects? Which type of defect has the strongest influence on Li adsorption? Most importantly, what is the underlying mechanism of enhanced Li adsorption on graphene with structural defects? Recently, we have studied these issues for adsorption of Na and Ca to graphene surface [30]. In this study, we have performed first-principle calculations based on DFT to thoroughly investigate these questions for Li–graphene systems.

2. Computational models

All DFT calculations were performed using the Vienna Ab-initio Simulation Package (VASP) [31]. The detail methodology is explained in Supplementary Information. We consider here two kinds of structural defects: vacancy and Stone–Wales (SW). Among the vacancy defects, single vacancies (SV) with a carbon atom missing in graphene (or in the outermost layer of graphite) have been experimentally observed using TEM [25] and STM [27]. Because of geometry, one dangling bond always remains in the case of SV. On the other hand, for a divacancy (DV) defect, the edge is always saturated. As explained in our previous work [30], a DV is thermodynamically more favored over an SV and it is the most common type of vacancy defects observed experimentally [32,33]. A DV defect (shown in Fig. 1a) can be obtained by removing a C–C dimer from pristine graphene. Transmission electron microscopy (TEM) experiments frequently show the existence of both the 555-777 and 5-8-5 defects [34]. Stone–Wales defect is 55-77 defects and gives us an idea about the role of heptagon. So we selected 5-8-5 DV defect in order to include octagon in our studies. Moreover, octagonal defect has been extensively observed in experiments [35,32]. Electronics [36] and mechanical [37] properties of graphene with octagonal defect have been extensively studied and it has been found as source of gap states in graphene semiconducting...
structures [38]. For adsorption studies, octagonal defect has also been extensively considered [39,40]. Future research considering 555-777 DV defect will be interesting and should be pursued.

As shown in Supplementary Fig. S1, five different percentages of DV defects are considered: 6.25% (Fig. S1b), 12.50% (Fig. S1c), 16.00% (Fig. S1d), 18.75% (Fig. S1e), and 25.00% (Fig. S1f). Like DV, SW defect (Fig. 1b) is another common structural defect observed experimentally [41]. As shown in Supplementary Fig. S2, we have considered four types of SW defects with different concentration: 25% (Fig. S2a), 50% (Fig. S2b), 75% (Fig. S2c), and 100% (Fig. S2d). For 100% SW defect, we get the Haeckelite structure [42], which is a sheet full of 5–7 rings with the lowest equilibrium energy (the total ground-state energy) per carbon atom [30]. Apart from these defective structures, extensive research has been carried out on graphene with tilted Stone–Wales defect [43] and polycrystalline graphene [44]. These studies open many new windows: How will different orientations and tilting angle of SW defect affect Li adsorption? Can polycrystalline graphene be a potential anode material for LIBs? Future research to address these issues is warranted and should be pursued.

3. Results and discussion

3.1. Analysis of adsorption potential for lowest defect density

To get insight into adsorption of Li on defective structure, we first consider the lowest defect density i.e. 6.25% DV and 25% SW defect. The lattice constant of graphene is 2.46 Å [45,46]. Two sites of high symmetry for adsorption: the sites on the top of a carbon atom (Top) and the site at the center of a hexagon (Hex) of the graphene sheet are considered for detailed analysis of adsorption potential for these lowest
defect densities. For each site, we consider three positions: over the defect (O-position), neighborhood of the defect (N-position), and away from the defect (A-position). Supplementary Figs. S3 and S4 explain this concept of site and position that we have considered. As explained in detail in our previous work [30], regarding different available positions for adsorption, we select the location that has the maximum defective neighborhood (MDN). For example, as shown in Fig. 1a, considering the Top site at the O position (Top-O), we can place adatom on any of the eight carbons enclosing the octagon. However, a closer look at the geometry reveals that we have only two different options: location 1 and 2 or 3 and 4. Location 1 or 3 is at the junction of an octagon, hexagon and pentagon, whereas for location 2 or 4, it is at the junction of an octagon and two hexagons.

Fig. 2 shows the lithiation potential for three different positions (O, N, A) at both Hex and Top sites. Here negative potential indicates that adsorption is not possible. As indicated in inset in Fig. 2 (red), lithiation is not possible in case of pristine graphene [28]. However, presence of DV defects favor lithiation. O-position (blue) has maximum potential as it has MDN. Lithiation potential decreases form O to A positions. In case of SW defect, lowest defect density (25%) does not favor absorption for any positions. However, we notice that O-position is the most favorable position. This means, if we increase the defect density, it will favor adsorption. Hence we have considered higher defect densities i.e. 50%, 75%, and 100% for further calculation.

3.2. Charge transfer analysis

To get deeper physical insight into adsorption, we performed bonding charge-density analysis [47]. Fig. 3 shows the bonding charge density passing through the bond between Li and the nearest carbon atom. The bonding charge density is obtained as the difference between the valence charge density of strain-free graphene–Li sheet and the superposition of valence charge density of the constituent atoms. A positive value (red) indicates electron accumulation, whereas a negative value (blue) denotes electron depletion. Changes in bonding charge distribution after introduction of defects clearly show that enhanced charge transfer from Li to underlying graphene sheet favors adsorption of adatom. To quantify the charge distribution, we performed Bader charge analysis [48]. Fig. 4 shows the charge transfer values for different defect sites and positions. The potential increases with increase in charge transfer. Beyond a threshold charge transfer of ~0.70e, Li adsorption is possible.

3.3. Adsorption potential and capacities for different defect densities

Analyzing Figs. 2–4, we notice that O position of Hex site (Hex-O) is the most favorable location of adsorption. Hence for initial distribution of Li, we have mainly focused on this location. For each defect density, to have certain capacity, we need adsorption of certain amount of Li adatoms. These adatoms can be placed over defective graphene in many different ways. For example, as shown Fig. 55, for 12.50% defect, we would like to have Li_{5}C_{28} (capacity = 398.4592 mAh/g) and Li_{6}C_{28} (capacity = 478.1510 mAh/g). As shown in upper and lower panel, lithium adatoms are placed in three different configurations. In fact, we can place adatoms in many other configurations i.e. *for every case; we have several options for the initial distribution.* For each configuration, adsorption potential

---

**Fig. 5** – Capacity and corresponding lithiation potential for different percentages of (a) DV and (b) SW defects. (A color version of this figure can be viewed online.)

**Fig. 6** – Maximum capacity for different DV and SW defect densities. (A color version of this figure can be viewed online.)
will be different. Naturally, if more adatoms are placed over and around the defect, potential will be more. If we compare configuration 1 and 2 in upper panel of Fig. S5, we notice for these cases, potentials are 0.0281 and 0.0523 eV respectively. For location 2, all adatoms are placed inside octagons while for location 1, one of them is placed outside resulting in lower potential. Likewise, as shown in Figs. S5–S11, for every case, we consider three among many possible configurations.

For each percentage of defects, we have carried out DFT calculations for different percentages of Li until adsorption is no longer possible i.e. potential becomes negative. Fig. 5a summarizes lithiation potential for five different DV defect densities. For highest defect density of 25% (Fig. S11), we notice the formation of Li5C8 at a potential of 0.84 eV, corresponding to a maximum capacity of 837 mAh/g. The favorable formation of Li5C8 has been confirmed in our recent experimental studies [29]. Fig. 5b shows Li adsorption to defective graphene with SW defects. The results indicate significant Li absorption for 100% SW defects i.e. for the Haeckelite structure. Error bar of different height indicates the variation in potential range for different capacities. Fig. 6 summarizes lithiation potential for five different DV and SW defect densities. For highest DV defect of 25%, the maximum capacity is as high as ~1675 mAh/g, corresponding to a lithiation potential of ~0.1 eV. In the case of SW defects, we observe the highest capacity of ~1100 mAh/g for the Haeckelite structure.

4. Conclusions
In summary, we have performed first-principles calculations to investigate the Li adsorption on graphene with various DV and SW defect densities. We confirm that lithiation is not possible in pristine graphene. However, presence of defect favors adsorption. The potential is larger when adatom is on and around the defective zone. We have demonstrated the underlying charge-transfer mechanism for enhanced adsorption. Our results provide deeper insight into adsorption and will help to create better anode materials for higher capacity and better cycling performance for LIBs. In addition, since the charge transfer occurring in both defects is identified to account for the enhanced adsorption of Lithium, we hope this work will provide the first theoretical understanding on the experimentally observed lithiation and attract more researchers’ attention on this important topic and promote the development of this field.

Acknowledgements
D.D., J.L., and V.B.S. gratefully acknowledge the support of the Army Research Office through contract W911NF-11-1-0171 and the National Science Foundation. N.K acknowledges funding support from the USA National Science Foundation (Award 0969895) and the John A. Clark and Edward T. Crossan Chair Professorship from the Rensselaer Polytechnic Institute. Authors would like to thank all three anonymous reviewers for their outstanding review that made our manuscript much better.

Appendix A. Supplementary data
Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.carbon.2014.08.068.

References


SUPPLEMENTARY INFORMATION

Methodology

All calculations are performed using the Vienna Ab Initio Simulation Package (VASP) [1] with the Projector Augmented Wave (PAW) [2,3] method and the Perdew-Burke-Ernzerhof (PBE) [4] form of the generalized gradient approximation (GGA) for exchange and correlation. For convergence studies, we determined a kinetic energy cut-off of 600 eV and a Fermi smearing width of 0.05 eV. The Brillouin zones of 4×4 and 5×5 super cell are sampled with the Γ-centered k-point grid of 9×9×1 and 7×7×1 respectively. In order to avoid the spurious coupling effect between graphene layers along the z-axis, the vacuum separation in the model structure is set to 18 Å. All atoms and cell-vectors are relaxed with a force tolerance of 0.02 eV/Å.

The lithiation potential $V$ is defined as [5,6]

$$V = -\frac{\Delta G_f}{z \cdot F}$$

(1)

where $F$ is the Faraday constant and $z$ is the charge (in electrons) transported by lithium in the electrolyte. In most nonelectronically conducting electrolytes $z = 1$ for Li intercalation. The change in Gibb’s free energy is

$$\Delta G_f = \Delta E_f + P\Delta V_f - T\Delta S_f$$

(2)

Since the term $P\Delta V_f$ is of the order of $10^{-5}$ eV$^5$, whereas the term $T\Delta S_f$ is of the order of the thermal energy (26 meV at room temperature), the entropy and the pressure terms can be neglected and the free energy will be approximately equal to the formation energy $\Delta E_f$ obtained from DFT calculations. The formation energy is defined as

$$\Delta E_f = E_{Li,G} - (nE_{Li} + E_G)$$

(3)
where $n$ is the number of Li atoms inserted in the computational cell, $E_{Li,G}$ is the total energy of the Lithiated Graphene ($Li_nG$) structure, $E_{Li}$ is the total energy of a single Li atom in elemental body-centered cubic Li, and $E_G$ is the total energy of a particular graphene structure. From DFT calculation, we have obtained $E_{Li}$ to be -1.8978 eV. If the energies are expressed in electron volts, the potential of the $Li_nG$ structures vs. $Li/Li^+$ as a function of lithium content can be shown as [7]

$$V = -\frac{\Delta E_f}{n}$$  \hspace{1cm} (4)

The composition range over which Li can be reversibly intercalated determines the battery capacity.

In our calculations, we have included spin polarization but not the van der Waals (VdW) interaction. The inclusion of VdW interaction is expected to affect our results based on PBE. But the charge transfer mechanism underlying the enhanced adsorption will remain unchanged. Since VdW interaction gives rise to stronger binding, its inclusion will lead to higher capacities. However, overall trend or major conclusion of this work will remain the same.

References


**FIGURES**

Figure S1: (a) Pristine graphene and graphene with DV defects (b) 6.25, (c) 12.50, (d) 16.00, (e) 18.75, (f) 25.00%. Systems shown here are 2X2 super cell in size with periodicity in their in-plane dimensions. For 16% defect, super cell is composed of 5X5 unit cell. For remaining cases, 4X4 unit cell is used. The super cell used in the calculation is marked in black. All systems are relaxed structure. (g) Unit cell considered creating the structure. One unit cell consists of 2 atoms.

In this study, we have considered triclinic system instead of square sheet. Since we are considering periodic systems *i.e.* there is no edge stress, overall conclusions for triclinic and square sheet will be same. To generate triclinic super cell, we used unit cell consisting of 2 atoms. For square sheet, we need unit cell consisting at least 4 atoms. For
DFT computation, we are using VASP package, which cannot handle too many atoms. For computational efficiency, it is desirable to have less number of atoms. Therefore, it is better to consider unit cell with less number of atoms.

Figure S2: Graphene with SW defects (a) 25, (b) 50, (c) 75, (d) 100%. Systems shown here are 2X2 super cell in size with periodicity in their in-plane dimensions. The super cell used in the calculation is marked in black. All systems are relaxed structure.
Figure S3: Li adsorption on DV Hex (a-c) and Top (d-f) site at (a,d) over the defect (O position) (b,e) neighborhood of the defect (N position) and (c,f) away from the defect (N position).
Figure S4: Li adsorption on SW Hex (a-c) and Top (d-f) site at (a,d) over the defect (O position) (b,e) neighborhood of the defect (N position) and (c,f) away from the defect (N position).

12.50 % DV Defect

Li₅C₂₈ (Capacity: 398.4592 mAh/g)

1. V = 0.0281 eV
2. V = 0.0523 eV
3. V = 0.0462 eV

Li₆C₂₈ (Capacity: 478.1510 mAh/g)

1. V = -0.1744 eV
2. V = -0.0054 eV
3. V = 0.0286 eV

Figure S5: Different relaxed configurations of Li₅C₂₈ and Li₆C₂₈ for 12.50% divacancy defect.

16.00 % DV Defect

Li₁₁C₄₂ (Capacity: 584.4068 mAh/g)

1. V = 0.14 eV
2. V = 0.1361 eV
3. V = 0.9991 eV

Figure S6: Different relaxed configurations of Li₁₁C₄₂ for 16.00% divacancy defect.
18.75 % DV Defect

$\text{Li}_7\text{C}_{26}$ (Capacity : 600.7538 mAh/g)

1 $V = 0.4145$ eV  
2 $V = 0.3012$ eV  
3 $V = 0.5845$ eV

$\text{Li}_{10}\text{C}_{26}$ (Capacity : 858.2197 mAh/g)

1 $V = 0.2103$ eV  
2 $V = 0.2923$ eV  
3 $V = 0.3712$ eV

$\text{Li}_{12}\text{C}_{26}$ (Capacity : 1029.90 mAh/g)

1 $V = 0.1587$ eV  
2 $V = 0.1285$ eV  
3 $V = 0.0885$ eV

Figure S7: Different relaxed configurations of $\text{Li}_7\text{C}_{26}$, $\text{Li}_{10}\text{C}_{26}$, and $\text{Li}_{12}\text{C}_{26}$ for 18.75% divacancy defect.
25.00 % DV Defect

Li$_7$C$_{24}$ (Capacity: 650.8166 mAh/g)

1. $V = 3.7196$ eV
2. $V = 3.0245$ eV
3. $V = 2.8213$ eV

Li$_{12}$C$_{24}$ (Capacity: 1115.7 mAh/g)

1. $V = 0.8337$ eV
2. $V = 0.9897$ eV
3. $V = 0.7648$ eV

Li$_{18}$C$_{24}$ (Capacity: 1673.5 mAh/g)

1. $V = 0.1930$ eV
2. $V = 0.0940$ eV
3. $V = 0.1666$ eV

Figure S8: Different relaxed configurations of Li$_7$C$_{24}$, Li$_{12}$C$_{24}$, and Li$_{18}$C$_{24}$ for 25.00% divacancy defect.
50.00% SW Defect

Li\textsubscript{6}C\textsubscript{32} (Capacity: 418.3821 mAh/g)

1. $V = 0.0946$ eV
2. $V = 0.0874$ eV
3. $V = 0.1385$ eV

Figure S9: Different relaxed configurations of Li\textsubscript{6}C\textsubscript{32} for 50.00% SW defect.

75.00% SW Defect

Li\textsubscript{6}C\textsubscript{32} (Capacity: 418.382 mAh/g)

1. $V = 0.1926$ eV
2. $V = 0.3098$ eV
3. $V = 0.2442$ eV

Li\textsubscript{8}C\textsubscript{32} (Capacity: 557.8428 mAh/g)

1. $V = 0.0946$ eV
2. $V = 0.1290$ eV
3. $V = 0.1102$ eV

Figure S10: Different relaxed configurations of Li\textsubscript{6}C\textsubscript{32} and Li\textsubscript{8}C\textsubscript{32} for 75.00% SW defect.
100.00% SW Defect

Li₈C₃₂ (Capacity: 557.8428 mAh/g)

1. V = 0.3803 eV
2. V = 0.3583 eV
3. V = 0.5036 eV

Li₁₄C₃₂ (Capacity: 976.2249 mAh/g)

1. V = 0.2146 eV
2. V = 0.2032 eV
3. V = 0.2020 eV

Li₁₇C₃₂ (Capacity: 1185.4 mAh/g)

1. V = 0.0443 eV
2. V = 0.0861 eV
3. V = 0.0713 eV

Figure S11: Different relaxed configurations of Li₈C₃₂, Li₁₄C₃₂ and Li₁₇C₃₂ for 100.00% SW defect.
FIGURE S12: Lithiation potential for different capacity for 25% DV defect. Here three points at each capacity corresponds to three different initial configurations.