

First-principles study on the performance of zigzag graphene nanoribbons for lithium-selenium cathode materials

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Abstract: The selenium-graphene system showcases the latest development of lithium-ion battery cathode material, which has attracted attention worldwide. By employing the first-principles calculation, we firstly find that both single Se atom and Se_n ($n=2,3,4,6,8$) clusters prefer to stick to the edge site of zigzag graphene nanoribbons (ZGNRs). Besides, the theoretical capacity of Li on Se_n @ZGNRs ($n=1,2$) is investigated comparatively. The Se_1 @ZGNRs system shows better capacity than that of Se_2 @ZGNRs. Our findings not only shed light on the adsorption behaviors between Li, Se atoms and ZGNRs theoretically, but also provide a new strategy for improving the performance of Li-Se cathode materials based on the aspect of Se atom number.

Key words: first principles; selenium; zigzag graphene nanoribbon; lithium selenium battery

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1 Introduction

Benefiting from the ultrahigh specific area, atoms or molecules modified two-dimensional (2D) graphene has been processed into sorbent materials used in diverse industrial fields, which range from sensors, electronic to catalysis^[1-2]. Moreover, graphene with a point-like Fermi surface (Dirac Cone) and a linear dispersion at the Fermi level exhibits intriguing ballistic transport properties. Graphene is also widely applied as electrode materials in lithium-ion batteries (LIBs) owing to its high Coulomb efficiency and outstanding electronic behaviors^[3-5].

Nowadays, high capacity cathode materials are urgently needed in long life rechargeable LIBs.

Selenium cathode has recently attracted great attention since lithium-selenium (Li-Se) batteries have some significant advantages, such as high discharge rate and good cycling performance^[6-7]. But same to the Lithium Sulfur (Li-S) batteries, the shuttle effect still exists in Li-Se batteries^[8]. The usage of composite materials for electrode can effectively weaken this shuttle effect. For Li-S batteries, the longer life time benefits from the strong adsorption properties of nanocarbon materials and their role in encapsulating and limiting sulfur^[9]. Similarly, Li-Se batteries may also show this physical mechanism. Selenium and sulfur have a comparable volumetric capacity, which can also be easily used in portable devices. Moreover, selenium has better electrical conductivity than sulfur, so it has better

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electrochemical performance and faster electronic conductivity^[10]. As the electrode, selenium will be a better choice. Sha et al^[11] constructed Se_n -decorated graphene through a facile high-energy ball-milling process and achieved the higher reversible capacity and better cycle stability. However, the physical and chemical interaction between Se clusters and graphene surface is rarely studied.

In this work, the prior Se atoms adsorption on ZGNRs and the performance of ZGNRs for Li-Se batteries are theoretically studied by first-principles calculation. The results show that both the single selenium atom and selenium atomic clusters are preferred to adsorb on the edges of ZGNRs. The theoretical capacity of lithium atoms adsorption on Se_n @ZGNRs is also evaluated. Our results provide a theoretical understanding for the Se @ZGNRs as cathode material in the Li-Se batteries.

2 Computational Methods

The calculations of electronic structures are carried out using the Vienna Ab-initio Simulation Package (VASP) based on density functional theory (DFT)^[12-15]. The exchange-correlation interaction is treated within the generalized gradient approximation (GGA) in the form of Perdew-Burke-Ernzerhof (PBE)^[16-18]. The cut-off energy is chosen to be 450 eV for the plane wave expansion. To achieve a balance between efficiency and accuracy, Monkhorst-Pack k-sampling with grid of $1 \times 1 \times 5$ and $1 \times 1 \times 15$ are used in structural optimization and static self-consistent calculation, respectively. The geometries are fully optimized until the forces on each atom are less than $0.1 \text{ eV} \cdot \text{nm}^{-1}$ and the energy convergence is less than $1.0 \times 10^{-5} \text{ eV}$. The van der Waals corrections are adopted for the adsorption with the scheme of Grimme DFT-D2 involved in the effect of dispersion relationship, which succeeds in describing interaction between graphene and the surface of SiO_2 ^[19].

In this work, the single layer ZGNRs with the width of 10 carbon atoms in both armchair and zigzag

direction is adopted as the initial supercell model, and Se and its clusters are adsorbed on the surface. This width will not be too large to show the graphene characteristics instead of ZGNRs, nor is it too small to show unreliable edge effects^[20]. 2 nm vacuum between edge-to-edge and layer-to-layer are added to eliminate the coupling between adjacent nanoribbons, while the crystal structure has periodicity in the z (zigzag) direction. In order to prevent the chemical reactivity between dangling bonds, the nanoribbon edges are passivated with hydrogen atoms. The adsorption energy (E_{ads}) of the Se_n clusters on the surface of ZGNRs is defined as

$$E_{\text{ads}} = E_{\text{Se}_n\text{@ZGNRs}} - E_{\text{ZGNRs}} - E_{\text{Se}_n}, \quad (1)$$

where $E_{\text{Se}_n\text{@ZGNRs}}$ is the total energy of Se_n @ZGNRs system, E_{ZGNRs} is the total energy of monolayer ZGNRs and E_{Se_n} is the total energy of free Se_n .

3 Results and Discussions

3.1 Single Se adsorption on ZGNRs

In this work, calculations are started with adsorption of a single selenium atom on ZGNRs. As shown in Fig. 1, the 1~8 and 1'~8' adsorption positions, including hole, bridge, and top sites along armchair direction, are considered to study the relative stability. The distance between two adjacent numbers is equal in y direction. We find that the energy at the edge site is smallest, which indicates indirectly that it is more stable at the edge, shown in Table 1. The same phenomenon is found in other studies^[21-22]. There is small fluctuation of energy near the middle of zigzag graphene nanoribbon, which is reasonable due to pseudo-periodicity at the center area of the nanoribbon.

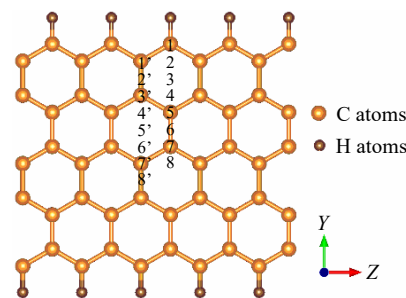
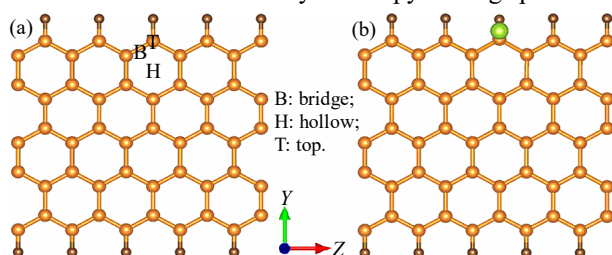


Fig. 1 The 1~8 and 1'~8' adsorption positions on ZGNRs

Table 1 Energy of the 1~8 and 1'~8' adsorption positions on ZGNRs eV

Position	Energy	Position	Energy	Position	Energy
1	-497.17	7	-496.21	5'	-495.07
2	-496.49	8	-495.86	6'	-495.86
3	-495.48	1'	-496.39	7'	-496.21
4	-495.96	2'	-496.07	8'	-495.95
5	-496.20	3'	-496.39		
6	-495.95	4'	-495.96		

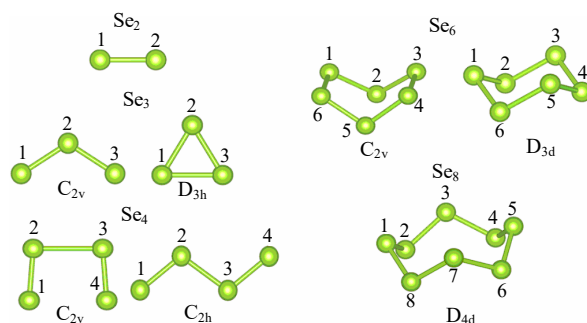
To further confirm that the edge site is the preferred location for Se adsorption, three different sites of Se adatom near the edge are taken into calculation again. As shown in Fig. 2(a), the bridge site refers to the midpoint position between two nearest-neighbor carbon atoms, the hollow site indicates the center of a carbon ring, and the top site represents the top of one carbon atom. After optimization, the selenium atom moves from the above considered three sites to the site between carbon and hydrogen atom near edge, as shown in Fig. 2(b). The adsorption energy is -1.78 eV and the distance between Se and the nearest carbon atom is 0.201 nm. Thus, we are able to reconfirm that the edge site is the most energetically favorable, meaning that single selenium atom is more likely to occupy the edge position.

**Fig. 2** Three high symmetry adsorption positions (a) and fully relaxed configuration of one Se adsorption on ZGNRs (b)

3.2 Se clusters adsorption on ZGNRs

The structures of selenium clusters on ZGNRs are then investigated. Eight cluster structures shown in Fig. 3, including Se_2 , C_{2v} and D_{3h} structures of Se_3 , C_{2v} and C_{2h} structures of Se_4 , C_{2v} and D_{3d} structures of Se_6 , and D_{4d} structure of Se_8 , are selected as adsorption models, which are comparable to the possible structures of Se_3 , Se_4 , Se_5 , Se_6 , Se_7 and Se_8 calculated by Hohl et al^[23] and

Li et al^[24]. In this work, the bond length and energy of selenium dimer are 0.220 nm and -5.29 eV, respectively. The bond length is in good agreement with the experimental results of 0.217 nm^[24-25]. Se_3 includes nearly degenerate (D_{3h}) and open (C_{2v}) structures. The bond lengths are 0.223 and 0.238 nm in C_{2v} and D_{3h} structures, respectively. The C_{2v} structure shows a slightly lower energy (-9.16 eV) than the D_{3h} structure (-9.06 eV). Se_4 has open (C_{2v}) and zigzag (C_{2h}) structures. The energy of C_{2v} (-12.96 eV) is again lower than C_{2h} structure (-12.62 eV). As for Se_6 , it has the symmetrical structures of C_{2v} and D_{3d} with D_{3d} showing higher stability (-20.71 eV) than C_{2v} (-20.31 eV). The D_{4d} structure of Se_8 , showing a bond length of 0.235 nm and angle of 109° , is well consistent with the experimental data^[26] and Hohl's data^[23]. All data and structural models are presented in Fig. 3 and Table 2.

**Fig. 3** Optimized structure of selenium clusters**Table 2** Bond length d , bond angles α and total energy E of Se clusters

Se cluster	d/nm	$\alpha/^\circ$	E/eV
Se_2	0.220		-5.29
$\text{Se}_3(\text{C}_{2v})$	0.223	115.3	-9.16
$\text{Se}_3(\text{D}_{3h})$	0.238	60	-9.06
$\text{Se}_4(\text{C}_{2v})$	$0.219(d_{12}, d_{34}),$ $0.268(d_{23})$	94.2	-12.96
$\text{Se}_4(\text{C}_{2h})$	$0.222(d_{12}, d_{34}),$ $0.241(d_{23})$	109	-12.62
$\text{Se}_6(\text{C}_{2v})$	$0.232(d_{12}, d_{23}, d_{45}, d_{56}),$ $0.251(d_{34}, d_{16})$	$99.9(\alpha_1, \alpha_3, \alpha_4, \alpha_6),$ $106.5(\alpha_2, \alpha_5)$	-20.31
$\text{Se}_6(\text{D}_{3d})$	0.236	102	-20.71
$\text{Se}_8(\text{D}_{4d})$	0.235	109	-28.14

Notes: d_{ij} is bond length between atoms i and j , α_i is bond angles at atom i .

The difference between ours and Hohl's work lies in the C_{2v} structure of Se_4 . The structure is built according to Hohl's parameters and the optimization leads to an angle of only 94.2° , which is same as Pan's data^[27], while the angle of the Hohl's data is 102° . Here we choose to use the C_{2v} structure of Se_4 obtained from our calculations. By comparing energy values of Se clusters, the most stable structures include Se_2 , C_{2v} structure for Se_3 , C_{2v} structure for Se_4 , D_{3d} structure for Se_6 , and D_{4h} structure for Se_8 .

After that, the above-mentioned stable structures of selenium clusters are placed at three highly symmetric point shown in Fig. 2(a) on the surface of ZGNRs. Generally, there are two adsorption forms of clusters on ZGNRs. The first form is parallel to ZGNRs, called "sleep-mode", and the second form is perpendicular to ZGNRs, named as "stand-mode". In both modes, geometric centers of selenium clusters are regarded as a point tentatively adsorbed on three different positions of edge sites. Thus, 30 types of adsorption structures are built as initial guesses. After full relaxation, five most stable structures are obtained, as shown in Fig. 4.

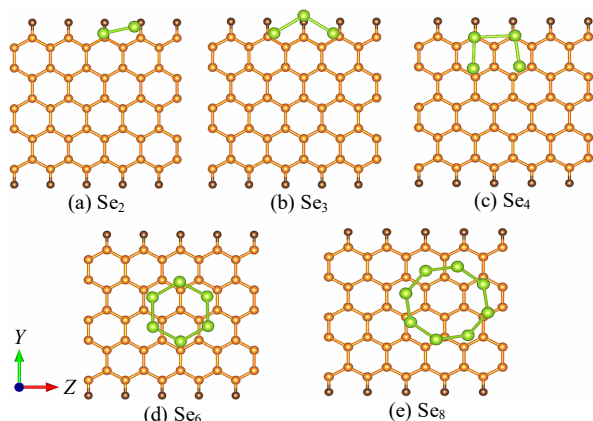


Fig. 4 The most stable structures of Se_n adsorbed on pristine ZGNRs

To better understand the changes before and after adsorption, the comparisons of structure parameters, including bond length between selenium (d_{Se-Se}), nearest distance between selenium and carbon (d_{Se-C}) and the angle of C-Se-C (θ_{C-Se-C}), are listed in Table 3. For $n < 4$ in $Se_n@ZGNRs$ system, the small distance between Se and nearest C may confirm that the two types of atom

may form covalent bond. However, Se_n ($n \geq 4$) clusters bind weakly with the ZGNRs by van der Waals forces, which may be related to lower adsorption energy. As to the energy, the adsorption energies show decrease tendency with cluster size increasing.

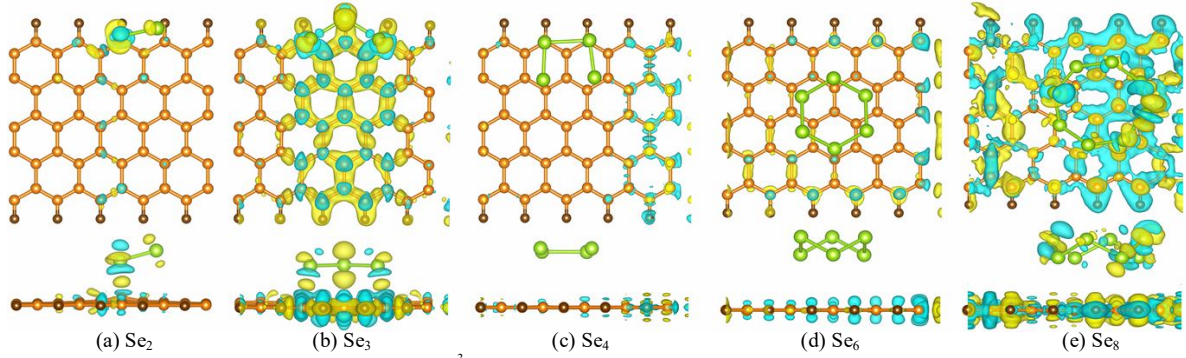
Table 3 Initial site including cluster form and structure parameters of Se_n on ZGNRs

Structure	Initial site	$d_{Se-Se}/$ nm	$d_{Se-C}/$ nm	$\theta_{C-Se-C}/$ ($^\circ$)	$E_{ads}/$ eV
ZGNRs- Se_2	sleep-B	0.224	0.221	30.2	-1.30
ZGNRs- Se_3	stand-H	0.235	0.221	30.2	-0.93
ZGNRs- Se_4	sleep-B	0.220	0.324	22.9	-0.58
ZGNRs- Se_6	stand-H	0.237	>0.3	—	-0.53
ZGNRs- Se_8	sleep-T	0.236	>0.3	—	-0.66

To further understand the interaction between Se_n clusters and ZGNRs, we compute the distribution of charge by calculating charge density difference. The charge distribution is calculated based on the formula:

$$\Delta\rho = \rho_{Se_n@ZGNRs} - \rho_{ZGNRs} - \rho_{Se_n}, \quad (2)$$

where $\rho_{Se_n@ZGNRs}$, ρ_{ZGNRs} and ρ_{Se_n} are the charge distributions of the Se_n clusters adsorbed on ZGNRs, the isolated ZGNRs and isolated Se_n , respectively. In Fig. 5(a~b), the increase and decrease of charge is distributed between the cluster and graphene for $n < 4$ in $Se_n@ZGNRs$ system. This is a common characteristic of the typical covalent bond. Shared electronic pair provides the binding of the clusters and ZGNRs. In Fig. 5(c~e), there is no charge distribution between Se_n clusters and ZGNRs, which shows that there is no covalent bond or ionic bond formation, which can be regarded as a sign for the van der Waals force between clusters and ZGNRs. This result is consistent with the result obtained by distance and adsorption energy. The interaction between Se_n clusters and ZGNRs is mainly caused by the dispersion force. As the number of selenium atoms increases, the interaction between Se_n and ZGNRs becomes stronger, so there is more charge density displayed on ZGNRs^[28]. In summary, clusters with less than four selenium atoms are chemically adsorbed on ZGNRs, while greater than or equal to four atoms are both physically adsorbed.



The value of rendering the isosurface is $33.6 \text{ e} \cdot \text{nm}^{-3}$. Yellow and blue correspond to charge increase and charge decrease, respectively.

Fig. 5 The charge redistributions by calculating charge density difference for $\text{Se}_n\text{@ZGNRs}$ in the side and top views

3.3 Theoretical capacity of lithium storage

The theoretical lithium-storage capacity calculations based on a single Se atom and Se dimer on ZGNRs are performed. The lithium atom and selenium atom form clusters are denoted as Li_xSe and Li_xSe_2 . The selenium atom is adsorbed on the edges of ZGNRs, which results in selenium atoms with strong edge states, with larger electron density and high activity^[29]. Moreover, the lithium atom is also more likely adsorbed on the hollow site at the edge of ZGNRs^[21,30]. Thus, Li atom is initially placed on top of the hollow site or functional group (between a hydrogen atom and a near-neighbor hydrogen atom) around the selenium atom at the edge site. The theoretical capacity is determined by calculating its lithiation voltages with respect to the potential of Li/Li^+ at various stages of lithiation using the following formula^[30]:

$$V_x = -\frac{E_{\text{Li}_x\text{Se}_n\text{@ZGNRs}} - E_{\text{Li}_{x-1}\text{Se}_n\text{@ZGNRs}} - \mu_{\text{Li}}}{\Delta x}, \quad (3)$$

where $E_{\text{Li}_x\text{Se}_n\text{@ZGNRs}}$ presents the total energy of selenium clusters adsorbed on the edge of ZGNRs with x Li atoms adsorbed. The chemical potential of Li, μ_{Li} is approximated by the energy of per atom in bulk Li. Δx means the number of Li atoms increased ($\Delta x=1$ here). When the lithiation potential V_x is bigger than zero, it is energetically favorable for the lithium atom to bond with the selenium clusters, and resulting in forming a stable compound (Li_xSe_n) on the edge of ZGNRs. When the lithiation potential becomes negative, the lithium atoms will begin to precipitate, resulting in the formation of lithium dendrites. Therefore, the achievable capacity

limit represents the maximum lithium content (x) that should keep the lithiation potential positive.

Fig. 6 shows optimized structure of Li_xSe clusters adsorbed on ZGNRs, as expected, the adsorption of Li atom occurs at the edge of ZGNRs. In Fig. 6(a), one single Li atom strongly prefers to occupy the hollow site at the edge of ZGNRs, similar to graphene^[31] and ZGNRs^[21,30].

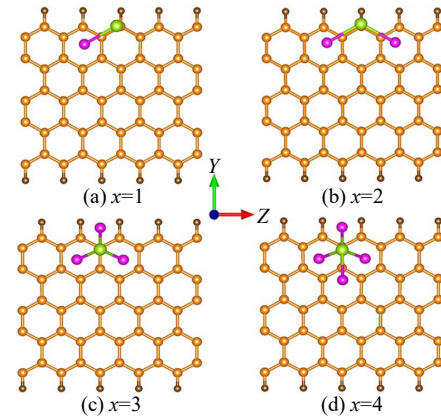


Fig. 6 Optimized structures of Li_xSe adsorbed on ZGNRs

The binding energy is obtained by:

$$E_b = -(E_{\text{Li}_x\text{Se}_n\text{@ZGNRs}} - E_{\text{Se}_n\text{@ZGNRs}} - xE_{\text{Li}}) / x, \quad (4)$$

where $E_{\text{Li}_x\text{Se}_n\text{@ZGNRs}}$, $E_{\text{Se}_n\text{@ZGNRs}}$ and E_{Li} are the total energy of Se_n clusters adsorbed on the edge of ZGNRs with x Li atoms adsorbed, Se_n clusters adsorbed on ZGNRs and isolated Li atom. In Table 4, some structural parameters of Li_xSe adsorption on ZGNRs, such as distances among Se, Li and the nearest-neighbor C ($d_{\text{Se-Li}}$, $d_{\text{Li-C}}$, $d_{\text{Se-C}}$), angle between selenium atom and nearest and second nearest neighbors ($\theta_{\text{C-Se-C}}$), and the binding energy of Li have been listed. Comparing $d_{\text{Se-C}}$, and $\theta_{\text{C-Se-C}}$ in Table 4, we find that the height of

selenium atom has increased, which indicates that the introduction of Li atom leads to the weakness of the bond between the selenium atom and ZGNRs. Thus, the interaction between Se and ZGNRs becomes weaker after Li adsorption. The Li atoms adsorption also affects the selenium-ZGNRs system. The distance Se-C increases and the binding energy of Li is decreased with the number of adsorbed Li atoms increasing. And the distance of Se atom will be further away from the ZGNRs, which means that the interaction between Se and ZGNRs is further weakened. But the distance between Li and Se is observed to be closer, which shows that the interaction between Li and Se will be stronger. To explain from the formation of bonds, due to the increase of Li atom, the C-Se bond is gradually broken, while the Li-Se bond will strengthen, which is more conducive to the formation of Li-Se clusters. The binding energy of a Li atom is 1.91 eV, which is larger than 1.55 eV in the previous work for the absence of selenium atom^[21]. This may be because the Li-Se interaction is stronger than Se-C interaction. The theoretical capacity of Li in the selenium-ZGNRs system is 4, reflected in the solid line in Fig. 7, while the theoretical capacity of Li on pristine ZGNRs was 1 in previous work^[30]. It is clear that selenium atom adsorption on ZGNRs is beneficial to increase the theoretical capacity of Li.

Table 4 Structural parameters of Li_xSe adsorbed on ZGNRs

x	$d_{\text{Se-Li}}/\text{nm}$	$d_{\text{Li-C}}/\text{nm}$	$d_{\text{Se-C}}/\text{nm}$	$\theta_{\text{C-Se-C}}/(^{\circ})$	E_b/eV
1	0.248	0.234	0.205	31.9	1.91
2	0.258	0.222	0.208	30.7	1.64
3	0.234	0.233	0.372	20.9	1.53
4	0.227	0.477	0.376	21.5	1.33

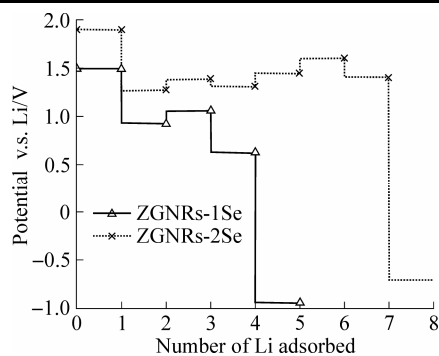


Fig. 7 The calculated lithiation potential of $\text{Se}_1/\text{Se}_2/\text{ZGNRs}$

We further calculate the lithium capacity of Se_2/ZGNRs system. The optimized structures of Li_x on Se_2/ZGNRs are shown in Fig. 8. Meanwhile, the relevant parameters are also listed in the Table 5. Compared to the case of Se/ZGNRs , the theoretical capacity of Li becomes bigger after adding one selenium atom, the value is 7, as shown in dotted line in Fig. 7. As the number of Li atoms increases, the distance becomes larger and the interaction becomes smaller between the two selenium atoms, corresponding to dissociation of the dimer into single Se atoms when interacting with surrounding Li atoms. This phenomenon implies that Li_xSe_2 is not as stable as Li_xSe adsorbed on ZGNRs. Therefore, better capacity in electrodes may be obtained in the single Se-graphene systems. These results may provide new clues for improving the performance of Li-Se batteries.

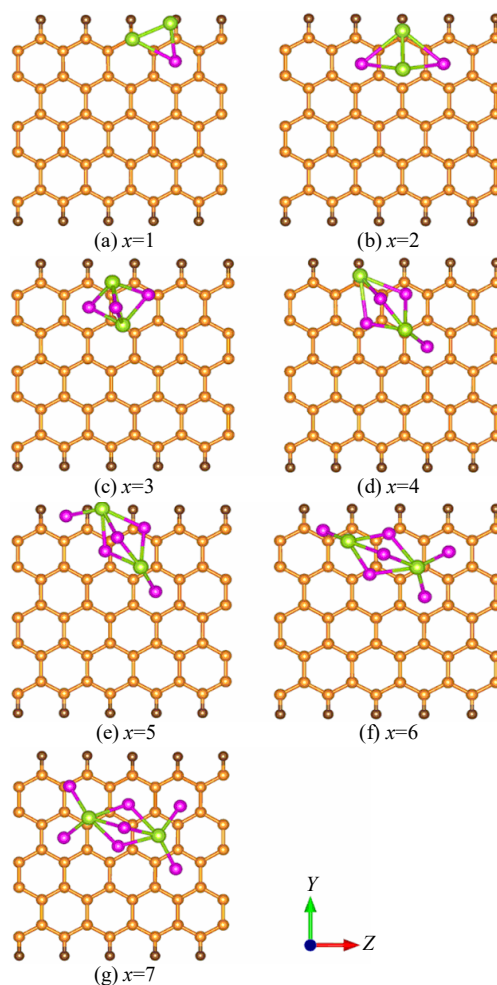


Fig. 8 Optimized structures of Li_x on Se_2/ZGNRs

Table 5 The structural parameters of Li_x on Se_2 @ZGNRs

x	d/nm						E_b/eV
	Se1-Li	Se2-Li	Li-C	Se1-C	Se2-C	Se1-Se2	
1	0.247	0.273	0.232	0.356	0.219	0.232	1.90
2	0.257	0.257	0.227	0.361	0.213	0.236	1.58
3	0.241	0.241	0.576	0.365	0.385	0.248	1.52
4	0.237	0.541	0.240	0.375	0.208	0.403	1.47
5	0.520	0.235	0.233	0.425	0.349	0.389	1.46
6	0.244	0.551	0.228	0.354	0.390	0.384	1.48
7	0.536	0.241	0.232	0.359	0.358	0.391	1.47

4 Conclusion

In summary, the structures of selenium and selenium clusters absorbed on zigzag graphene nanoribbons are studied and the atomic lithium capacities of Se_1/Se_2 @ZGRNs are explored by DFT computation. The results show that a single selenium atom is more easily adsorbed on the edge of ZGNRs, i.e., the C-H bridge site. The selenium atom in Se_n ($n < 4$) clusters are covalently bonded with ZGNRs, while the interaction between Se_n ($n \geq 4$) and ZGNRs is mainly stabilized by the van der Waals force. It is also found the insertion of lithium may increase the distance between selenium atom and ZGNRs. The Li_xSe and Li_xSe_2 clusters adsorbed on ZGNRs show maximum capacity values of 4 and 7, respectively. As the number of Li atoms increases, the interaction between selenium atoms decreases and atomized Se may bring higher capacity than clustered Se in ZGNRs. Our results may provide new clue on the performance improvement of the selenium-ZGNRs as cathode material in lithium-selenium battery.

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锯齿型石墨烯纳米带用于锂硒正极材料性能的第一性原理研究

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摘要: 硒-石墨烯体系是一种新型的锂离子电池正极材料, 引起了广泛的关注. 通过第一性原理的计算, 发现单个 Se 原子和 Se_n ($n=2,3,4,6,8$) 团簇都更偏向于吸附在锯齿型石墨烯纳米带(ZGNRs)的边缘位置. 此外, 研究了锂吸附在 Se_n@ZGNRs ($n=1,2$) 上的理论容量. Se₁@ZGNRs 系统显现出比 Se₂@ZGNRs 更好的容量. 本文不仅从理论上阐述了 Li、Se 原子与 ZGNRs 之间的吸附行为, 而且从 Se 原子数的角度出发, 为提高锂硒正极材料的性能提供了新的策略.

关键词: 第一性原理; 硒; 锯齿型石墨烯纳米带; 锂硒电池

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