Essential Electronic Properties of Stage-1 Li/Li⁺-Graphite-Intercalation Compounds for Different Concentrations

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Abstract: We use first-principles calculations within the density functional theory (DFT) to explore the electronic properties of stage-1 Li- and Li⁺-graphite-intercalation compounds (GIC) for different concentrations of LiCₓ/Li⁺Cₓ, with x = 6, 12, 18, 24, 32 and 36. The essential properties, e.g., geometric structures, band structures and spatial charge distributions are determined by the hybridization of the orbitals, the main focus of our work. The band structures/density of states/spatial charge distributions display that Li-GIC shows a blue shift of Fermi energy just like metals, but Li⁺-GIC still remains as in the original graphite or exhibits so-called semi-metallic properties, possessing the same densities of free electrons and holes. According to these properties, we find that there exist weak but significant van der Waals interactions between interlayers of graphite, and 2s-2pₓ hybridization between Li and C. There scarcely exist strong interactions between Li⁺-C. The dominant interaction between the Li and C is 2s-2pₓ orbital-orbital coupling; the orbital-orbital coupling is not significant in the Li⁺ and C cases, but dipole-diploe coupling is.

Keywords: first-principles; graphite intercalation compounds

1. Introduction

Green energy is one of the most important issues in the world today. The limited resources, such as fossil fuels, will be consumed eventually. In addition, the concomitant environmental pollution is also inevitable. This therefore gives rise to the need for efficient storage of electrical energy. Apart from the finite resources on earth, solar power has the most potential for humans. As years passed, rechargeable batteries have emerged as a solution to the energy storage problem. Many previous theoretical and experimental studies focused on lithium batteries and lithium-ion batteries because of the low costs, high safety and long cycle life. For the most part, the anodes are composed of carbon and non-carbon materials. The former is the well-known graphite, and the latter can be lithium, sodium or other ionic clusters. This kind of anode is almost always presented as graphite-intercalation compounds (GICs), that is to say, the lithium atoms (or other atoms) are intercalated into the graphite layers.

Graphite with its layered structure is easily intercalated by alkali-metal atoms. The carbon-layered system is purely composed of a hexagonal symmetric lattice, in which there exist weak but significant van der Waals (vdW) interactions. The vdW interactions modify the low-lying energy band structures and dominate the essential physical properties of the graphite of GIC. The electronic properties strongly depend on the stacking configurations the graphitic layers. In general, there are three well known kinds of stacking configurations: AA (simple hexagonal), AB (Bernal), and ABC (rhombohedral) [1–3]. Previous studies [4] revealed that the Li-GICs and A-GICs (A stands for an alkali metal such as Na, K, Rb, or Cs)
present different structures in stage-1: LiC₆ and AC₈, respectively. Additionally, the AA-stacking configuration is the most stable one for Li-GIC of stage-1 type [5], whereas other stage-n types (n = 2,3,4 . . . ) form the AB-stacking configuration. The comparisons between Li-GICs and A-GICs have been widely discussed in the past years, but few theoretical and experimental research papers on Li-ion-GICs and alkali-ion-GICs are available. The geometric properties of Li-GICs, such as disorder on surface [6] or interlayer distances [7], have been studied for years. However, many studies exclusively focused on Li-atom intercalation/deintercalation, but ignored Li-ion cases.

In this work, we display the comparison between Li-GICs and Li⁺-GICs, and mainly focus on the orbital hybridizations in lithium and lithium-ion GICs by presenting the essential structural and electronic properties. We consider the different concentrations on the uniform situations of intercalations, i.e., this paper only covers the stage-1 type for different concentrations. In addition, the optimal adatom position is located in the hollow site [8–11] of the hexagonal carbon layers. The theoretical calculations, including the tight-binding model and DFT method [12–15], are utilized to investigate the total ground state energies, optimal geometric structures, energy band structures, density of states and the spatial charge distributions. For instance, the DFT method is used to examine the band structures and interlayer binding, finding that for any number of layers, Bernal few-layer graphenes (AB stacking) are the most stable [12]. Furthermore, the band structures predicted by DFT on ABA-stacked and ABC-stacked trilayer graphenes are fitted to a tight-binding model [13,15]. Moreover, the intercalation-induced conduction-electron densities can be predicted. The rich and unique phenomena in Li-GICs and Li⁺-GICs are expected to show significant differences under a systematic comparison with each other.

2. Theoretical Calculations

The density functional theory (DFT) [16–19] has been widely utilized for the many-electron systems in physics and chemistry for years. Specifically, the Vienna ab initio simulation package (VASP) [20] evaluates an approximate solution within the density functional theory by solving the Kohn-Sham equations. We used first-principle calculations with the VASP in this study. The VASP applies Bloch’s theorem because it is suitable for dealing with the problems of bulk materials with periodic boundary conditions. The exchange-correlation energy depending on the electron-electron interactions was calculated from the Perdew-Burke-Ernzerhof functional under a generalized gradient approximation (GGA) [21]. First, all the atoms in the relaxation process were adjusted to form the optimized structures with the lowest total ground energy. The spatial charge density can be solved by a numerically self-consistent scheme. Furthermore, we can use the above results to investigate the fundamental physical properties. The first Brillouin zone was sampled in a Gamma scheme by a 10 × 10 × 10 k-point mesh for optimization and a 30 × 30 × 30 k-point mesh for electronic structures. The energy convergence was set to 10⁻⁵ eV for two simulation steps. The maximum Hellmann-Feynman force on each atom was less than 0.01 eV/Å. The calculations for Li⁺ ion in this work were performed by reducing the number of electrons by fixing the NELECT tag in the INCAR file, and the Vander Waals interactions were considered with the tag IVDW = 11, which is under the DFT-D3 method of Grimme.

3. Results and Discussions

3.1. Geometric Structures

The geometric symmetries of graphite are diversified by the chemical intercalation. The Li/Li⁺ can be easily intercalated into the interlayer spacing because of the week but significant van der Waals interactions. There are three frequent types of absorptions positions, the hollow sites, the top sites, and the bridge sites, for the intercalant atoms. The hollow-site position possesses the lowest ground energies, that is to say, the hollow-site position is the most stable geometric configuration [22,23] The pristine structures of LiCₓ/Li⁺Cₓ display the same stacking type, stage-1, but distinct concentrations, listed in
Table 1. The changes between the interlayer distances of Li-GIC/Li$^+$-GIC are very different from each other.

Table 1. Optimized interlayer distances for state-1 AA-stacking graphite and Li/Li$^+$ GICs with PBE functional methods.

| Interlayer Distance (Å) | LiC$_x$ | LiC$_{12}$ | LiC$_{18}$ | LiC$_{24}$ | LiC$_{32}$ | LiC$_{36}$ | Li$^+$C$_6$ | Li$^+$C$_{12}$ | Li$^+$C$_{18}$ | Li$^+$C$_{24}$ | Li$^+$C$_{32}$ | Li$^+$C$_{36}$ | Graphite |
|-------------------------|---------|------------|------------|------------|------------|------------|---------|------------|------------|------------|------------|------------|---------|
| LiC$_6$                 | 3.815   |
| LiC$_{12}$              | 3.863   |
| LiC$_{18}$              | 3.924   |
| LiC$_{24}$              | 3.954   |
| LiC$_{32}$              | 3.978   |
| LiC$_{36}$              | 3.964   |
| Li$^+$C$_6$             |         |
| Li$^+$C$_{12}$          |         |
| Li$^+$C$_{18}$          |         |
| Li$^+$C$_{24}$          |         |
| Li$^+$C$_{32}$          |         |
| Li$^+$C$_{36}$          |         |
| Graphite                | 3.550   |

For the atom cases, the interlayer distances of LiC$_6$, LiC$_{12}$, LiC$_{18}$, LiC$_{24}$, LiC$_{32}$ and LiC$_{36}$ are 3.815 Å, 3.863 Å, 3.924 Å, 3.954 Å, 3.978 Å and 3.964 Å, respectively; for the ion cases, the interlayer distances of Li$^+$C$_6$, Li$^+$C$_{12}$, Li$^+$C$_{18}$, Li$^+$C$_{24}$, Li$^+$C$_{32}$ and Li$^+$C$_{36}$ are 3.082 Å, 3.283 Å, 3.374 Å, 3.451 Å, 3.510 Å and 3.555 Å, respectively. See Table 1 for details.

The heights of LiC$_x$ and Li$^+$C$_x$ decrease with higher concentrations. Apparently, compared to the pristine graphite lattice with an experimental interlayer distance of 3.550 Å [1], the height of the former will be close to that of pristine graphite when the concentration rises; on the contrary, the height of the latter will be close to that of the pristine graphite lattice when the concentration declines (Figure 1).

Figure 1. The interlayer distances with different concentrations. The blue, green, and red lines are the interlayer distances of Li-GICs, Li$^+$-GICs, and AA-stacking graphite.
3.2. Band Structures and Density of States

The pristine AA-stacking graphite possesses an unusual electronic structure, including the same amounts of free electrons and holes within $-0.5 \text{ eV}~0.5 \text{ eV}$, according to the band structure and density of state (Figure 2), and an obvious band overlap is revealed in the $k_z$-dependent energy dispersion along $\Gamma A$. That is to say, the AA-stacking graphite behaves like a semimetal. The low-lying energy bands ($\pi$ bands) are dominated by the C-2$p_z$ orbitals; the C-(2$s$, 2$p_x$, 2$p_y$) orbitals, generating the $\sigma$ bands, appear at $E \leq -3.0 \text{ eV}$ and strongly contribute to form the planar geometric structures. However, the electronic band structures exhibit very different changes after the intercalation of Li and Li$^+$. 

![Figure 2](image_url)

For intercalations of Li atoms, the asymmetry of the electron and hole bands becomes much more noticeable. Apparently, the Fermi level presents a blue shift, compared to the pristine graphite, and does not intersect with any valence bands (Figure 3). That is to say, the free conduction electrons are all created by the intercalations of Li atoms and replace the pristine carriers (both electron and hole). The blue shift of the Fermi level is determined by the negative energy with the minimum density of state and the $E_F$ ($E = 0$); the values are calculated to be, respectively, 1.800 eV, 1.326 eV, 1.138 eV, 0.991 eV, 0.882 eV and 0.810 eV for $x = 6, 12, 18, 24, 32$ and 36, as shown in Figure 4. These results indicate that the C-2$p_z$ orbitals are easily affected by the Li-C bonds and sensitive to the concentrations of Li-atom intercalation.

The intercalations of Li$^+$ ions are quite different from the Li case. The band structures do not exhibit the apparent shift of the Fermi level, estimated to be 0.088 eV, 0.042 eV, 0.036 eV, 0.026 eV 0.018 eV and 0.026 eV for $x = 6, 12, 18, 24, 32$ and 36, respectively, as shown in Figure 4; that is, the Fermi level maintains a position similar to the pristine graphite. Moreover, the initial $\sigma$ bands display shoulder structures in the orbital-projected density of states near $-2.6 \text{ eV}~-2.9 \text{ eV}$ at the $\Gamma$ point, and present a blue shift relatively to the Li ones; in other words, the $\sigma$ bands are deeper or more stable in the Li intercalations than in the Li$^+$ ones.
that the C-2pz orbitals are easily affected by the Li-C bonds and sensitive to the concentrations of Li-atom intercalation.

3.3. Charge Distributions and Charge Transfer

The spatial charge distributions ($\rho$) and variations ($\Delta \rho$) of Li- and Li$^+$-GICs are illustrated in Figures 4 and 5. The $\rho$ is directly obtained from the calculated charge density, but the $\Delta \rho$ is a value subtracting the charge density of the pure Li (or Li$^+$) and of the pure C charge density from the charge density of the Li-GIC (or Li$^+$-GIC). They are all shown on a x-z plane and useful for understanding the chemical bonding change after intercalations. For Li-atom intercalations, the $\rho$ and $\Delta \rho$ indicate that significant hybridizations of Li-C bonds with red and yellow colors in Figure 6 (within the red dashed frame) depend on the concentration; the variations become obvious with an increase of concentrations, i.e., the charge transfer is strongest in LiC$_6$, but weakest in LiC$_{36}$. Moreover, the variations are close to the C atoms but not the Li atoms, indicating that the charge transfer took place from the Li atom to the C atom. Additionally, the charge transfer mainly appears on the C atoms directly neighboring Li atoms.
3.3. Charge Distributions and Charge Transfer

The spatial charge distributions and variations of Li-GICs.

Figure 5. The spatial charge distributions and variations of Li-GICs.

For Li$^+$-ion intercalations, the variations present quite different characteristics. The $\Delta \rho$ between the Li$^+$ ions and the C atoms are broader and lighter than for the Li-atom cases, shown with light green and yellow colors in Figure 6 (within the red dash frame). In addition, the $\Delta \rho$ between the neighboring C atoms become more obvious with an increase of concentrations, as seen by the light blue colors in Figure 6 (within the black dash frame); moreover, the variations between the Li$^+$ ions and the C atoms are slightly closer to the former. That is to say, the charge transfer occurs from the C atoms to the Li$^+$ ions. This is similar to the Li-atom case in the sense that the carbon atoms not directly neighboring the Li$^+$ ions are seldom affected. By the Bader analysis in the VASP calculations, the Li-GICs exhibit charge transfers for LiC$_6$, LiC$_{12}$, LiC$_{18}$, LiC$_{24}$, LiC$_{32}$ and LiC$_{36}$, respectively; the Li$^+$-GICs exhibit charge transfers for Li$^+$C$_6$, Li$^+$C$_{12}$, Li$^+$C$_{18}$, Li$^+$C$_{24}$, Li$^+$C$_{32}$ and Li$^+$C$_{36}$, respectively, as shown in Table 2. The charge transfers show apparent differences between the Li-GIC and the Li$^+$-GIC. For the former, the charge transfers from the Li atoms to the C atoms so that the charges per Li atom exhibit a minus value. Moreover, there are slightly differences in charge transfers of the Li atoms with different concentrations. However, the C atoms obtain charges from the Li atoms, where the values of charge transfers of C atoms increase with the concentration. In other words, the higher the concentrations are, the stronger is the C-Li bonding. On the contrary, in the Li$^+$ cases, the Li$^+$ ion attracts charges from the C atoms. Even though the calculated values show that the charge transfers are much more in the Li$^+$C$_6$ than in the Li$^+$C$_{36}$, the charge transfers of the C atoms are still less than 0.3 charges, which result in the relatively weak interactions.
Table 2. The charge transfers of Li-GICs and Li⁺-GICs.

|                | Charge Transfer (e/atom) |
|----------------|--------------------------|
|                | C                        | Li                        |
| LiC₆           | 0.144                    | −0.865                    |
| LiC₁₂          | 0.073                    | −0.871                    |
| LiC₁₈          | 0.049                    | −0.878                    |
| LiC₂₄          | 0.037                    | −0.880                    |
| LiC₃₂          | 0.028                    | −0.884                    |
| LiC₃₆          | 0.025                    | −0.883                    |
| Li⁺C₆          | −0.030                   | 0.191                     |
| Li⁺C₁₂         | −0.015                   | 0.176                     |
| Li⁺C₁₈         | −0.009                   | 0.173                     |
| Li⁺C₂₄         | −0.007                   | 0.163                     |
| Li⁺C₃₂         | −0.005                   | 0.159                     |
| Li⁺C₃₆         | −0.004                   | 0.155                     |

4. Conclusions

In summary, we present the current work from first-principles calculations within the GGA method. Our work provides a comparison between these two cases and gives the evidence for the orbital hybridizations. We find that the changes of essential physical properties are very different between Li- and Li⁺-GICs, e.g., the interlayer distances, energy band structures, density of states and the spatial charge distributions, and the results clearly reveal that the Li-C bonds are generated from the 2s-2pₓ orbital hybridizations, which leads to the high charge transfers from Li to C of about 0.86–0.88 electrons as well. On the contrary, the variations of Li⁺-GICs are relatively weak, and the charge transfers that Li⁺ obtains from C merely range from 0.163–0.191 electrons. The dominant effects between Li and C are obviously the orbital-orbital interactions; but between Li⁺ and C, the main effects might be the dipole-dipole interactions. The saturated electronic configurations of the Li⁺ ions, similar to the inert gas helium [He], lead to a low contribution of free electron carriers.

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