# First-principles studies of lithium storage in reduced graphite oxide

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## ARTICLE INFO

## ABSTRACT

The present work performs a first-principles study of the lithiation of graphite oxides with low oxygen content, which resemble reduced graphite oxide materials. The chemical nature of the Li structure formed is analysed, leading to the conclusion that the nature of lithium binding in these materials is completely different from that observed in pristine graphite. The stability of the lithium structures formed under different loadings is studied, with the finding that the lithiation potentials predicted are within the ranges of the values observed experimentally.

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## 1. Introduction

Rechargeable Li-ion batteries (LIBs) appear nowadays as promissory energy storage media for many applications, ranging from portable electronic devices up to electric vehicles (EV). However, for the more demanding applications uses such as EV and load-levelling applications, the challenge that remains is to improve the energy and power densities without increasing weight [1–5]. Therefore, a large amount of effort is being undertaken in the scientific and engineering community in the development of new electrode materials for this type of batteries.

Carbonaceous materials present a lot of advantages due to their excellent properties such as good thermal and electronic conductivity and great surface area, among others. In summary, these properties make them attractive materials for innumerable applications, particularly in the field of energy carriers, like hydrogen storage and electrochemical systems. Among the latter, the commercial anodes of Li-ion batteries are a typical example. In fact, graphite is the most commonly used carbon material in the manufacture of the anodes of Li-ion batteries, allowing Li ions to be stored up to a $LiC_6$ stoichiometry, which implies a maximum theoretical capacity of 372 mAh g$^{-1}$ [6]. Recently, materials based on carbon nanostructures such as nanotubes [7–9] and oxidized graphene nanoribbons [10] obtained by unzipping of the carbon nanotubes [11], have been shown to outperform the Li-ion storage capacity of ordinary graphitic materials. Similarly, graphene nanosheets have been found to yield a capacity of 460 mAh g$^{-1}$ for 100 cycles work [12] and in the case of disordered graphene nanosheets the reported reversible capacity has been even larger, ranging between 794 and 1054 mAh g$^{-1}$ [13]. Oxidized graphene nanoribbons have shown an initial capacity of 1400 mAh g$^{-1}$ and a reversible capacity of 800 mAh g$^{-1}$ [10]. Something similar happens with graphite oxide with different degrees of oxidation [14] and reduced graphite oxide [15]. However, up to date storage in oxidized graphitic systems has received relatively little attention in the theoretical field [16] in comparison with studies of pristine graphitic materials [17–21]. On the other hand, highly porous structures composed of carbon nanotubes or graphite oxide can be decorated with different metals (Ti, Ni, Co, Mn, V) to promote the intercalation of lithium. These experiments also indicate that it would be possible to increase the maximum ratio of 1:6 (Li:C) found for graphite. Thus, theoretical advances in the understanding of the absorption/desorption mechanism of Li$^+$ ions for the new carbon materials are critical to increase the actual performance and to acquire knowledge in the experimental limitations of the carbonaceous anode materials.

In the present work we investigate lithiation of mildly oxidized graphitic nanostructures, sometimes referred as reduced graphite oxide (RGO) [16], by means of first-principles calculations. We analyse the chemical nature of the modified carbonaceous-Li structures and consider the stability of them under different Li-loadings.

### 1.1. Methodology

#### 1.1.1. Calculation details

All DFT calculations were performed using the Quantum Espresso package [22] with Van der Waals interactions. The

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Kohn-Sham orbitals and charge density were expanded in plane-waves basis sets up to a kinetic energy cutoff of 30 and 300 Ry for all atoms respectively. Ultra soft pseudopotentials were employed with the Perdew-Wang approximation for exchange and correlation in the PW91 functional [23–25]. The application of this functional to a system closely related to the present one has been validated in a very recent article [26]. The Brillouin zone was sampled with $3 \times 3 \times 1$ irreducible Monkhorst-Pack k-point grid [27]. The convergence threshold for the total energy at each electronic calculations was set to $1 \times 10^{-6}$ Ry. Geometry optimizations were performed employing the Broyden-Fletcher-Goldfarb-Shanno (BFGS) algorithm (for stress minimization) and total forces acting on each ion were minimized to reach less than $1 \times 10^{-3}$ Ry/a.u. by movement of the ionic positions.

### 1.2. Model for reduced graphite oxide

The RGO structures were represented by means of a unit cell made of two carbon sheets of 32 C atoms each, stacked in an AB arrangement as in the case of graphite. The unit cell was tetragonal $(0.986 \times 0.854 \times c)$ $nm^3$ with periodic boundary conditions in the x,y,z coordinates and the c value was equal to twice the interlayer distance $(d)$.

In order to represent the RGO structures, different amounts of epoxy (-O-) and hydroxyl (-OH) groups were randomly arranged to represent amorphous oxides, as proposed by Liu *et al.* [28]. In the present work we consider an amorphous oxide with low oxygen content and in the ratio of 2:1 between (OH:O) functional groups, which is within the [1.06:3.25] interval of oxides most frequently observed in the experiments. The unit cell used to get the results presented here is shown in Fig. 1.

We have performed previously a complete study of the properties of this system. It is pertinent here a comment concerning the stability of RGO structures with respect to exfoliation, so that we shortly revisit here the results of our previous work. While the exfoliation energy for pristine graphite layers was 0.31 J/m$^2$, the result for the present RGO structure yielded the same value within the calculation accuracy. For structures with larger oxygen content, the exfoliation energy increased up to 1.89 J/m$^2$ [29]. The reason why graphite oxides dissolve relatively easily in aqueous solutions is to be found in the strong interaction of the oxidized surface species with the solvent via hydrogen bonds. This problem will be probably reduced in the case of nonpolar solvents.

### 1.3. The lithiation potential and specific capacity

We denominate with the term *lithiation* the process that occurs when lithium is inserted/intercalated in the active anode material, in the present case reduced graphite oxide. The lithiation potential, $V_{lit}$, can be represented by the following equation, as has been employed to characterize electrode materials by other authors [30,31]:

$$V_{lit} = -\frac{\Delta G_f}{z \cdot F} \tag{1}$$

where z is the number of electrons involved in the electrochemical reaction, here 1, and F is the Faraday constant, 96485 C/mol. The change in the formation Gibb's free energy is:

$$\Delta G_f = \Delta E_f + P\Delta V_f - T\Delta S_f \tag{2}$$

where, $\Delta E_f$, $\Delta V_f$ and $\Delta S_f$ are the internal energy change, the volume change and the entropy change of formation, respectively. P and T are the pressure and absolute temperature, respectively. Equation (1) can be straightforwardly deduced from a thermodynamic cycle where a lithium cation is taken under equilibrium conditions from a reference pure Li electrode material into a working electrode made

of the material under consideration. Since the term $P\Delta V_f$ is in the order of $10^{-5}$ eV and the entropy term is in the order of the thermal energy, $k_B T$ (that is, Boltzmann constant multiplied by the temperature, which amounts about 25 meV at 298 K), the entropy and pressure terms can be neglected in comparison with the internal energy, which is of the order of 1 to 4 eV for the different systems and we can approximate the change in the formation Gibb's energy to the internal energy $\Delta G_f \simeq \Delta E_f$ obtained from DFT calculations. The internal energy of the Li-graphite oxide compound is defined as follows:

$$\Delta E_f = E_{Li_xGO} - E_{GO} - xE_{Li} \tag{3}$$

where $E_{Li_xGO}$ is the total energy of the $Li_xGO$ structure with $x$ Li atoms intercalated, $E_{GO}$ is the total energy of a particular GO structure and $E_{Li}$ is the total energy of a single Li atom in the elemental body-centered cubic Li structure. If the energies are expressed in electron volts, the potential in volts of the $Li_xGO$ structure vs. Li$^+$/Li$^0$ as a function of lithium content can be obtained from [16]:

$$V_{Lit} = \frac{-\Delta E_f}{x \cdot e_0} \tag{4}$$

where $e_0$ is the elementary charge. The theoretical capacity of the electrodes and also that of the total battery cell is determined by the amount of active material in it. It is expressed as the total quantity of electric charge involved in the complete electrochemical reaction of the electrode material. The specific Capacity is defined as [4]:

$$C = \frac{zF}{atomic\ weight} \tag{5}$$

where atomic weight is the weight of the $Li_xGO$ structure.

## 2. Results and Discussion

### 2.1. Structural and Electronic properties of lithium absorbed in RGO

Due to their relatively low oxygen content, the RGO structures considered here present different regions, some oxidized and others resembling the pristine graphite structure. While in the latter case the carbon atoms show local $sp^2$ hybridization, in the former there is a change to $sp^3$ hybridization producing a corrugation effect in the carbon layers. We have thus considered two possibilities for the lithiation process of these structures: *a)* The Li atom is absorbed preferentially in the functionalized region (named as "Li-O") and *b)* The Li atom is absorbed in the area far away from the functionalized groups (named as "Li-C"). In *a*, the resulting lithiation potential as calculated according to equation (4) is 1.12 V and in *b* it is 0.13 V. It is remarkable that for the structure where de Li atom is near the non-functionalized section, the lithiation potential is very similar to the intercalation potential of Li in pristine graphite, as it is found in experiments [32], while for the Li-O structure the potential is much higher. In order to determine the relative stability of the different structures when more lithium ions are introduced in the RGO structure, we calculated the binding energy ($E_b$) per Li atom as follows:

$$E_b = \frac{E_{Li_xGO} - E_{GO} - xE_{Li,vac}}{x} \tag{6}$$

where $E_{Li,vac}$ is the total energy of a single Li atom in vacuum. The Li atom presented a binding energy of −1.60 eV in the Li-C structure and −2.59 eV in the Li-O structure. This means that absorption of the Li atom is much more favourable close to the oxygen functional groups than near the carbon atoms in the pristine graphite. To elucidate the chemical nature of this phenomenon, we calculated the electronic density differences between the electron densities of the