

Study on the First-Principles Calculations of Graphite Intercalated by Alkali Metal (Li, Na, K)

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First-principles calculations of formation energy and energy barrier were done to examine the energetics of alkali metal graphite intercalation compounds (AM-GICs). The results showed that Li, K can be intercalated into the graphite layer under the high intercalated density, while Na was hardly intercalated into it, which was due to the energetic instability of Na-GICs. In addition, the ion jumps between sites in the graphite presented that Na can hardly move in ordered graphite layers, while K can move smoothly. Therefore, it can be expected that K-GICs will be an advantaged alternative as the battery anode material in theory.

Keywords: First-principles, AM-GICs, Formation energy, Energy barrier

1. INTRODUCTION

It is well known that lithium can be intercalated into graphite to form lithium-graphite intercalation compounds (Li-GICs), because the presence of weak van der Waals forces between the inter-layer[1]. Li-GICs have been actively investigated since the early of 1980s due to the discovery of the reversible electrochemical intercalation of lithium in graphite, which is widely used in rechargeable lithium ion batteries[2-8]. In theoretical studies, some first-principles calculations of the thermodynamics and kinetics of Li_xC_6 have reported that very fast Li diffusion in bulk graphite, which may have important implications for lithium ion battery anode optimizations[9-11]. An important and characteristic property of Li-GICs is the staging structure, which is formed by intercalated lithium layers that are periodically arranged in a matrix of graphene layers depending on the Li densities[12]. However, a certain intercalated concentration of intercalated Li usually shifts the stacking pattern of the carbon planes to an AA stacking whereas original graphite consists of carbon planes which are

shifted with each other (AB stacking)[13]. So far there are many experimental and theoretical studies pay close attention to Li-GICs[2-13].

On the one hand, lithium ion batteries have governed the current worldwide rechargeable battery market due to their outstanding property, but on the other hand, other alkali metal GICs (AM-GICs) are being actively researched as cost-effective electrodes in batteries. Recently, unlike Li, sodium is one of the more abundant elements on Earth and exhibits similar chemical properties to Li, indicating that Na chemistry could be applied to a similar battery system[14-18]. Despite the gravimetric capacities being lower for sodium than lithium insertion, a reversible sodium capacity of 300mAh/g has been achieved in experimental research, close to that for lithium insertion in graphitic carbon anode materials[16]. However, it has been reported that lithium can easily be intercalated into graphite, but it is hard for sodium, which results in the performance of sodium ion batteries are lower than lithium ion batteries[19]. In addition, K-GICs have attracted a good deal of attention to be superconductors[20].

Until now a great many of electrochemical techniques and theoretical methods have been used to study insertion properties and mechanisms of Li-GIC, but there are few studies of Na-GICs and systematic differences between Li, Na and K-GICs. In the present work, we have focused on these differences of AM-GICs (AM=Li, Na, K) from first-principles calculations. It presents results of the stability of AM-GICs with the observed or hypothetical structures on the formation energies, as well as the mobility of the ion in the graphite from the calculated energy barrier of the ion jump between sites in the graphite.

2. COMPUTATIONAL METHOD

The total energies of AM-GICs were performed with total-energy code CASTEP (Cambridge Sequential Total Energy Package), which employs pseudopotentials to describe electron-ion interactions and represents electronic wave functions using a plane-wave basis set, based on first-principles density functional theory (DFT). The generalized gradient approximation (GGA) with the exchange-correlation potential proposed by Perdew, Burke and Ernzerhof (PBE), the ultrasoft pseudopotential and the projected augmented wave (PAW) method was used for calculations[21-23]. The k-space integral and the plane-wave basis was chosen to ensure that the total energy was converged at the 1 meV/atom level. The kinetic cutoff energy of 700 eV for the plane wave expansion of the wave functions and the k-points sampling with the spacing of 0.3 Å for the Monkhorste-Pack scheme in the reciprocal space was found to be sufficient. The self-consistent total energy in the ground state was effectively obtained by the density-mixing scheme. The convergence threshold for self-consistent field (SCF) tolerance was set to 1.0×10^{-6} eV/atom. Finite basis set corrections were also included.

The formation energies E_f , which estimated the stability of AM-GICs, were obtained from the total energies of the supercell by following equation[24]: $E_f = E_{AM} + E_G - E_{AM-GICs}$, where E_{AM} , E_G and $E_{AM-GICs}$ are total energies of alkali metals, original graphite (AB stacking) and AM-GICs, respectively. E_{AM} has been calculated to consider the alkali metal bulk structure having a body

centered cubic (bcc) structure. Note that configurations with smaller formation energy are more stable than configurations with larger E_f .

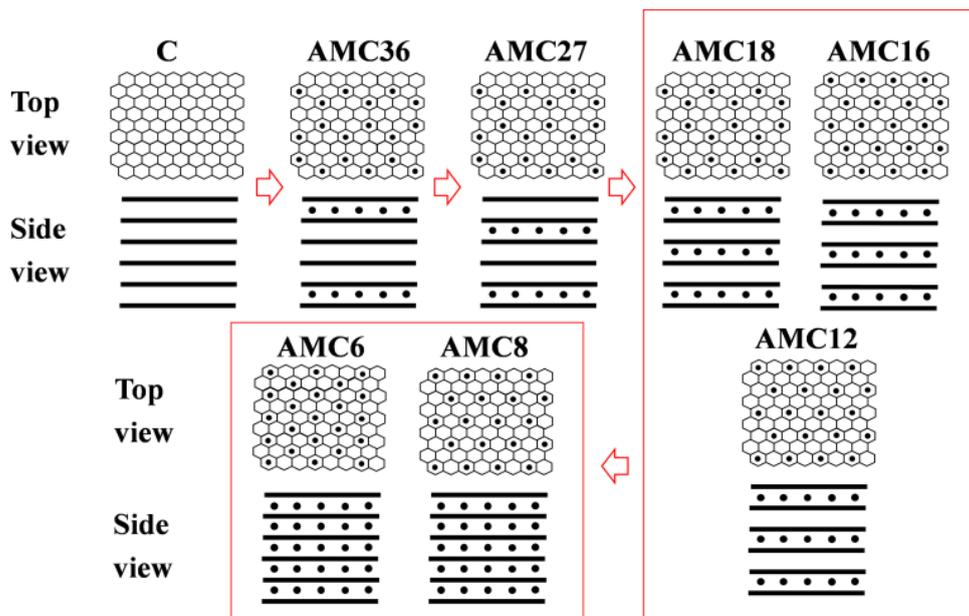


Figure 1. Staged structures of AM-GICs

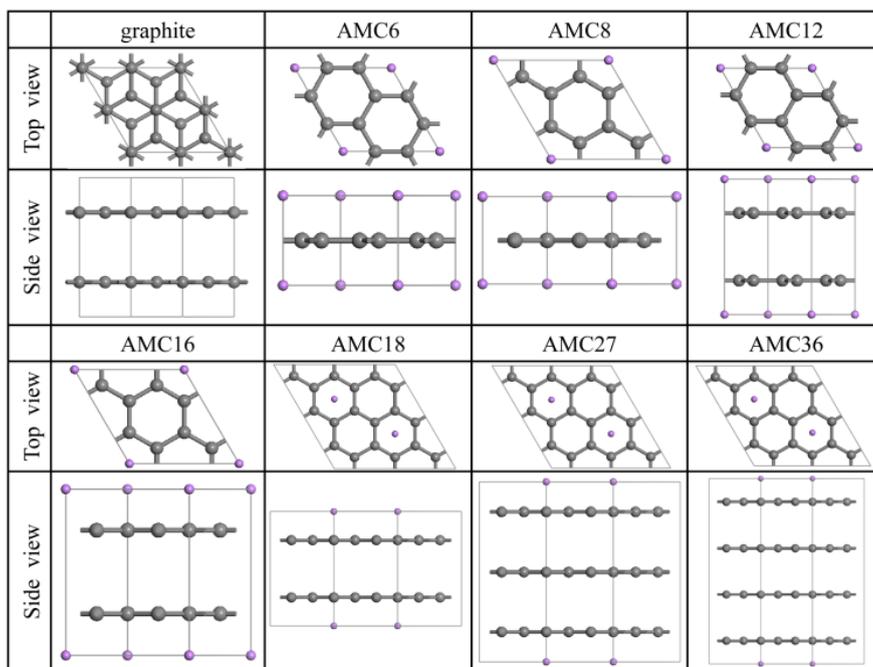


Figure 2. The calculation models of AM-GICs

In intercalated process, several different staged structures of Li-GICs are known, depending on the concentration of intercalated lithium and these are represented by LiC_n [12]. In a recent calculated report of AM-GICs, the calculation models were considered as two different staged structures,

corresponding to two lower order structures[25]. However four different staged structures of Li-GICs are known, and the stage order index denotes the number of graphene layers between adjacent intercalate layers. The first staged structures are higher order structures, and then gradually lower order structures, as schematically illustrated in Figure1. The most symmetric position between graphene layers (the center of a hexagonal ring formed by carbon atoms) is the one which is energetically favorable for all alkali metal atoms. As experimentally reported for Li-GICs, we assumed calculation models of AM-GICs to be the AA stacking as shown in Figure2, containing AMC_{36} , AMC_{27} , AMC_{18} , AMC_{16} , AMC_{12} , AMC_8 and AMC_6 .

In order to determine the structure of hypothetical AM-GICs, geometrical optimization using total energy minimization algorithm had been performed. Lattice parameters and atomic arrangements were changed under the constraint condition of the assumed space groups, using the Broyden–Fletcher–Goldfarb–Shannon optimization procedure. In the geometry optimizations, all forces on the atoms were converged to less than $0.03 \text{ eV}/\text{\AA}$, the total stress tensor was reduced to the order of 0.05 GPa , and the maximum ionic displacement was within 0.001 \AA . However, in case of the graphite, the AB stacking structure can be described as belonging to the Space Group 194, $P63/mmc$ as experimentally reported, and we did not carry out the cell optimization. It is well known that GGA has been used to study GICs may overestimate the interlayer distance of graphite, while GGA does not reproduce the weak van der Waals interaction in graphite interlayer[26-28].

In addition, the diffusion behavior of the Li, Na and K ion in graphite interlayer was clarified by employing the method of the transition state (TS) search based on the traditional linear and quadratic synchronous transit (LST/QST) method[29] as available implemented through CASTEP code. In order to exclude the influence of boundary conditions, an alkali metal ion was inserted into the large enough super cell model C_{36} as the example calculation model of the TS search.

3. RESULTS

After geometry optimization, we can be able to study the stability of AM-GICs structure formed by calculating formation energies (E_f), as shown in Figure3. It can be found that formation energies are gradually decreased with increasing concentration of intercalated alkali metal ion. The formation energies of Li-GICs, K-GICs are greater than zero and each compound can remain energetically stable until the high density of LiC_6 and KC_6 , which is consistent with experimental reported[30]. On the other side, it can be stated that NaC_{18} , NaC_{16} are hardly stable, which formation energies are close to the zero. Especially, assumed structures of NaC_{12} , NaC_8 , NaC_6 have been impossible under the higher density of intercalated Na[31]. The results of formation energies are similar to the earlier report of first-principles study of AM-GICs[25], and further clearly illustrate that the maximum intercalated density structures of AM-GICs are LiC_6 , NaC_{16} , KC_6 , respectively. Such energetic instability under the high density means it is difficult for Na to be intercalated into the graphite, while the Li and K can intercalate into it.

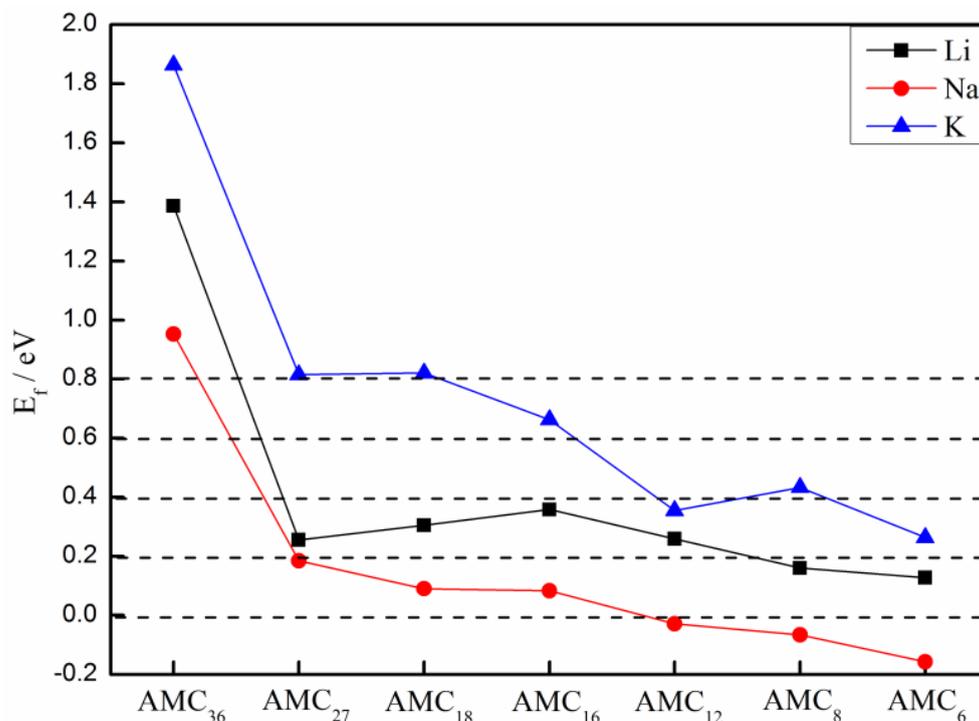


Figure 3. The formation energies of AM-GICs with different intercalated density of alkali metal

Next, the geometry optimized structures were discussed to clarify the reasons for the stability of compounds. The distances between the carbon layers intercalated with alkali metal ions are illustrated in Figure 4. The distance is obtained as follows: $d = d_1 - d_2$, where d , d_1 and d_2 are the distance between the carbon layers intercalated with alkali metal ions, the distance between two intercalated alkali metal ion layers and the distance between the carbon layers intercalated without alkali metal ions, respectively. There is a positive correlation between these distances (d) and the radius of the alkali metal ion, whether the differences of all intercalated densities. In the geometry optimized calculation of structures, this result, the greater ionic radius, the greater distance between the carbon layers is not surprising.

Due to the high density of intercalated compounds LiC_6 , KC_6 have been observed in the experiment as already mentioned [30], it is clear that the ionic size of the alkali metal is not a reason for the energetic instability of the Na-GICs. Furthermore, Figure 5 shows the C-C bond lengths of carbon six-membered ring in the carbon layer intercalated with alkali metal ions. It illustrates that the graphite structure with the increasing intercalated density of AM-GICs become more unstable and receive greater strain, which C-C bond lengths are more stretched. The C-C bond lengths of AM-GICs under the same intercalated density almost perform as follows order: $\text{Na} > \text{Li} > \text{K}$, which are consistent with the energy results that K-GICs, Li-GICs are more stable than Na-GICs as already mentioned previously. It can be clearly found that all the C-C bond lengths of K-GICs are stretched less than that of Li-GICs, thus there is smaller strain and higher stability in their structures. It must be noted, however, the C-C bond lengths of Na-GICs are significantly greater than that in K-GICs, which are opposite to the ionic radius. This shows that graphite becomes stressed while Na is intercalated into it, so it is almost impossible to form a stable structure of Na-GICs under the high intercalated density.

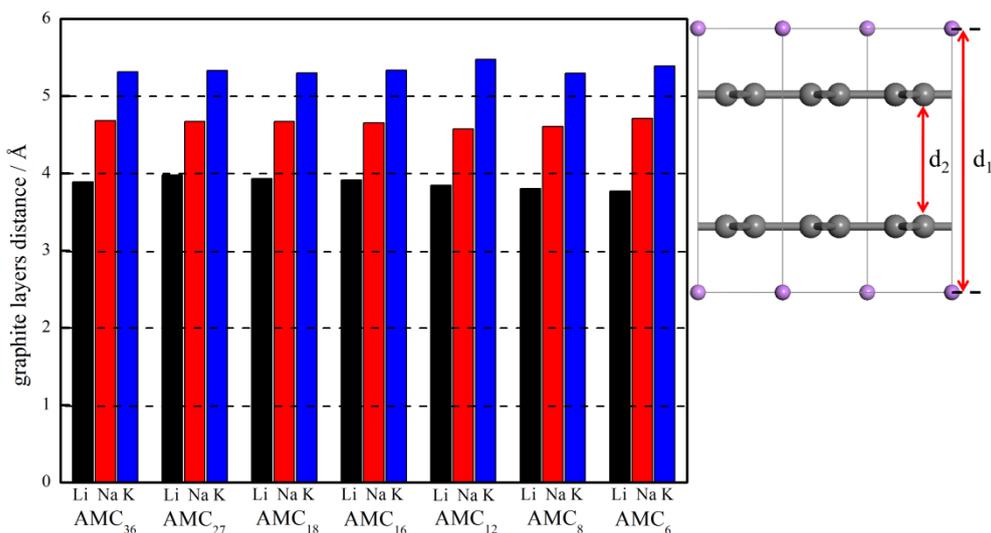


Figure 4. The distances between the carbon layers intercalated with alkali metal ions

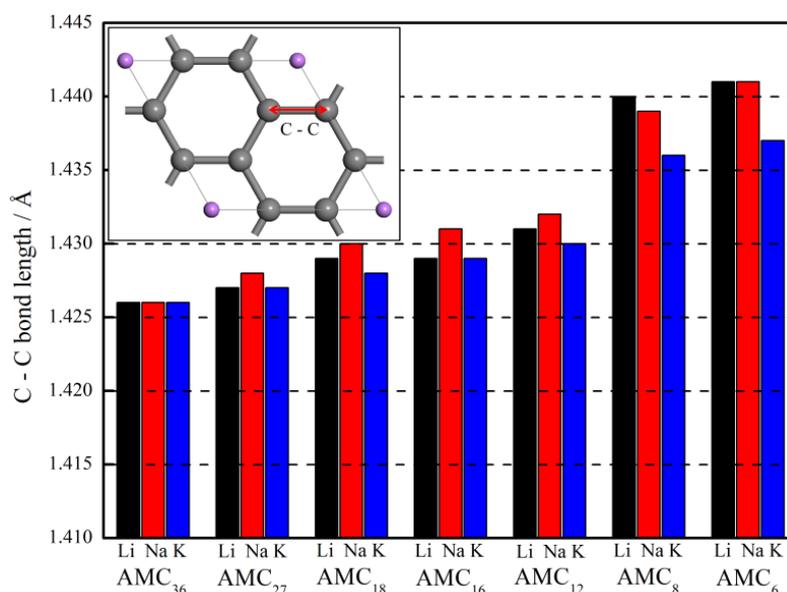


Figure 5. The C-C bond lengths of carbon six-membered ring in the carbon layer intercalated with alkali metal ions

Finally, we investigated the mobility of the alkali metal ion in graphite layers by calculating energy barriers of the ion jumps between sites in the graphite, as results shown in Figure6. In earlier energy barriers calculation, researchers deduced that the larger radius ions more smoothly move in the graphite[25]. However, through our theoretical calculations, it can be clearly stated that the energy barrier of Na is the highest among that of the three alkali metal ions, and the lowest one is K. It means that Na hardly moved in ordered graphite layers, K moved more smoothly. This has nothing to do with the size of the ionic radius. Combined with the previous discussion of the structural stability, it is proved that Na is hardly stored and moved in ordered graphite layers. Compared with experimental

reported that Na which used the hard carbon as the negative electrode material, is only stored between disordered graphite layers and in closed nanopore parts[16, 19, 32], it can be deduced that the perfect graphite structure is not an excellent electrode material for the sodium ion battery. However, we find that the migration of K in graphite layers is easier than that of Li. It indicates that there is a greater diffusion rate of K in the graphite which is consistent with the previous report that K-GICs is one of the potential applications in the field of superconductivity[20].

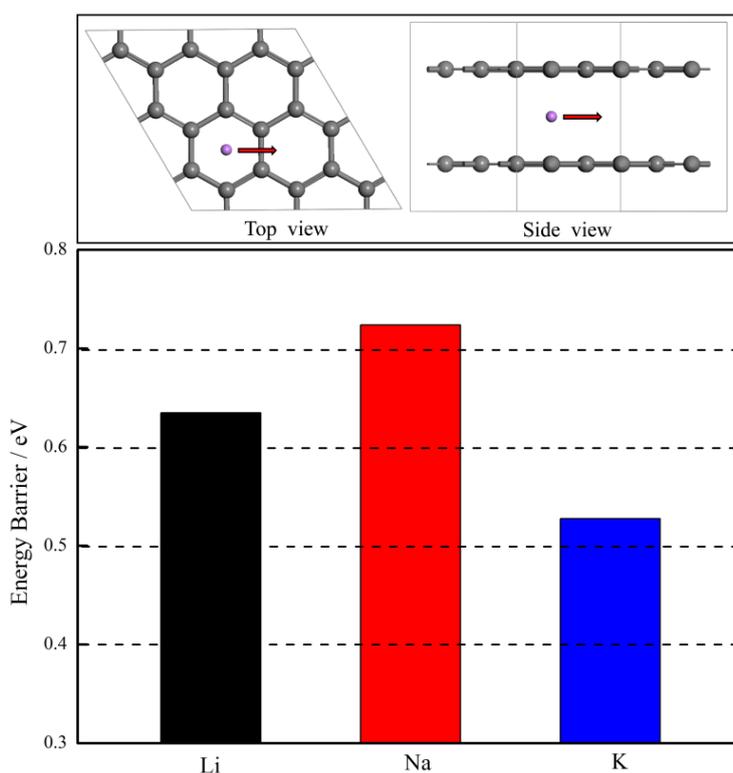


Figure 6. The energy barriers of the alkali metal ion jumps between the sites in the graphite

4. CONCLUSIONS

The energetics of alkali metal graphite intercalation compounds were obtained by first-principles calculations on the formation energies. It indicated that Li, K can be intercalated into the graphite layer under the high intercalated density, while Na was hardly intercalated into it, which was due to the energetic instability of Na-GICs. The graphite is stressed when alkali metal ions intercalated into it, with the greater pressure and the worse stability of the structure. In this work, the pressure performs as follows order: $\text{Na} > \text{Li} > \text{K}$, which is oppositely correlated with the stability of their structures: $\text{K} > \text{Li} > \text{Na}$. In addition, the results of the energy barrier calculation showed that while Na hardly moved in ordered graphite layers, K moved more smoothly. Thus, compared to Na, K is expected to be an advantaged alternative to Li for using graphite as the battery anode material in theory.

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