Lithium incorporation at the MoS$_2$/graphene interface: an *ab initio* investigation

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Abstract

Based on *ab initio* calculations, we examine the incorporation of Li atoms in the MoS$_2$/graphene interface. We find that the intercalated Li atoms are energetically more stable than Li atoms adsorbed on the MoS$_2$ surface. The intercalated atoms interact with both graphene sheet and MoS$_2$ layer, increasing the Li binding energies. However, the equilibrium geometries are ruled by the MoS$_2$ layer, where the intercalated Li atoms lie on the top (Li$_T$) and hollow (Li$_H$) sites of the MoS$_2$ layer. We calculate the Li diffusion barriers, along the Li$_T$ $\rightarrow$ Li$_H$ diffusion path, where we find similar energy barriers compared with that obtained for Li adatoms on the MoS$_2$ surface. Our results allow us to infer that the Li storage capacity increases at MoS$_2$/G interfaces, in comparison with Li adatoms on the MoS$_2$ surface—however, with no reduction on the mobility of the intercalated Li atoms. Those properties are interesting/useful to the development of Li batteries based on MoS$_2$.

(Some figures may appear in colour only in the online journal)

Two-dimensional (2D) materials have attracted numerous studies addressing technological applications as well as fundamental science. In the past few years, graphene has been the subject of the majority of studies in those 2D systems [1, 2]. Indeed, graphene exhibits a strong technological appeal mainly due to the development of new electronic nano-devices [3]. On the other hand, (recently) other 2D layered structures, composed of few atoms, have been considered as interesting/promising materials for several applications: in particular, molybdenum di-sulfide (MoS$_2$) for the development of electronic devices [4–6], and Li batteries (LIBs) [7]. MoS$_2$ is a hexagonal layered structure, in which each layer is composed by S–Mo–S atoms covalently bonded, stacked along the [0001] direction, while the layer–layer interaction is weak, mediated by van der Waals (vdW) forces. Such layered structure promotes the intercalation of Li ions.

Very recently, epitaxial layers of MoS$_2$ have been successfully synthesized on graphene sheet [8, 9]. MoS$_2$/G, despite the large lattice mismatch between MoS$_2$ and graphene. In this case, there are no chemical bonds at the MoS$_2$/G interface, and the MoS$_2$ layers are attached to the graphene substrate through vdW interactions. Recent experimental studies indicate that MoS$_2$/G composites present a set of quite interesting/suitable electrochemical properties to the development of high performance LIBs. It has been suggested that such high performance of LIBs, based on MoS$_2$/G systems, is due to ‘synergistic effects between layered MoS2 and graphene’ [10–12]. In this work we try to clarify the rule played by those ‘synergistic effects’ to the Li incorporation in MoS$_2$/G.

We have performed a theoretical *ab initio* study of Li atoms in the MoS$_2$/G interface (MoS$_2$/Li/G). Initially we verify the energetic stability of the MoS$_2$/G interface, and then the energetic properties of Li atoms adsorbed on the MoS$_2$ surface (Li/MoS$_2$), and on the graphene sheet (Li/G). For the MoS$_2$/Li/G system, we have considered a number of different configurations for the Li atoms in the MoS$_2$/G interface region. Based on the calculation of the Li binding energies, we find an energetic preference for the MoS$_2$/Li/G system, in comparison with the Li/MoS$_2$ and Li/G configurations. The energetically stable geometries of Li atoms at the interface region are the same as those...
obtained for Li adatoms on the MoS$_2$ surface—namely, Li atoms lying on the top site (Li$_T$) aligned with the Mo atom, and on the hexagonal hole site (Li$_H$) of MoS$_2$. We find that the Li$_T$ configuration is energetically more stable than Li$_H$ by 0.1 eV for both systems, MoS$_2$/Li/G and Li/MoS$_2$, thus suggesting the same Li$_T$ $\rightarrow$ Li$_H$ jumping rate for the intercalated (MoS$_2$/Li/G) and adsorbed (Li/MoS$_2$) Li atoms. Such suggestion is supported by calculated Li diffusion barriers along the Li$_T$ $\rightarrow$ Li$_H$ diffusion path.

Our calculations were performed based on the density functional theory (DFT), within the PBE-GGA approach [13], as implemented in the SIESTA code [14]. The Kohn–Sham orbitals were expressed by a double-zeta plus polarization (DZP) basis set [15]. The MoS$_2$/G interface was described by using the slab method, composed of a monolayer of MoS$_2$, a single graphene sheet, and a vacuum region of 18 Å. In order to minimize the lattice mismatch effects between MoS$_2$ and graphene ($\sim$28%), we have considered a surface (or interface) periodicity of $7 \times 7$ and $9 \times 9$ for the MoS$_2$ and graphene, respectively. In this case, the lattice mismatch reduces to $\sim$0.6%. All the atomic positions are relaxed within a force convergence criterion of $10$ meV Å$^{-1}$.

Initially we examine the energetic stability and the equilibrium geometry of the MoS$_2$/G interface, composed of a monolayer of MoS$_2$ attached to the graphene sheet. The Mo$_2$S/G binding energy ($E^b$) was obtained by comparing the total energies of the isolated systems, MoS$_2$ and graphene ($E$[MoS$_2$] and $E$[G], respectively), and the total energy of the MoS$_2$/G (final) system, $E$(MoS$_2$/G), $E^b = E$[MoS$_2$] $+ E$[G] $- E$(MoS$_2$/G). We find that the formation of MoS$_2$/G system is an exothermic process, with $E^b$ of 21 meV/C-atom, and MoS$_2$–G the equilibrium distance ($h$) of 3.66 Å. Those results are in agreement with the recent studies performed by Ma et al. [16]. Here we confirm the experimentally verified weak interaction between the graphene sheet and the MoS$_2$ [8]. Indeed, similar weak interaction has been verified for graphene adsorbed on SiO$_2$ or HFO$_2$ [17–20]. We are aware that DFT-GGA calculations underestimate the binding energy of systems ruled by vdW interactions [21], however, we believe that the present description of the MoS$_2$/G host structure is suitable enough for our purposes in the present study.

Motivated by the recent experimental findings, aiming at the development of LIBs based on stacked layers of MoS$_2$ [7, 22, 23], the adsorption of Li atoms on the MoS$_2$ surface and Li incorporation into the MoS$_2$ bulk have been the subject of recent $ab$ initio total energy studies [24, 25]. The energetic stability of Li adatoms on the MoS$_2$ sheet was examined based on the calculation of the Li binding energy ($E^b_{Li}$),

\[ E^b_{Li} = E[Li] + E[MoS_2] - E[Li/MoS_2]. \]

$E[Li]$ and $E[MoS_2]$ represent the total energies of an isolated Li atom and the pristine MoS$_2$ monolayer, respectively, and $E[Li/MoS_2]$ represents the total energy of the Li adsorbed MoS$_2$. We have considered Li adatoms on the top (T) and hollow (H) sites of the MoS$_2$ monolayer surface (figure 1(b)). We obtained $E^b_{Li}$ of 1.95 and 1.84 eV for a Li adatom lying on the T site (Li$_T$) and H site (Li$_H$), respectively. The binding energy difference ($\Delta E^b_{Li}$) indicates that the Li$_T$ configuration is more stable than Li$_H$ by 0.11 eV. At the equilibrium geometry, the Li$_T$ adatom lies directly above one Mo atom, being three-fold coordinated with the nearest neighbor S atoms. The Li–S equilibrium bond length ($d_{LiS}$) is 2.46 Å, with a vertical distance ($h$) of 1.57 Å. On the H site, the center of the hexagonal hole of MoS$_2$, the Li$_H$ adatoms also form three Li–S bonds, with $d_{LiS} = 2.48$ Å and $h = 1.62$ Å. The calculated Li binding energies, and the equilibrium geometries are in good agreement with the recent DFT calculation performed by Li et al. [24]. The projected density of states (PDOS) of the Li$_T$ adatoms (black line in figure 1(c)) confirms the hybridization of the Li adatom on the MoS$_2$ surface. Through the integration of the PDOS, we find an electronic charge transfer of 0.42 electrons from the Li adatom to the MoS$_2$ sheet.

On the graphene sheet the Li adsorption is an exothermic process [26]. Here we obtained $E^b_{Li}$ of 1.06 eV for a Li adatom on the hollow site (figure 1(d)). At the equilibrium geometry the Li adatom lies at 1.82 Å from the graphene sheet, with $d_{LiC} = 2.33$ Å. In [26], for the same (energetically more stable) configuration, the authors obtained $E^b_{Li} = 1.10$ eV, and Li vertical distance of 1.71 Å. For both systems, Li/MoS$_2$ and Li/G, the atomic displacements of the host elements (bonded to the Li adatom) are very small, that is, the MoS$_2$ and graphene lattice structures are weakly perturbed upon the presence of Li adatoms.

Having described the Li interaction with the separated systems, Li/MoS$_2$ and Li/G, let us start our investigation of Li incorporation in MoS$_2$/G. Here we have considered two configurations, Li adatoms lying on the MoS$_2$ surface (Li/MoS$_2$/G), and Li atoms embedded in the MoS$_2$/G interface (MoS$_2$/Li/G) (figure 1(a)). In Li/MoS$_2$/G the Li adsorption energy and the equilibrium geometry are the same as those obtained for Li/MoS$_2$. This is somewhat expected, since the MoS$_2$–G interaction is weak, whereas the MoS$_2$/Li/G system exhibits a very different picture, in which the Li atoms feel the presence of the graphene sheet. That is, the Li binding energy and equilibrium geometry depends on the atomic structure around the Li atom at the MoS$_2$/G interface. Here, the energetic stability and the equilibrium geometry were mapped by considering a set of 32 different configurations of Li atoms embedded in the MoS$_2$/G interface.

Our total energy results reveal that the MoS$_2$/Li/G system is energetically more stable than Li/MoS$_2$/G (on average) by 0.41 ± 0.01 eV, thus indicating that the incorporation of Li atoms at the MoS$_2$/G interface is more likely than the Li adsorption on MoS$_2$/G or MoS$_2$ surfaces. For the MoS$_2$/Li/G system we obtained averaged binding energies ($E^b_{Li}$) of 2.36 (Li$_T$) and 2.26 ± 0.01 eV (Li$_H$). Similarly to the Li/MoS$_2$/G system, there is an energetic preference for the Li$_T$ configuration by 0.10 eV ($\Delta E^b_{Li}$). In fact, we did not find any stable or metastable configuration other than Li$_T$ and Li$_H$. In figure 2(a) we present a given structural model of MoS$_2$/Li/G where we find $E^b_{Li}$ of 2.36 (Li$_T$, figure 2(a1)), and 2.26 eV (Li$_H$, figure 2(a2)). Those results allow us to infer that the energetic stability of the Li atoms at the MoS$_2$/G
interface is ruled by the MoS$_2$ sheet. Indeed, the calculated Li binding energies of the separated systems, namely Li/G (1.06 eV) and Li/MoS$_2$ (1.95 and 1.84 eV), indicate a stronger interaction between the Li adatom and the MoS$_2$ surface. The Li–S equilibrium bond length is slightly stretched when compared with the Li/MoS$_2$/G system—we find $d_{LiS}$ between 2.49 and 2.61 Å, and vertical distances ($h$) between 1.64 and 1.77 Å. The calculated PDOS of Li$_T$ adatoms in the MoS$_2$/G interface (red line in figure 1(c)) confirms the dominant role played by the MoS$_2$ layer, since it is very similar to the PDOS obtained for Li adatoms on the MoS$_2$ surface (black line in figure 1(c)).

Despite the dominant role played by the MoS$_2$ layer, the influence of the graphene sheet, on the energetic properties of MoS$_2$/Li/G, can be verified by considering two particular geometries, namely: (i) the intercalated Li atom lying on the T site of MoS$_2$ (Li$_T$), aligned with the hollow site of graphene (figure 2(b)), and (ii) the intercalated Li atom lying on the H site of MoS$_2$, aligned with the hollow site of graphene (figure 2(c)). In (i) the Li$_T$ interaction with the MoS$_2$/G interface is strengthened, and $E^b_{Li}$ increases to 2.40 eV, while the binding energy of Li$_H$ reduces slightly to 2.24 eV, compared with the averaged values of $E^b_{Li_T}$, 2.36 and 2.26 eV, respectively. For this particular configuration—namely (i)—the total energy difference between Li$_T$ and Li$_H$, $\Delta E^b_{Li_T}$, increases to 0.16 eV.

Meanwhile, in (ii) the binding energy of Li$_H$ increases to 2.33 eV, becoming the same as that for Li$_T$, $\Delta E^b_{Li} = 0$. Those findings allow us to infer that in (i), the Li atomic jumping rate from the T to H sites (Li$_T$ → Li$_H$) will be reduced, while in (ii) Li$_T$ → Li$_H$ will be increased, when compared with the averaged MoS$_2$/Li/G configuration, where $\Delta E^b_{Li} = 0.10$ eV. Our results of Li binding energies and equilibrium geometries are summarized in table 1.

In order to get a more complete picture of Li diffusion in the MoS$_2$/Li/G system, we estimate the Li$_T$ → Li$_H$ diffusion barrier. Here, along the Li$_T$ → Li$_H$ diffusion path, the Li energy barrier was obtained by keeping fixed the Li coordinates parallel to the MoS$_2$/G interface, while both the

Table 1. Calculated binding energies ($E^b$ in eV), and the equilibrium vertical distances ($h$ in Å) of Li adatoms on the T ($E^b_T$ and $h_T$) and H ($E^b_H$ and $h_H$) sites of the MoS$_2$ surface (Li/MoS$_2$), on the graphene sheet (Li/G), and intercalated in the MoS$_2$/G interface (MoS$_2$/Li/G) for the structural models presented in figures 1(a)–(c).

| Model      | $E^b_T$ | $h_T$ | $E^b_H$ | $h_H$ |
|------------|---------|-------|---------|-------|
| Li/MoS$_2$ | 1.95    | 1.57  | 1.84    | 1.62  |
| Li/G       | 1.06    | 1.71  | —       | —     |
| Figure 1(a)| 2.36    | 1.67  | 2.26    | 1.70  |
| Figure 1(b)| 2.40    | 1.72  | 2.24    | 1.71  |
| Figure 1(c)| 2.33    | 1.64  | 2.33    | 1.77  |
Li adatom on the T site of MoS$_2$

Structural model of a given MoS$_2$ with Li adatoms on the MoS$_2$ surface is very interesting/promising system for LIBs. The Li atoms are energetically more stable at the MoS$_2$ bulk, and due to the larger diffusion barrier of Li can be attributed to the formation of Li–S chemical bonds at the interlayer regions of the graphene.

Therefore, for the most common configuration, where the intercalated Li atom lies on the T site of the MoS$_2$ layer and hollow site of the graphene, and (c) the intercalated Li atom lies on the H site of the MoS$_2$ layer and hollow site of the graphene, we find a diffusion barrier of 0.19 eV for Li adatom on the MoS$_2$ monolayer surface, in good agreement with [24]. For the particular configurations discussed above, the diffusion barrier increases to 0.23 eV in (i) (figure 3(c)), while it reduces to 0.15 eV in (ii) (figure 3(d)). Meanwhile, for the most common configuration, namely where $\Delta E_{\text{ads}}^{\text{Li}} = 0.10$ eV as depicted in figure 2(a), we find a Li diffusion barrier of 0.18 eV (figure 3(b)), i.e. practically the same as that obtained for the Li/MoS$_2$ system. Thus, we can infer that the diffusion barriers of Li atoms intercalated in the MoS$_2$/G interface are (on average) similar to the diffusion barrier verified for Li adatoms on the MoS$_2$ monolayer surface.

Li/MoS$_2$ ($\sim$1.6 Å) and Li/G (1.7 Å) systems, we find that it is smaller than the equilibrium vertical distance between the graphene sheet and the MoS$_2$ monolayer (3.66 Å), even by including the vdW interaction to describe the MoS$_2$/G interface. In this case, we find a MoS$_2$–G equilibrium vertical distance of 3.40 Å.

Aiming to provide further support to the last statement, we have performed additional calculations fixing the MoS$_2$–G vertical equilibrium distance to 3.40 Å. In this case, we find (i) $E_{\text{li}}^{\text{ads}} = 2.26$ (Li/T) and 2.16 eV (Li/H), $\Delta E_{\text{ads}}^{\text{Li}} = 0.10$ eV, and (ii) Li/T $\rightarrow$ Li/H energy barrier of 0.18 eV. Thus, (i) supports the energetic stability of Li/T embedded in the MoS$_2$/G interface, and in (ii) we find that the energy barrier of Li adatoms will be maintained upon the reduction of the MoS$_2$–G vertical distance, due to the inclusion of the vdW interaction.

In summary, based on ab initio calculations, we examined the energetic stability of Li atoms embedded in the MoS$_2$ surface. Our total energy results reveal that there is an energetic preference for Li atoms intercalated in the MoS$_2$/G interface (MoS$_2$/Li/G), when compared with Li adatoms on the MoS$_2$ surface (Li/MoS$_2$ and Li/MoS$_2$/G), thus indicating an increase on the Li storage capacity at the MoS$_2$/G interfaces, in comparison with Li adatoms on the MoS$_2$ surface. The equilibrium geometries of the Li intercalated systems are ruled by the MoS$_2$ layer, where the Li atoms lie on the T (Li/T) and H (Li/H) sites of the MoS$_2$. Although the Li atoms feel the presence of the graphene interface, the mobility of Li atoms in MoS$_2$ bulk can be enhanced by increasing the interplanar (stacking) distance between the MoS$_2$ layers. Indeed, the total energy calculation performed by Li et al [24] supports such statement. They find that the (Li/T $\rightarrow$ Li/H) energy barrier reduces from 0.49 eV in MoS$_2$ bulk to 0.21 eV in MoS$_2$ surface. The higher diffusion barrier of Li can be attributed to the formation of Li–S chemical bonds at the interlayer regions of the MoS$_2$ bulk. Within this scenario, MoS$_2$/Li/G represents a very interesting/promising system for LIBs.
sheet, on average we find similar Li$^+ \rightarrow$ LiH diffusion barriers for the MoS$_2$/Li/G and Li/MoS$_2$ systems. We can infer that, in addition to the increase on the Li storage capacity, there is no reduction on the mobility of the intercalated Li atoms, when compared with that of Li adatoms on the MoS$_2$ surface. These findings suggest that MoS$_2$/G interfaces are interesting/promising systems to the development of Li batteries based on MoS$_2$.

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