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First-principles insight into Li and Na ion storage in graphene oxide*

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The structural, electronic, and adsorption properties of Li/Na ions on graphene decorated by epoxy groups are investigated by first-principles calculations based on density functional theory. Our results show that the concentration of epoxy groups remarkably affects the structural and electronic properties of graphene. The bandgaps change monotonically from 0.16 eV to 3.35 eV when the O coverage increases from 12.5% to 50% (O/C ratio). Furthermore, the highest lithiation potential of 2.714 V is obtained for the case of graphene oxide (GO) with 37.5 % O coverage, while the highest sodiation potential is 1.503 V for GO with 12.5% O coverage. This clearly demonstrates that the concentration of epoxy groups has different effects on Li and Na storage in GO. Our results provide a new insight into enhancing the Li and Na storage by tuning the concentration of epoxy groups on GO.

Keywords: graphene oxide, lithiation potential, sodiation potential, first-principles

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1. Introduction

Graphene, a monolayer of honeycomb carbon with sp^2 hybridization, has attracted intensive attention since its discovery in 2004[1,2] because of its fascinating electrical, mechanical, and thermal properties and potential applications in many technological fields such as nanoelectronics, sensors, nanocomposites, batteries, supercapacitors, and hydrogen storage.[3–7] However, the large-scale production of pure graphene sheets remains challenging. Graphene oxide (GO) is a promising, low-cost, and easily up-scalable candidate precursor to prepare graphene platelets.[8,9] At the same time, GO has different compositions with various oxidation levels based on the synthesis processes and conditions,[10–14] and thus shows great potential in different fields, such as two-dimensional electronics[15,16] and optoelectronics,[17] sensor devices,[18,19] and supercapacitor electrodes in energy storage.[20] Although the exact structures of GO remain unresolved,[21,22] it is well accepted that the main functional groups on GO are epoxy and hydroxyl groups.[23,24] GO has different functional groups with various oxygen densities, which is currently of particular interest to scientists.[25–33]

It is still a major challenge for energy storage to meet the demand of a consistent power supply, both in portable devices and in larger devices like electric vehicles, backup inverters, and so on. Traditional Li-ion battery technology (developed in 1990s) has been widely used due to its high operating potential, long life, and relatively simple design.[34] However, the electrochemical capacity of the graphite negative electrode of Li-ion batteries is relatively low, and has already reached its theoretical gravimetric capacity of approximately 372 $mA{\cdot}h{\cdot}g^{-1}$.[35] Therefore, new electrode materials that can offer high gravimetric capacity with cycling efficiency comparable to graphite are under investigation.[36–38] Recently, much attention has been paid to enhance the capacities of anodes as well as cathodes using carbon-based materials,[39–43] like oxidized graphene with epoxy as a promising sustainable carbonaceous cathode material for rechargeable Li storage with a high capacity of 360.4 $mA{\cdot}h{\cdot}g^{-1}$ at 50 $mA{\cdot}g^{-1}$.[42] Chouhan *et al.* found GO sheets as an anode material with a high specific capacity of $\sim$ 860 $mA{\cdot}h{\cdot}g^{-1}$.[43] Moreover, GO as an anode material in Na-ion batteries has shown a discharge capacity of 272 $mA{\cdot}h{\cdot}g^{-1}$ at a current density of 50 $mA{\cdot}g^{-1}$,[44] which paves a new path to obtaining high-performance and low-cost Na-ion batteries. However, the electrochemical characteristics of GO with different epoxy concentrations as an electrode material in Li and Na storage are still unclear. Thus, in this work, the structural, electronic, and adsorption properties of Li/Na ions on GO with an epoxy group are systematically studied by first-principles calculations.

2. Methodology

All the calculations in the present work were performed using the Vienna *ab initio* simulation package[45,46] with the projector augmented wave[47,48] method. The Perdew and Wang functional (PW91) with generalized gradient approximation was employed to describe the exchange correlation interactions.[49,50] The cut-off of the plane-wave kinetic energy was set to be 520 eV. The energy and ionic force convergence tolerances were 10^{-4} eV and 0.01 $eV{\cdot}Å^{-1}$, respectively, which achieve a sufficiently high accuracy.[31,51] Brillouin

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zone integrations were approximated by using $21 \times 21 \times 1$ and $25 \times 25 \times 1$ k-point meshes with a Γ centered grid for geometry optimizations and static calculations, respectively. Using these parameters, we obtain a C–C bond length of 1.42 Å for pristine graphene, which agrees well with the experiments.[52]

The 2×2 graphene, including eight C atoms with one or more epoxy groups, was used to model different degrees of single-side oxidation (see Fig. 1). In addition, to avoid the spurious coupling effect between periodic graphene layers along the z direction, the vacuum space was set to be 20 Å. For the case of Li atom adsorption on the same side of epoxy groups, the single Li atom was initially put at the hollow site nearest the O atom, and the Li–O bond length was set to be about 1.70 Å. The model of Na-adsorbed GO is similar to that of Li-adsorbed GO because of the similarity of Na and Li. Based on the Li-adsorbed GO model, we obtained Li–O bond lengths of 1.86 Å for the GO sheet with O coverage of 12.5%, agreeing well with the theoretical results and experimental observations.[42,53] In this work, the formation energy ($E_{\rm f}$) and the lithiation potential (LP) as a function of the O concentration in epoxy functionalized graphene have been calculated. The LP can be determined by the following equation:

$$\mathrm{LP} = -\frac{\Delta G_{\rm f}}{zF}, \tag{1}$$

where z is the number of electrons involved in the electrochemical reaction, and F is the Faraday constant. The change in Gibb's free energy is

$$\Delta G_{\rm f} = \Delta E_{\rm f} + P\Delta V_{\rm f} - T\Delta S_{\rm f}. \tag{2}$$

At room temperature, the volume effects ($P\Delta V_{\rm f}$) and entropic effects ($T\Delta S_{\rm f}$) will be very small, and are in the order of 10^{-5} eV and 26 meV, respectively.[51,53,54] Therefore, the entropy and pressure terms can be neglected and the change in free energy will be approximately equal to the change in formation energy $\Delta E_{\rm f}$ that is obtained from density functional theory calculations. The change in formation energy is defined as

$$\Delta E_{\rm f} = E_{\mathrm{Li}_x\mathrm{GO}} - (xE_{\rm Li} + E_{\rm GO}), \tag{3}$$

where $E_{\mathrm{Li}_x\mathrm{GO}}$ is the total energy of the Li_xGO structure, and x is the number of Li atoms inserted in the computational cell. $E_{\rm Li}$ is the total energy of a single Li atom in the body centered cubic (bcc) structure, and $E_{\rm GO}$ is the total energy of the substrate GO structure. If the energies are expressed in units of eV, the potential of the Li_xGO structures versus Li/Li+ as a function of Li content can be obtained as follows:[51,53]

$$\mathrm{LP} = -\frac{\Delta E_{\rm f}}{xe}, \tag{4}$$

where e is the electron charge.

Similarly, the sodiation potential (NP) of the Na atom over the GO is calculated as follows:

$$\mathrm{NP} = -\frac{\Delta E_{\rm f(Na)}}{xe}, \tag{5}$$

where x is the number of Na atoms inserted in the computational cell. $\Delta E_{\rm f(Na)}$ is the formation energy, which is defined as

$$\Delta E_{\rm f(Na)} = E_{\mathrm{Na}_x\mathrm{GO}} - (xE_{\rm Na} + E_{\rm GO}), \tag{6}$$

where $E_{\mathrm{Na}_x\mathrm{GO}}$ is the total energy of the Na_xGO structure, $E_{\rm Na}$ is the total energy of a single Na atom in bcc metallic Na, and $E_{\rm GO}$ is the total energy of the GO structure.

3. Results and discussion

3.1. Structural and electronic properties of GO

First, the geometries of GO are investigated. In the present calculations, four different oxidation levels are considered: 12.5% (C_8O_1), 25% (C_8O_2), 37.5% (C_8O_3), and 50% (C_8O_4). Figure 1 shows the most stable configuration at each oxidation level. As shown in Fig. 1, the adsorbed O atoms prefer the bridge positions between two C atoms to form epoxy bonds (C–O–C). The O–C bond lengths are 1.475 Å, 1.459 Å, 1.444/1.443 Å, and 1.434 Å, respectively (as shown in Figs. 1(a)–1(d)). The O–C bond length decreases monotonically with the increase in O coverage, which is similar to the result of Ref. [55]. It can be seen that the O/C ratio has an important influence on the geometric structure of GO. The corresponding structural parameters of the GO with different O/C ratios are listed in Table 1. From Table 1, we can see that the distance between two C atoms bonding to an O atom ($d_{\rm C-C}$) is a non-monotonic function of the O/C ratio. The shortest $d_{\rm C-C}$ is 1.474 Å, corresponding to the O/C ratio of 25%. This result is different from the previous theoretical studies, where two O atoms adsorbed on the opposite sides of the graphene form two epoxide groups.[55]

Next, we calculate the formation energies of GO with different O/C ratios. The formation energy is defined as[25]

$$E_{\rm f} = E_{\rm tot} - (E_{\rm G} + nE_{\rm O}), \tag{7}$$

where $E_{\rm tot}$ is the total energy of the graphene sheet with O atoms, $E_{\rm G}$ is the total energy of the graphene sheet, $E_{\rm O}$ is the energy of an isolated O atom, and n is the number of O atoms.

The calculated formation energies of GO with O/C ratios of 12.5%, 25%, 37.5%, and 50% are listed in Table 1, and are −3.907 eV, −4.363 eV, −4.453 eV, and −4.637 eV, respectively. It is found that the formation energies of GO sheets decrease with increasing O/C ratio, which agrees well with a previous report.[55]

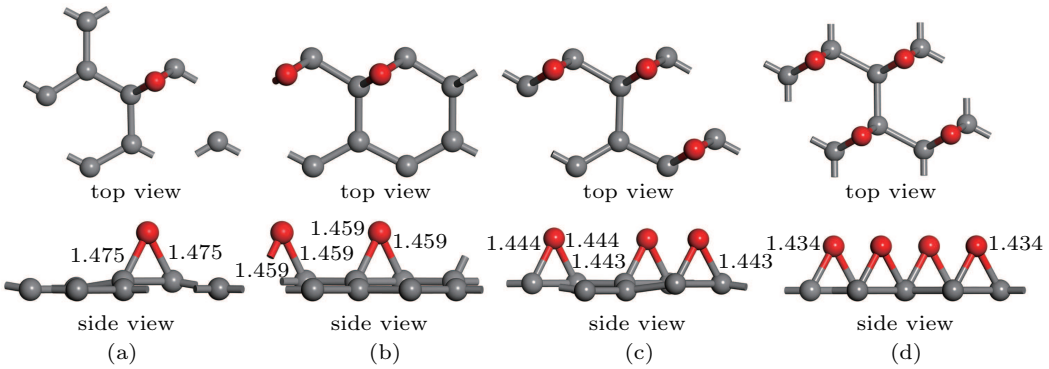


Fig. 1. Relaxed configurations of GO with epoxy groups with different O/C ratios: (a) 12.5% (C_8O_1), (b) 25% (C_8O_2), (c) 37.5% (C_8O_3), and (d) 50% (C_8O_4). Grey spheres represent C atoms, and red spheres represent O atoms.

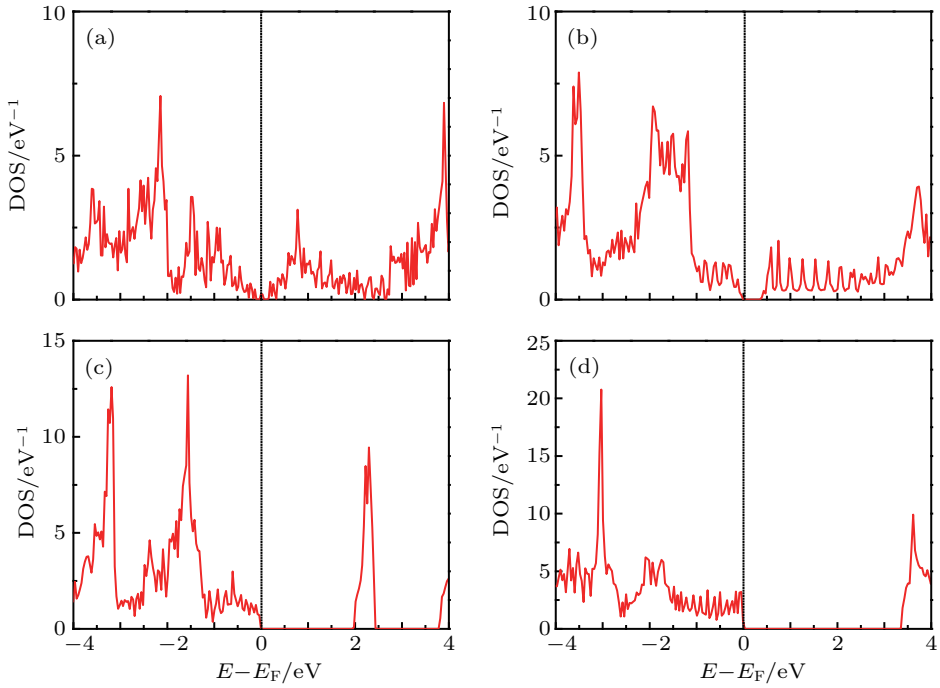


Fig. 2. Total DOS of GO with O coverages of (a) 12.5% (C_8O_1), (b) 25% (C_8O_2), (c) 37.5% (C_8O_3), and (d) 50% (C_8O_4). The Fermi levels are set to zero.

The electronic properties of GO with epoxide groups were also investigated. Figure 2 shows the calculated density of states (DOS) of GO with different O/C ratios. It shows that the DOS of GO is essentially sensitive to the O/C ratio. From Fig. 2, we can see that the bandgap increases monotonically from 0.16 eV to 3.35 eV (listed in Table 1) with increasing O/C ratio, which is similar to the result of Ref. [55]. However, the result of 0.16 eV at the O/C ratio of 12.5% is obviously far below 0.87 eV in Ref. [9], and the result of 0.39 eV at 25% O coverage is in disagreement with the 1.25 eV reported in Ref. [55]. This result may be caused by O atoms absorbed on both sides of the graphene plane in Ref. [55]. Therefore, the effect of O coverage on the electronic properties of GO can be neglected when the O/C ratio of GO is below or equal to 25%.

As for the case of GO with a higher than 25% (37.5% and 50%) O/C ratio, the bandgaps (1.98 eV at the 37.5% O/C ratio and 3.35 eV at the 50% O/C ratio) are obviously increased. These results are in line with previous results at the 50% O/C ratio (3.93 eV in Ref. [25], 3.14 eV in Ref. [31], 3.54 eV in Ref. [29], and 3.24 eV in Ref. [9]).

Table 1. Calculated distance between two C atoms bonded to an O atom (d_{C-C}), C–O bond length (d_{C-O}), formation energies, and band gap energies (E_g) of GO with different O/C ratios.

	O/C	d_{C-C}/Å	d_{C-O}/Å	E_f/eV	E_g/eV
C_8O_1	12.5%	1.494	1.475(B)	–3.907	0.16
C_8O_2	25%	1.474	1.459(B), 1.459(B)	–4.363	0.39
C_8O_3	37.5%	1.471/1.513	1.443(2-B), 1.444(B)	–4.453	1.98
C_8O_4	50%	1.504	1.434(4-B)	–4.637	3.35

3.2. Adsorption of Li on GO

Since GO has potential application in the field of energy storage, we examined the adsorption property of Li/Na ions on the same side of the epoxy groups. First, the structural properties of Li absorption on GO are studied. Figure 3 shows the structures of Li atom adsorption on GO with different O/C ra-

tios. It is found that the binding of the O atom (nearest to the Li atom) and Li atom will break the O–C bond except for in the case of a GO sheet with an O/C ratio of 50% (Fig. 3(d)), thus making the O atom move to the top site of one of the C atoms. These results are the same as those in previous theoretical calculations[25,53] and experimental observations.[56]

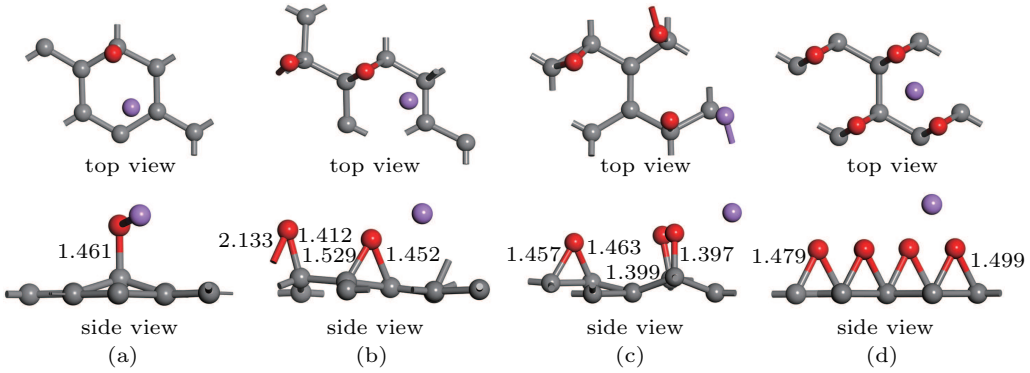


Fig. 3. Relaxed configurations of a Li atom on GO with different O/C ratios: (a) 12.5% (C_8O_1), (b) 25% (C_8O_2), (c) 37.5% (C_8O_3), and (d) 50% (C_8O_4). The grey spheres stand for C atoms, the red spheres for O atoms, and the purple spheres for Li.

To investigate the lithiation of GO for the epoxy group as a function of O coverage, we calculate the LP and gravimetric capacity of GO for different O/C ratios. The corresponding results are listed in Table 2. First, we can see that the LPs are about 1.569 V and 1.568 V, respectively, when GO sheets have low O coverage at a 12.5% O/C ratio and 25% O/C ratio. These values are consistent with a previous results: close to 1.663 V.[53] A similar LP of 1.44 V was also found by Chouhan.[43] The discrepancy of 0.13 V may be caused by the different cell size used in our calculations. We also find that the capacity decreases monotonically with the increase in O coverage. Therefore, the highest capacity is 478 mA·h·g^{-1} in the case of the 12.5% O/C ratio. Next, Table 2 shows that the LP reaches a maximum value of 2.714 V at the 37.5% O/C ratio. But in the case of the highest oxidized sheets at the 50% O/C ratio, the LP drops to −0.142 V. Our results show that the LPs increase non-monotonically with the increase in O coverage. In Table 2, we also present the relaxed structural parameters of GO–Li. The C–C bond lengths are defined as the distances between two C atoms bonded to an O atom. It is found that the longest O–Li and C–C bond lengths and the shortest C–O bond length appear in the case of the GO sheet with a 37.5% O/C ratio.

To investigate the effect of different O coverage on LP, the Bader charge of GO-adsorbed Li at different O/C ratios has been analyzed. The values of Bader charge are 0.1066*e*, 0.1163*e*, 0.1144*e*, and 0.2019*e* at different O/C ratios (12.5%, 25%, 37.5%, and 50% O/C ratio), respectively. It is shown that the Li Bader charge values are insensitive to the increase in O/C ratio except for the case of the 50% O/C ratio. At the 50% O/C ratio, the Bader charge is 0.2019*e*, which is larger than those of three other ratios, indicating that the interaction between Li and GO is weakened, and thus the LP is the lowest.

Table 2. Calculated C–C bond length (d_{C-C}), C–O bond length (d_{C-O}), O–Li bond length (d_{O-Li}), formation energies of Li adsorption on GO, LP, and gravimetric capacity for the GO with different O/C ratios.

	O/C	d_{C-C}/Å	d_{O-Li}/Å	E_f/eV	LP/V	Gravim. capacity /mA·h·g^{-1}
$C_8O_1Li_1$	12.5%	1.413–1.501	1.859	–3.455	1.569	478
$C_8O_2Li_1$	25%	1.414–1.519	1.904, 1.831	–3.454	1.568	209
$C_8O_3Li_1$	37.5%	1.393–1.548	2.205, 1.882, 1.906	–4.599	2.714	186
$C_8O_4Li_1$	50%	1.504–1.527	2.611(2), 1.854(2)	–1.744	–0.142	167

3.3. Adsorption of Na on GO

For the adsorption of Na on graphene-based materials, the previous theoretical studies were mainly concerned with the absorption of Na atoms on graphene with defects such as monovacancy, divacancy, and Stone–Wales defects.[44,57]

To confirm the influence of the epoxy groups on the Na adsorption in GO, GO with four different O/C ratios of 12.5%(C_8O_1), 25%(C_8O_2), 37.5%(C_8O_3), and 50%(C_8O_4) have been investigated. The optimized configurations of a GO-absorbed Na atom are shown in Fig. 4. Similar to the case of lithiation, the introduction of a Na atom breaks the O–C bond except for in cases of O/C ratios of 25% and 50% (Figs. 4(b) and 4(d)). Then the O atom moves to the top of the C atom, and the shortest O–C bond length arises at the O/C ratio of 37.5% (Fig. 4(c)). This result is similar to that of GO-absorbed Li.

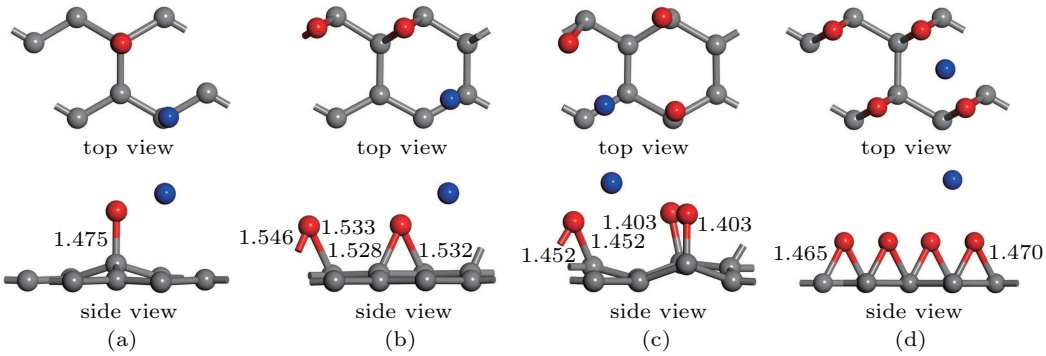


Fig. 4. Relaxed configurations of a Na atom on GO with different O/C ratios: (a) 12.5% (C_8O_1), (b) 25% (C_8O_2), (c) 37.5% (C_8O_3), and (d) 50% (C_8O_4). The grey spheres stand for C atoms, the red spheres for O atoms, and the blue spheres for Na.

Similar to Li storage in functionalized graphene, the corresponding results of Na storage in GO are listed in Table 3. First, it is found that the highest NP is 1.503 V for the GO at a 12.5% O/C ratio. With the increase in O coverage, the NP decreases. When the O/C ratio reaches 50%, the NP decreases to −0.169 V. Owing to the larger ionic radius of Na than that of Li, the distances between Na and O atoms in Na–GO structures are larger than those in the Li–GO system with all O coverages. Correspondingly, the NPs for Na storage in GO are lower than those of Li storage in GO. Typically, Na adsorption at the O/C ratio of 12.5% has the smallest formation energy (E_f) of −2.806 eV; meanwhile, Li adsorption at the O/C ratio of 37.5% obtains the smallest formation energy (E_f) of −4.599 eV. This means that the most favorable O coverage for Na adsorption on GO is different from that for Li adsorption on GO. In Table 3, we also present the relaxed structural parameters of GO–Na configurations, where the C–C bond lengths are represented by the distances between two C atoms bonding to an O atom. Furthermore, the bond lengths between O and Na atoms are larger than those between O and Li atoms. Additionally, the C–C bond length of 1.555 Å near the O atom is the longest at the 37.5% O/C ratio, which is the same as that of Li adsorption on the GO sheet. This shows that the NPs are affected by the epoxy concentration in GO–Na systems. Moreover, the NP in the range of 1.36–1.50 V in GO at 12.5%–37.5% O/C ratios agrees well with the theoretical results.[57]

Table 3. Calculated C–C bond length (d_{C-C}), O–Na bond length (d_{O-Na}), formation energies of Na adsorption on GO, NP, and gravimetric capacity for the GO with different O/C ratios.

	O/C	d_{C-C}/Å	d_{O-Na}/Å	E_f/eV	NP/V	Gravim. capacity /mA·h·g^{-1}
$C_8O_1Na_1$	12.5%	1.413–1.498	2.527	–2.806	1.503	478
$C_8O_2Na_1$	25%	1.414–1.522	2.397, 2.548	–2.665	1.363	209
$C_8O_3Na_1$	37.5%	1.395–1.555	2.267, 2.263, 2.263	–2.761	1.459	186
$C_8O_4Na_1$	50%	1.507–1.541	2.969(2), 2.316(2)	–1.133	–0.169	167

Similar to Li storage in functionalized graphene, the Bader charges of Na adsorption on GO at 12.5%, 25%, 37.5%, and 50% O/C ratios are also examined, and the results are 0.1528e, 0.1829e, 0.1551e, and 0.4696e, respectively. It is found that the Bader charge values of Na are larger than those of Li at the same O coverage. Therefore, the NPs for Na storage in GO with different O coverages are lower than those for the Li storage counterpart. It can be deduced that the Bader charge value is one significant factor affecting the LPs/NPs.

4. Conclusion

In summary, the structural, electronic, and Li/Na adsorption properties of GO with epoxy groups have been fully investigated by means of density functional calculations. It is found that the bandgaps of GO with 12.5%, 25%, 37.5%, and 50% O/C ratios are 0.16 eV, 0.39 eV, 1.98 eV, and 3.35 eV, respectively. The O–C bond lengths are 1.475 Å, 1.459 Å, 1.444/1.443 Å, and 1.434 Å, respectively, and the corresponding formation energies are −3.907 eV, −4.363 eV, −4.029 eV, and −4.637 eV, respectively. Therefore, the concentration of epoxy groups can modify the structural and electronic properties of GO. Moreover, with the moving of the O atom from the bridge site to the top site, the O–C bond length decreases monotonically for the O coverage in the range of 12.5%–37.5% in GO after one Li atom adsorption. Meanwhile, for the Na adsorption case, the O atom moving from the bridge site to the top site only occurs at an O coverage of 12.5%. Furthermore, the highest LP 2.714 V is obtained in the case of 37.5% O coverage while the highest NP is 1.503 V at the O/C ratio of 12.5%; this indicates that the O coverage in GO has a different effect on the LP/NP. The Bader charge value can well explain the LPs being higher than the NPs.

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