Van der Waals density functional study of the energetics of alkali metal intercalation in graphite

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We report on the energetics of intercalation of lithium, sodium and potassium in graphite by density functional theory using recently developed van der Waals density functionals. First stage intercalation compounds are well described by conventional functionals like GGA, but van der Waals functionals is crucial for higher stage intercalation compounds and graphite, where van der Waals interactions are important. The vdW-optPBE functional gave the best agreement with reported structure and energetics for graphite and LiC₆ and was further applied for intercalation of Na and K. The enthalpy of formation of LiC₆ and KC₈ were found to be -16.4 and -27.5 kJ/mol respectively. NaC₆ and NaC₈ were unstable with positive enthalpies of formation (+20.8 and +19.9 kJ/mol). The energetics of stacking of graphene and intercalant layers was investigated from first to fifth stage intercalation compounds. Higher stage compounds of Li and K were stable, but with smaller enthalpy of formation with increasing stage order. The higher stage Na compounds possessed positive enthalpy of formation, but less in magnitude than the energy difference of 0.6 kJ/mol between graphite with AB and AA stacking. The abnormal behaviour of the lower stage Na intercalation compounds were rationalized by the lower energy involved in the formation of the chemical bond between carbon Na relative to the corresponding bond with Li or K. The chemical bond between alkali metal and carbon is characterized by charge transfer from the alkali-metal to carbon resulting in ionized alkali-metals. The intercalation induces only a subtle increase in the in-plane C-C bond lengths, with longer C-C bonds in the vicinity of the alkali metals but without breaking the hexagonal symmetry.

Introduction

Graphite is a layered hexagonal material with sp² hybridized carbon-carbon bonds within the graphene layers and weak van der Waals (vdW) interactions between the layers [1]. Electron acceptors or donors are easily intercalated into graphite due to the weak inter-planar vdW bonds and because the intraplanar π-bands consisting of C 2p orbitals readily donates or accepts electrons. Graphite intercalation compounds (GIC) with electron donors such as alkali metals display a rich variety of phases with different compositions and crystal structures. LiC₆ and KC₈ are examples of first stage GICs with alkali metals intercalated between all the graphene layers [1]. The order of the stage refers to the number of graphene layers between two adjacent layers of intercalated alkali metal atoms. A first stage Na-GICs has never been observed, and only higher stage compounds such as NaC₆₄, where Na is only intercalated in every eighth layer, have been reported [2].

Alkali metal GICs (AM-GICs) are important as electrodes in rechargeable lithium ion batteries [3-10]. Na-GIC has drawn attention recently due to the potential as anode in a Na-ion battery as an alternative to Li-batteries [11-15]. Graphite is also used as a cathode material in electro-winning of aluminium, where sodium intercalation is known to cause chemical expansion of the cathode, change the wetting properties of the cathode and possibly influence the cathode wear [16]. Finally, K-GICs are known to be superconductors [17].

Previous density functional theory (DFT) studies of alkali metal GICs have primarily focused on Li-GICs [16-21] and K-GICs [22], while Na-GICs and systematic differences between Li-, Na- and K-GICs have received less attention [23]. The local density (LDA) and generalized gradient approximations (GGA) have been used to study GICs, although these exchange correlation density functionals do not treat non-local van der Waals interactions properly. While GGA does not reproduce the weak interlayer interaction in graphite [24-27], LDA can mimic a fraction of the van der Waals interactions and give a reasonable unit cell parameter c [27-32], which has obscured the inability of LDA to properly account for vdW interactions [33]. With respect to energetics LDA also severely overestimates the Li-C binding energy [34]. The lack of models for vdW interactions is a fundamental limitation of traditional DFT, and much effort has been devoted to solve this problem. Empirical methods based on...
the Lennard-Jones potential have been used to describe the structure of carbon compounds [35-37]. Semi-empirical methods based on both DFT (LDA, GGA) and empirical corrections proposed by Hasegawa et al. [33] and Grimme [38, 39] (vdW-D) are alternative ways to describe vdW interactions. Rydel et al. have constructed a tractable non-local correlation density functionals for flat surfaces and slabs [40] and applied it to graphite and other layered structures [26, 41]. Langreth and Lundqvist’s non-local functional (vdW-DF) was the first to be implemented in DFT [26, 42-44]. The self-consistent implementation based on the algorithm of Roman-Perez and Soler [45] has been applied in studies of graphite [46-49], K-GICs [22] and Ce-GICs [50]. Several van der Waals density functionals (vdW functionals) have recently been developed to include dispersion in DFT exchange correlation functional and implemented in VASP [42, 51, 52]. These functionals have been tested on cases where hydrogen bonds, dispersion bonds and mixed bonding are present with good results [51, 53]. These new vdW functionals have so far not been used to study graphite intercalation compounds. A non-empirical physical treatment of the vdW interactions is necessary to compare DFT calculations on graphite and AM-GICs, and to determine the energetic stability of AM-GICs.

Here we report on a DFT study of graphite intercalation compounds with Li, K and Na by DFT functionals including weak London dispersion interactions. The recently established vdW functionals were applied to graphite and the first stage Li-GICs. The vdW-optPBE functional gave the best agreement with experimental data for graphite and LiC6 and was used to study the energetics of Li, Na and K GICs and their polytypes from stage I to stage V. First stage Na-GICs were found to be unstable while LiC6 and KC8 were the most stable first stage Li- and K-GICs, respectively. Intercalation caused subtle changes in the electronic density of states and the in-plane C-C bond lengths.

**Computational Details**

Density functional theory (DFT) calculations were performed using the VASP code [54-58], with the five vdW functionals vdw-revPBE, vdw-optPBE, vdw-optB88, vdw-optB86b, vdw-DF2 were evaluated by comparing the DFT results with experimental lattice parameters and cohesive energies of graphite (P6/mmc [63]) and LiC6 (P6/mmm [64]), the binding energy of graphite and the enthalpy of formation of LiC6. The enthalpy of formation is particularly important for the present aim to investigate the energetics and stability of AM-GIC polytypes. Lattice parameters, especially the long unit cell parameter c, and the binding energy gives additional insight to how well the functionals reproduce the weak inter-planar van der Waals interactions. The calculated unit cell parameters and cohesive energy (binding energy corresponding to the sublimation energy) are summarized in Tables 1 and 2. GGA did not give a stable lattice constant for the unit cell parameter c of graphite and was not reported (c increases slightly with each ionic step due to the underestimated interlayer interaction).

All functionals reproduced the experimental lattice parameter a of graphite, implying that the in-plane C-C bonds are well described. The lattice parameter c, which is perpendicular to the graphene planes and along the direction of the weak van der Waals interactions, displayed much larger deviations from the experimental value, reflecting the challenge of reproducing vdW interactions by DFT. LDA gave a small lattice parameter c and a too high cohesive. Compared to GGA all the five vdW functionals improve the treatment of interplanar interaction by introducing dispersion. However, vdw-optB88 and vdw-optB86b overestimate the interlayer interaction and gives a small lattice parameter c and high cohesive energy. The functionals that underestimated the interlayer interactions in graphite, like LDA, vdw-optB88 and vdw-optB86b, were disregarded as they gave even larger deviations in the lattice parameter c of LiC6 where the Li-C interactions dominate. The calculated lattice parameter a was in excellent agreement with the experimental value for all the functionals.

For first stage GICs, like LiC6, Li-C interactions dominate over vdW forces and the compounds are well described by the conventional GGA functional. For higher stage intercalation compounds, and in the infinite stage limit of pure graphite, vdW interactions dominate, and a suitable vdW functional must be used. The vdw-optPBE and vdw-DF2 functionals performed well with respect to lattice parameters and cohesive energies of
both graphite and LiC₆, while the vdW-revPBE functional gave significant deviations in the lattice parameter c of graphite.

### Table 1

<table>
<thead>
<tr>
<th></th>
<th>a [Å]</th>
<th>Δ [%]</th>
<th>c [Å]</th>
<th>Δ [%]</th>
<th>Ecoh [eV/atom]</th>
<th>Δ [%]</th>
<th>Reference</th>
</tr>
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<td>LDA</td>
<td>2.446</td>
<td>-0.7</td>
<td>6.590</td>
<td>-1.80</td>
<td>10.10</td>
<td>+57.2</td>
<td></td>
</tr>
<tr>
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<td></td>
<td>/</td>
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<td></td>
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<td></td>
</tr>
<tr>
<td>vdW-revPBE</td>
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<td>+5.9</td>
<td>8.63</td>
<td>+17.2</td>
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<tr>
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<td>6.834</td>
<td>+1.8</td>
<td>8.99</td>
<td>+22.0</td>
<td></td>
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<tr>
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<td>+0.1</td>
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<td>9.14</td>
<td>+24.1</td>
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<tr>
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<td>0.0</td>
<td>6.593</td>
<td>-1.8</td>
<td>9.26</td>
<td>+25.6</td>
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<tr>
<td>vdW-DF2</td>
<td>2.472</td>
<td>+0.3</td>
<td>6.975</td>
<td>+3.9</td>
<td>8.54</td>
<td>+15.9</td>
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<tr>
<td>Exp.</td>
<td>2.464</td>
<td>/</td>
<td>6.711</td>
<td>/</td>
<td>7.37</td>
<td>/</td>
<td>[63]</td>
</tr>
<tr>
<td>GGA</td>
<td>2.47-</td>
<td>&gt;7.5</td>
<td>/</td>
<td>/</td>
<td></td>
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<tr>
<td></td>
<td>2.473</td>
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<td>2.453</td>
<td>6.784</td>
<td></td>
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<td>vdw-DF2</td>
<td>2.47-</td>
<td></td>
<td>6.45-</td>
<td>8.08</td>
<td>[48]</td>
<td></td>
<td>[22, 26, 42, 47-49, 68]</td>
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<tr>
<td>2.476</td>
<td>7.52</td>
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<tr>
<td>a at ~300K, L. Brewer (unpublished), originally cited in ref. [28]</td>
<td></td>
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</tbody>
</table>

The effect of the weak vdW interactions can also be assessed by calculating the interlayer binding energy of graphite as a function of the interlayer spacing. The calculated binding energy (corresponds to the attractive energy between graphene layers) as a function of interlayer distance with a fixed lattice constant $a = 2.46$ Å is shown in Fig. 1. The minimum binding energy defines the equilibrium interlayer distance. The functional vdW-revPBE gave the best agreement with experiments. vdW-DF2 reproduced the lattice parameters, while vdW-optPBE, vdW-optB86b and vdW-optB88 overestimated the binding energy even more than vdW-DF2. LDA gave a bit too low binding energy and underestimated the interplanar distance along the c-axis, while GGA could not yield a minimum in the bonding energy. PBEsol improved the treatment of interlayer interaction, but still the calculated binding energy was too low relative to experimental data.

In order to estimate the enthalpy of formation of LiC₆ the functionals were also applied to lithium metal [74]. The enthalpy of formation was then estimated from the change in cohesive energy $E_{coh}$ for the reaction

$$\text{Li(s)} + 6 \text{C(graphite)} = \text{LiC}_6(s)$$  \hspace{1cm} (1)

The internal energy of reaction (1) is estimated as

$$\Delta E_f = - (E_{coh, \text{LiC}_6} - E_{coh, \text{Li}} - 6 \times E_{coh, \text{C in graphite}})$$  \hspace{1cm} (2)

where $E_{coh}$ is the cohesive energy. The enthalpy of formation can be expressed as

$$\Delta H_f = \Delta E_f + pV$$  \hspace{1cm} (3)

since the $pV$ term can be neglected. The change in cohesive energy of reaction (1), corresponding to the enthalpy of formation of LiC₆ calculated by the different functionals, is summarized in Table 3.
Fig. 1 Interlayer binding energy of graphite as a function of interlayer separation (d) calculated by LDA, GGA and five different vdW functionals, in all calculation lattice constant a was fixed as 2.46 Å. The range of experimental energies are shown as a grey region [70–73] and the 5 experimental interlayer distance is given as the vertical line at 3.355 Å. Markers are the calculated value and lines are guides to the eye. Experimental binding energies reported shown in the figure are 31±2, 43, 52±5 and 35(+15 -10) meV/atom [70–73]

Table 3 The calculated enthalpy of formation of LiC₆ using vdW-optPBE compared to the experimental enthalpy of formation.

<table>
<thead>
<tr>
<th></th>
<th>ΔH [eV/f.u.]</th>
<th>ΔH [kJ/mole]</th>
<th>Δ [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>LDA</td>
<td>-0.453</td>
<td>-43.7</td>
<td>214</td>
</tr>
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<td>vdW-optPBE</td>
<td>-0.084</td>
<td>-8.1</td>
<td>-42</td>
</tr>
<tr>
<td>vdW-optPBE88</td>
<td>-0.169</td>
<td>-16.3</td>
<td>+18</td>
</tr>
<tr>
<td>vdW-optB86b</td>
<td>-0.231</td>
<td>-22.3</td>
<td>+60</td>
</tr>
<tr>
<td>Exp. 455K [75]</td>
<td>-2.280</td>
<td>-220</td>
<td>+1483</td>
</tr>
</tbody>
</table>

The calculated enthalpy of formation of LiC₆ has been reported to -13.9±1.2 kJ/mol [75]. Taking into account the enthalpy of fusion of Li, which is 2.38 kJ/mol at 453.69 K [76], the vdW-optPBE functional demonstrates the best agreement with the experimental value. LDA and vdW-DF2 overestimated the exothermic enthalpy of formation.

The preferred functional was chosen as a compromise to simultaneously describe the lattice parameters, cohesive energy and the enthalpy of reaction (1). vdW-optPBE was found as the most suitable vdW functional to describe graphite and Li-GICs as it resulted in an excellent agreement with the experimental value of the enthalpy of formation of LiC₆ and reasonable lattice parameters and cohesive energies of graphite and LiC₆.

2. Energetics of graphite and the first stage alkali metal GICs (AM-GICs)

Graphite has three polytypes; hexagonal P6₃/mmc, P/6₃mmc and rhombohedral $R\bar{3}m$. The difference in cohesive energy of these three using the vdW-optPBE functional was less than 1 meV, which is within the convergence limit of the calculations. In the following only the $P\bar{6}₃/mmc$ graphite polymorph was considered. The graphene layers in the $P\bar{6}₃/mmc$ polymorph are ordered in an AB stacking sequence along the c-axis, while the artificial AA stacking sequence has 0.6 kJ/mol (7 meV/atom) higher energy. The equilibrium interplanar distance in graphite changes from 3.42 Å with AB stacking to 3.58 Å for AA stacking. In the first stage Li-GICs the AA stacking sequence has lower total energy than the AB, in concordance with the literature [1] as shown further below.

Polytypes of AM-GICs differ in the relative position of the alkali metal layers and the graphene layers along the long c-axis. The positions of the intercalants, the alkali metal atoms, on a particular site in one layer tends to exclude the placement of the intercalants on the similar sites in the nearest neighbour intercalant layer. In the nearest layer the intercalants will thus occupy equivalent intercalation sites [1], with concomitant changes in unit cell symmetry and space group. Due to the different possible stacking sequences there is a high number of possible GICs polytypes. The different polytypes are identified by a nomenclature previously used for intercalation compounds [1, 22, 69]. The polytypes of LiC₆ and KC₈ considered in this work are shown in Figure 2. LiC₆ may have the unit cell $/Aα$/ or $/AαAβAγ$/…, where A represents the graphene layer and α, β, γ represent the equivalent sites for alkali metal atoms. Correspondingly, KC₈ may have the unit cell $/Aα$/ or $/AαAβAγAδ$/….

The same considerations apply to Na-GICs, LiC₈ and KC₈, although they have not been observed experimentally.

![Diagram of MC₆ with in-plane p(√3 x √3)R30° structure](image)

**Fig. 2** MC₆ with in-plane p($\sqrt{3} \times \sqrt{3}$)R30° structure (a) and MC₈ with in-plane p(2 x 2)R0° structure (b). Carbon is represented by brown spheres, while the spheres with the other colours represent alkali metals [77]. α, β, γ and δ represent the equivalent intercalation sites.

The calculated enthalpy of formation of different polytypes of
the GICs, as defined for LiC₆ by equation (2), for Li, K and Na are shown in Fig. 3 to 5, where the crystal structures are also illustrated. Endothermic enthalpy of formation means that the compound is unstable with respect to reference state of the pure elements, while exothermic enthalpy of formation implies that the polytype structure is stable. The absolute value of the formation energy reflects the relative stability; the more negative the value the more stable the intercalation compound is with respect to the pure elements.

The most stable Li-GIC was found to be LiC₆-/Aα/, in agreement with experiments [64]. The polytype LiC₆-/AαBβγ/ has slightly higher energy than the most stable compound as illustrated in Fig 3, reflecting that it has also been observed at low temperatures [78]. The polytype LiC₆-/AαBαγ/, which has never been reported, has higher energy than the pure substances. LiC₆-/Aα/ is also found to be less stable than LiC₆-/Aα/ (Fig. 3), following from the exothermic energy of the reaction

\[ \text{LiC}_6(s) = \text{LiC}_6(s) + 2 \text{C(graphite)} \]  

The calculated energies of formation for K-GIC polytypes are different from the corresponding Li-GICs, as illustrated in Fig. 4. For K-GICs KC₈-/Aα/… is more stable than KC₆-/Aα/…, while KC₈-/AαBβγAδ/… is found to be the most stable polytype, in concordance with experiments [79].

The energetics of the Na-GICs polytypes is fundamentally different from the Li- and K-GICs. None of the possible first stage Na-GICs are stable with respect to the reference state of sodium metal and graphite, reflecting the lack of experimental observations of such compounds [2].

3. Energetics of higher stage alkali metal GICs (AM-GICs)

AM-GICs can have higher stage intercalation compounds with overall lower alkali content. The structure of these compounds is characterized by its stage number \( n \) which refers to the number of graphene sheets between the two nearest AM intercalant layers. The stacking sequence of the graphene layers inside the sandwich structure of higher stage AM-GICs (\( n \geq 2 \)) has been proposed to be ABAB…[1], corresponding to the stacking in graphite. Several polytypes of the higher stage AM-GICs are possible as in case of the first stage GIC, and we have calculated the energetic stability of the relevant possible polytypes for stage I to V GICs. Higher stage GICs were not investigated due to the computational challenges with the large unit cell and number of atoms in such systems. In an odd stage structure, the intercalant atoms in the nearest neighbour layer take the same intercalation site, while in an even stage structure, they are more likely occupy equivalent intercalation sites. Figure 6 illustrates a stage II and a stage III Li-GICs.

The calculated enthalpy of formation with respect to the reference state (graphite and alkali metal) is reported in Fig. 7. The enthalpy of formation per mol atom are plotted as a function of the alkali metal mole fraction in the first and higher stage Li-GICs, Na-GICs and K-GICs respectively. The compositional position of the GIC compounds is also given at the top of the figure. Dotted lines represent AM-GICs with AA graphene stacking (AM-GIC-AA) while solid lines represent AM-GICs with AB graphene stacking (AM-GIC-AB).

![Fig. 3 Illustration of the enthalpy of formation in kJ/mol (meV/f.u.) of first stage Li-GICs relative to the reference state corresponding to pure graphite and Li metal. LiC₆-/Aα/ is the most stable compound. Arrow lengths are not to scale.](image-url)
Fig. 4 Illustration of the enthalpy of formation in kJ/mol (meV/f.u.) of first stage K-GICs relative to the reference state corresponding to pure graphite and K metal. The compound at the lowest position is the most stable structure. Arrow lengths are not to scale.

Fig. 5 Illustration of the enthalpy of formation in kJ/mol (meV/f.u.) of first stage Na-GICs relative to the reference state corresponding to pure graphite and Na metal. The compound at the lowest position is the most stable structure. Arrow lengths are not to scale.
We find that for stage II \( (n=2) \) AM-GICs AA stacking is more stable than AB, while for \( n \geq 3 \), AB stacking is most stable, although the energy differences are subtle. For Li-GICs and K-GICs, all higher stage compounds were stable with respect to their neighbouring compounds, hence the energy of reaction (5) is exothermic

\[
\text{GIC stage } n-1 + \text{GIC stage } n+1 = 2 \text{GIC stage } n \quad (5)
\]

The stable higher stage GICs should in principle be possible to observe experimentally if the overall stoichiometry can be controlled precisely. The enthalpy of formation of Li and K GICs with AB stacking sequence approach zero when \( n \to \infty \) \((x_M \to 0)\), which corresponds to pure graphite, while the GICs polytypes with AA stacking approach the value 0.6 kJ/mol, which is the calculated energy difference between natural AB graphite and artificial AA graphite. The energetics of Na-GICs is more sophisticated, and all the Na-GICs investigated here \((n \leq 5)\) possess an endothermic enthalpy of formation, which implies that the lower stage Na-GICs is unstable in good agreement with the lack of experimental evidence for these compounds [2, 80].

**Discussions**

1. **Crystal structure after intercalation**

Intercalation of alkali metal atoms in graphite causes chemical expansion along the c-axis perpendicular to the graphene layers. The interlayer distance of the first stage GIC is shown in Fig. 8 together with the corresponding values for graphite with AA and AB stacking. The radii of Li, Na, K metal atoms and cations are also displayed in Fig. 8. The interlayer distances in AM-GICs clearly reflect the size of the intercalants. K⁺ has by far the largest ionic radius and yields the strongest chemical expansion upon intercalation, while Li-GIC exhibit only minor chemical expansion. The expansion along the c-axis mainly reflects the radii of the alkali metal cations.

\[
\begin{array}{cccccc}
\text{C}_6 & \text{C}_{12} & \text{C}_{18} & \text{C}_{24} & \text{C}_{30} & \text{C}_{40} \\
\text{NaC}_{6n} & \text{NaC}_{8n} & \text{NaC}_{8n} & \text{LiC}_{6n} & \text{LiC}_{6n} & \text{LiC}_{6n} \\
\text{AA} & \text{AB} & \text{AA} & \text{AB} & \text{AA} & \text{AB} \\
\end{array}
\]

Fig. 7 The enthalpy of formation per mol atom of AM-GICs plotted as a function of composition given as the mole fraction of the alkali metal ion \((x_M)\). The location of the different stage GICs are also given at the top of the figure. * refer to the enthalpy of formation of artificial graphite AA compared to graphite. “I” and “II” refers to stage I and II. Dotted lines correspond to AM-GICs with AA graphene stacking (AM-GIC-AA) while solid lines correspond to AM-GICs with AB graphene stacking (AM-GIC-AB). The lines are guides to the eye.

The in-plane C-C bond lengths in the graphene layers are also perturbed by the intercalation process. While the in-plane C-C bond lengths in pure graphite are equal, the distortion of the carbon rings by intercalation yields “long” and “short” C-C bond lengths as shown in Fig. 9. Here "L" denotes the long C-C bonds closest to the intercalants and “S” short C-C bonds further away from the intercalants. This pattern of long and short in-plane C-C bonds does not break the hexagonal symmetry of the AM-GIC. The in-plane C-C bond lengths of AB and AA graphite are
included in Fig. 9 for comparison. Intercalation causes an expansion of the carbon rings, as expected from the charge transfer (see below) to the graphene layers. A larger difference between the long and short bond lengths is a possible rationalization for the lower stability of LiC₆ (NaC₆) compared to LiC₈ (NaC₈). The difference between the short and long bond lengths in K-GICs is however very small. NaC₆ differs from LiC₆ and KC₆ by displaying slightly longer C-C short and long bonds.

Further insight in the stability of the AM-GICs is provided by calculation of the artificial interlayer binding energy by fixing the lattice parameter $a (=4.33 \, \text{Å})$ and variation in the interlayer distance along $c$ for the first stage GICs. These calculations are performed in a similar way to the interlayer binding energy of graphite, shown in Fig. 1. The estimated interlayer binding energies of LiC₆, NaC₆ and KC₆, relative to an infinite interlayer distance, were 1.48, 0.61 and 0.86 eV/f.u., respectively. NaC₆ had the lowest binding energy, which reflects the instability of the first stage Na-GIC and its abnormal intercalation behaviour relative to Li- and K-GICs.

2. Electronic structure after intercalation

It is also interesting to investigate the effect of electron donors like alkali metals on the electronic structure of the graphite host. The total density of state (DOS) of graphite (top) and three first stage AM-GICs (bottom) is shown in Fig. 10. While graphite is a semi-metal with close to zero band gap and negligible DOS at the Fermi energy there is a finite DOS at the $E_F$ for the AM-GICs, which explains why the AM-GICs are metallic. All three AM-GICs have quite similar DOS in the vicinity of $E_F$ and are expected to possess similar electronic properties, independent on the type of alkali metal. The charge densities of the three AM-GICs (not shown) are also quite similar. This reflects the strong charge transfer from the alkali metal to carbon as elucidated further below.
between Li 2s and carbon orbital energies, implying that Li completely donates its 2s electron to the carbon p\_z orbitals. Integrating the PDOS of MC\_x from E\_F, graphite to E\_F, MC\_x yields numbers very close to 1 for Li-, Na- and K-GICs investigated, implying virtually complete charge transfer from the alkali metal atoms to the carbon. These calculations demonstrate that the alkali metals become completely ionized with a formal charge of +1 as expected from in the periodic table of the elements. Interkalation of the electron donors like alkali metals in carbon does therefore results in charge transfer from the donor to the carbon host in line with the expectations.

![Partial DOS of graphite and LiC\_6](Image)

**Fig. 11** Partial DOS of graphite (top) and LiC\_6 (bottom).

3. Abnormal behavior of Na-GICs corresponding to Li- and K-GICs

The minor difference in the electronic structures of the three AM-GICs could not explain the abnormal behavior of Na-GIC corresponding to the other two alkali metal GICs. Further insight in the abnormal behavior of Na-GICs can be obtained by de-convolution of the enthalpy of formation of GICs into several hypothetical reactions as illustrated in Figure 13 for NaC\_6. Hess law can then be applied since the internal energy is a state function. The three reaction steps are; 1) the reconstruction of the carbon host from the graphite reference state to the position of the carbon atoms in the intercalation compound, 2) reconstruction of the alkali metal from the reference bcc structure to the position of the alkali atoms in the intercalation compound, and 3) The intercalation of the hypothetical alkali layer into the carbon host. Reaction step 1) is endothermic due to the change in the stacking sequence of the graphene layers, increase in the layer spacing and finally due to elongation of the in-plane C-C bond length. The reaction step 2) is also an endothermic process due to the breaking of the metallic bond in one direction and elongation of the atomic distance to the spacing corresponding to the atomic spacing in the alkali layer in the intercalation compound. Finally, reaction step 3) is exothermic due to the charge transfer from the alkali metal to carbon and formation of the chemical bond.

<table>
<thead>
<tr>
<th>ΔE_1 [eV]</th>
<th>ΔE_2 [eV]</th>
<th>ΔE_3 [eV]</th>
<th>ΔH_f [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiC_6</td>
<td>0.101</td>
<td>0.657</td>
<td>-0.928</td>
</tr>
<tr>
<td>NaC_6</td>
<td>0.236</td>
<td>0.278</td>
<td>-0.298</td>
</tr>
<tr>
<td>KC_6</td>
<td>0.326</td>
<td>0.143</td>
<td>-0.673</td>
</tr>
</tbody>
</table>

**Table 4** The enthalpy of formation and the energy of the three reactions steps, illustrated in Fig. 12, for LiC\_6, NaC\_6 and KC\_6.

Conclusions

Alkali metal atoms are easily intercalated in graphite due to the weak van der Waals (vdW) interactions between the graphene layers. The vdW interactions, which are not properly accounted for by conventional density functional theory (DFT), were well described by vdW-optPBE vdW exchange correlation functional. LiC\_6 and KC\_6 were shown to be the most stable intercalation compounds with Li and K, in agreement with experiments. In contrast, stage I to stage V Na-GICs were shown to be energetically unstable, reflecting the absence of experimental observation of lower stage Na-GICs. This instability was rationalized by the low interplanar binding energy of Na-GICs.

The stage I and stage II AM-GICs prefer an AA stacking sequence of the graphene layers, while in stage III and higher stage AM-GIC AB stacking of graphene layers, as in pure graphite, is the most stable configuration. The intercalation raises the Fermi energy, transforming the semi-metal graphite to metallic GICs. The chemical bonds between alkali metal atoms and carbon atoms are characterized by complete charge transfer from AM to carbon. The energy gain due to the charge transfer from Na to carbon atoms is not sufficient to cause an exothermic enthalpy of formation of the first stage GIC of Na.

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Fig. 12 The hypothetical reaction cycle for the formation of AM-GICs from the elements using NaC₆ as an example. ΔE₁ and ΔE₂ correspond to the energy required for the reconstruction of graphite and alkali metal into the layers corresponding to the intercalation compound. ΔE₃ corresponds to the energy gain from the charge transfer when the artificial alkali metal layer intercalates the carbon host.

Notes and references

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