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First-Principles Understanding of the Staging Properties of the Graphite Intercalation Compounds towards Dual-Ion Battery Applications

Wenchong Zhou and Patrick H.-L. Sit*

ABSTRACT: Graphite-based dual-ion batteries are a promising alternative to the lithium-ion batteries for energy storage because of its potentially lower cost, higher voltage, and better safety. Among the most important materials in the dual-ion battery are the graphite and graphite intercalation compounds (GICs), whose properties determine the performance of electrodes. The GICs are formed at both anode and the cathode sides during the charging process in which the graphene sheets and the intercalants are arranged in an ordered way called the staging of GICs. Staging is one of the important structural features of GICs related to the volume expansion of the electrodes, the charging rate, and the capacity of the battery. However, the details of the staging mechanism, such as the structural properties, the electronic structure, and the voltage dependence on the stages are still poorly understood. In this regard, we perform density functional theory studies to explore these issues in GICs. Using staging models, we examine the stability of GICs at different stages of intercalation with a range of species (i.e., Li, Na, K, PF₆, BF₄, TFSI, AlCl₄, and ClO₄). We then study the contribution of intercalants to the electronic band structures in GICs. In addition, the voltage profiles of the dual-ion batteries with different intercalation species, intercalation stages, and battery capacities are also analyzed. The present work is important for the better understanding of graphite-based dual-ion batteries and helpful in development of novel energy storage systems.

1. INTRODUCTION

Rechargeable batteries are undoubtedly one of the most important inventions in the modern society which have fueled the technological advancement in portable electronics such as cell phones, cameras, and laptops. There is promising potential for rechargeable batteries in energy applications such as grid powers and electric vehicles. The surplus energy generated from the renewable energy sources can be collected and stored by the batteries and be used without the constraints from time and place using the grid powers. In addition, the internal combustion engines of most vehicles using the fossil fuels can be replaced by electric motors powered by rechargeable batteries, eliminating the problematic emission of greenhouse gases or other toxic pollutants.

Many types of rechargeable batteries have been developed and commercialized. Among them, lithium-ion batteries (LIBs) have dominated the market because of their high volume and gravimetric energy density. However, the unbridled usage of transition-metal oxides in LIBs and the environmental impact from the abandoned batteries have challenged the continued large scale application of LIBs. Moreover, the safety issues of LIBs have not been completely resolved. Together with their high cost, LIBs are a less-than-ideal solution for the green energy storage with low cost, good environmental friendliness, and safety. Efforts have been devoted to exploring new materials for better battery performance. One example is the graphite material, which has been used as the anode of LIBs as it provides better cycling performance, higher specific capacity, and more negative redox potential than other anode materials such as chalcogenides and polymers. Because of its lamellar structure and redox-amphoteric property, the graphite has been considered as the cathode materials of dual-graphite batteries, also called dual-ion batteries (DIBs) with an emphasis on the importance of both the anions and cations in the charge/discharge processes. The graphite-based DIBs potentially have a higher working voltage, better safety, and lower cost compared to the conventional LIBs. In DIBs, the working principle involves the reversible intercalation of the cations and anions into the graphite electrodes: the simulta-
neous insertion of the electrolyte cations and anions into the graphite anode and cathode happens during charging; the release of these ions from the graphite back to the electrolyte solvent happens during the discharging process.23,24

Graphite intercalation compounds (GICs) formed between the intercalants and the graphite are among the most important materials in DIBs.25 GICs can be described by different stages.25 The stage feature is usually characterized by the stage index, which is the number of graphene sheets between two adjacent intercalated layers. For example, stage 1 GICs correspond to compounds with each graphene interlayer intercalated, while stage 2 GICs are intercalated in every other interlayer. Figure 1 shows the structures of different stages of GICs. The Daumas–Hérold domain theory states that the GICs could consist of many microscopic domains at the same stage, but the intercalants in different domains can be located at different interlayers.26 The stage transition can take place by the diffusion of the intercalants from one domain to another, which has been suggested to be kinetically limited.27

There have been a few experimental studies of staging in GICs and its relation to the DIB performance.23,24,28–31 Besides the common salt ions and organic solvents being adopted in DIBs, the ionic liquids (ILs) with the organic cation such as 1,2-dimethyl-3-propylimidazolium (DMPI+) and the anion chloroaluminate (AlCl4−) have also been used, which could further improve the safety of DIBs with the non-flammable nature of ILs.32,33 Moreover, using the freestanding meso-carbon microbead film cathode, the intercalation process of the PF6− anions has been studied experimentally, and stage 1 was achieved at the charging voltage of 5 V.34 On the other hand, stage 3 was attained with a charging voltage of 2.45 V for AlCl4− anions intercalation, and the flexuous graphite was developed for aluminum ion batteries.35,36 While these works gave important understanding of anion intercalation in GICs and DIBs, density-functional theory simulations are useful to provide microscopic understanding and insights which are difficult to obtain by experiments alone. However, many of the previous theoretical works focused on GICs of a single type. For example, Li–GICs for LIB applications37 and the AlCl4− intercalation for aluminum-ion batteries38 were studied. Moreover, for DIBs, there have been studies on PF6−–GICs39 and TFSI–GICs.40 To provide better comparison of the salts used in DIBs, it is important to systematically study the different cations and anions with the explicit stage models.

In this regard, the stability of the Li, Na, and K–GICs was studied and compared.41 However, as the study was on their application in alkali metal-ion batteries, anion intercalation was not studied. Another work studied a series of GICs including K4C56, Li4C56, Li(DMPO)4C64, Li(DBE)4C110, ClO4C18, and PF6C18.42 While this work has provided key understanding of the GICs, it focused only on the structure and energetics of these GICs, but their application in the DIBs was not discussed.

In our previous work, we studied the on-set voltage of the DIBs by considering initial intercalation of one intercalant into the simplified graphene bilayer models.43 We identified the contribution of extraction, ionization and solvation steps to the on-set voltage. Building on this, we study in the current work the intercalation of multiple intercalants at different stages using the full graphite models. We explore systematically the properties of staging in GICs and their effects on the voltage and specific capacity of DIBs.

In this work, using first-principles calculations, we studied the stabilities of different GICs with the formation energy calculations. We examined the electronic band structures of the intercalated graphite compounds at different stages. A systematic analysis was carried out on the electronic band

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**Figure 1.** Illustration of the structures of stage 4, stage 3, stage 2, and stage 1 GICs.
structures of the staged structures. Also, we compared the voltage profiles of different anion-based batteries upon charging using Li/Na/K metals as the counter electrodes. Last, the voltage profile at different stages of intercalation versus the capacity of the LiPF$_6$-based DIB was examined in detail.

The rest of the paper is organized as follows. In Section 2, the computational details are presented. In Section 3.1, the structural properties of the GICs and the model construction criteria are described. In Section 3.2, we compare the stability of the GICs at various stages and with different intercalants. Following that, the electronic structures of the GICs are examined in Section 3.3. The cell voltages of the batteries based on our staging models are compared in Section 3.4. Finally, we summarize the main conclusions in Section 4.

2. COMPUTATIONAL DETAILS

Calculations of the structural, energetic, and electronic properties were performed using the Plane-Wave self-consistent field (PWscf) module of the Quantum Espresso package$^{43,44}$ with the Perdew–Burke–Ernzerhof (PBE) exchange–correlation functional$^{46}$ and the ultrasoft pseudopotentials method. The DFT-D3 approach was used to treat dispersion corrections. The energy cutoffs were set as follows: for the calculations involving lithium, because of the inclusion of the 1s electrons, we used the high cutoffs of 78 Ry and 624 Ry for the wave functions and the augmented part of the charge density, respectively; for the other calculations, we used the cutoffs of 48 and 480 Ry for the wave functions and the augmented part of the charge density, respectively. These cutoff settings have been tested and adopted in our previous work. The Monkhorst–Pack grids for the Brillouin zone sampling are listed in Table S1 of Supporting Information. For larger supercells, the $k$ points are appropriately scaled down as per the size of the unit cell so that the same level of convergence is maintained. In the calculation of the electronic band structure and density of states (DOS), a much denser set of sampling grid points was applied. For the solvation energy calculations, we used the COnductor-like Screening MOdel (COSMO) solvation model$^{49,50}$ implemented in the NWChem package$^{51}$ together with the 6-31g* basis sets$^{52,53}$ and the PBE functional.

In Section 3.1.1, we constructed the relatively sparsely intercalated stage 1 models, as shown in Figure S1, that is, C$_6$A$_2$ ($A = $PF$_6$, BF$_4$, ClO$_4$, AlCl$_4$, and TFSI) and C$_{24}$M ($M = $ Li, Na and K) to identify the favorable positions of the intercalants in the GICs. To study the in-plane distance between two intercalants, a larger model of C$_{128}$A$_2$ with A represents only PF$_6$, BF$_4$, ClO$_4$, AlCl$_4$, or TFSI as shown in Figure S2a. On the other hand, for the metal atoms, the C$_{72}$M$_2$ model was used which is shown in Figure S2b. For the case of the TFSI intercalant, which is linear in shape, two models of C$_{96}$TFSI with two intercalants separating along the $a$- and $b$-directions as shown in Figure S2c,d, respectively, are taken into consideration of the orientation of the two intercalants.

Based on the position and in-plane distance results, as discussed in Section 3.1.1, we built the stage 1, stage 2, stage 3, and stage 4 models with the unit cell stoichiometries or compositions of C$_{12}$A$_2$, C$_{56}$A$_4$, C$_{54}$A$_4$, and C$_{72}$A ($A = $PF$_6$, BF$_4$, ClO$_4$, or AlCl$_4$) for GICs intercalated by anion molecules. In the case of TFSI–GICs, we used the unit cell models of C$_{32}$TFSI (stage 1), C$_{48}$TFSI (stage 2), C$_{72}$TFSI (stage 3), and C$_{96}$TFSI (stage 4). For the small monoatomic Li, Na, and K intercalants, a higher concentration was considered. For Li–GICs, we adopted the unit cell stoichiometries of C$_8$Li (stage 1), C$_{12}$Li (stage 2), and C$_{18}$Li (stage 3). For Na–GICs and K–GICs, we have the stoichiometries of C$_8$M (stage 1), C$_{12}$M (stage 2), and C$_{24}$M (stage 3), where M = Na or K. The in-plane structures for our unit cells of the stage 1 models (C$_8$Li, C$_8$K, C$_{12}$PF$_6$ and C$_{32}$TFSI) are shown in Figure 2. For a better clarity, the side views of unit cell PF$_6$/TFSI/Li/K–GICs in different stages are shown in Figure S3. Larger supercells of these unit cells were constructed when multiple intercalations were studied as discussed in the later sections. These stoichiometries are in accordance with suggestions in the previous work. Additional justification of adopting these stoichiometries for different stages are provided in Section 3.1.1. All the structures of the stage models were fully relaxed with variable cell relaxation along $z$-direction.

3. RESULTS AND DISCUSSION

3.1. Structural Properties of GICs. 3.1.1. In-Plane Structure. We first examined the in-plane intercalation structures of GICs. We compared the different occupation sites of the intercalant relative to the graphene sheets. The energy difference of the PF$_6$/BF$_4$/ClO$_4$/AlCl$_4$/TFSI intercalants at different positions are within 1 kcal/mol, indicating that there is very little site preference. This is because of the negligible interaction between the molecular intercalants and the graphene sheets due to the large interlayer expansion. In contrast, the Li/Na/K intercalants show a strong preference of locating at the center of the carbon six-member ring between the two graphene sheets. This site preference comes from the strong interaction with the carbon atoms in the graphene layers of graphite. The center position of the metal intercalant allows interaction of the metal with six carbon atoms in the ring and therefore is the most stable site.

Then, we studied the in-plane distance between two intercalants in the same intercalated layer. It is expected that a closer distance would lead to a stronger repulsion. A lower-bound distance is related to the maximum number of intercalants for a specific area of the intercalated layer, corresponding to the maximum capacity of the battery.

As expected, the system with the larger the distance between the two intercalants, the lower the energy. For the molecular
intercalants (PF₆/BF₆/ClO₄/AlCl₄), the distance was measured between the two center atoms of the molecules which was fixed using constraint optimization. Using the system with the intercalants furthest apart as the reference (set its energy as 0 kcal/mol), we plotted in Figure 3 the relative energy (RE) as a function of the in-plane distance between the two intercalants in the same intercalated layer of stage 1 Li–GIC, Na–GIC, K–GIC, PF₆–GIC, BF₄–GIC, ClO₄–GIC, AlCl₄–GIC, and TFSI–GIC. C₂₃TFSI_a and C₂₆TFSI_b represent the systems with the two TFSI intercalants aligning in a- and b-directions, respectively.

![Figure 3](https://dx.doi.org/10.1021/acsomega.0c01950)

**Figure 3.** RE as a function of the in-plane distance between two intercalants in the same intercalated layer of stage 1 Li–GIC, Na–GIC, K–GIC, PF₆–GIC, BF₄–GIC, ClO₄–GIC, AlCl₄–GIC, and TFSI–GIC. C₂₃TFSI_a and C₂₆TFSI_b represent the systems with the two TFSI intercalants aligning in a- and b-directions, respectively.

For the molecular intercalants (PF₆/BF₄/ClO₄/AlCl₄), an in-plane distance of less than 5 Å gives a very large RE (>7 kcal/mol or 0.3 eV) as a result of the strong repulsion between the molecules in the same layer. Meanwhile, the RE becomes less than 2 kcal/mol or 0.1 eV when the distance is larger than or equal to 7.38 Å (here, 7.38 Å is the distance of 3 blocks of carbon rings along a or b axis, in which the lattice parameter is 2.46 Å). Therefore, to avoid the strong repulsion, the in-plane distance should be larger than or equal to 7.38 Å for anion molecule intercalants (PF₆/BF₄/ClO₄/AlCl₄). This minimum distance also justifies the use of C₉₆Li stoichiometry (A = PF₆, BF₄, ClO₄, and AlCl₄) for the fully occupied stage 1 model. For example, a 6 × 6 graphene sheet of 72 carbons can hold at most 4 intercalants, which results in a maximum capacity of 124 mA h g⁻¹ for a fully intercalated stage 1. This theoretical value can also be considered as the upper bound of the maximum capacity. Figure S4a shows the top view and the distance information of the stage 1 model with four PF₆ molecules intercalated. Other molecular intercalants BF₄/ClO₄/AlCl₄ have the same in-plane structure as PF₆, and thus, they are not shown.

For the TFSI intercalant, we tested the in-plane distances in the a- and b-directions. The RE for TFSI–GICs in Figure 3 significantly changes from less than 5 kcal/mol or 0.2 eV to more than 12 kcal/mol or 0.5 eV when the distance is further shortened from 7.38 Å along the a-direction and 8.52 Å along the b-direction. Moreover, we found, upon structural optimization, the linear TFSI intercalants are tilted leading to longer separation among the terminal fluorine atoms of the two TFSIs. Therefore, we concluded that the in-plane distances between the center nitrogen atoms should be 7.38 Å along the a-direction and 8.52 Å along the b-direction with the shortest distance between two nearby fluorine atoms of the two TFSIs longer than 3 Å, as shown in Figure S4b. For the fully intercalated stage 1 of TFSI–GIC, the maximum capacity of 93 mA h g⁻¹ can be achieved under this in-plane distance criterion. Such an arrangement is also in agreement with the use of the stoichiometry C₂₄TFSI (stage 1). Experimentally, the maximum stoichiometries of stage 1 PF₆–GIC, BF₄–GIC, and TFSI–GIC were suggested to be C₂₃₋₄PF₆, C₂₃₋₄BF₄, and C₂₆₋₇TFSI, respectively. The carbon to intercalant ratios are close but slightly larger than those of our present stage 1 models C₁₆A for PF₆, BF₄, ClO₄, and AlCl₄, and C₂₆TFSI. Our present stage 1 models set the upper bounds of the intercalation densities in different cases.

For Li/Na/K GICs, we have found that the distances smaller than 4.26 Å for Li and 4.92 Å for K will lead to significant repulsion (i.e., the relative energies >12 kcal/mol or 0.5 eV) as shown in Figure 3. It is somewhere in between for the case of Na atom intercalants. These lower-bound distances are consistent with the previous experimental work. This is also consistent with the use of the stoichiometries of C₉₆Li and C₉₆K for the stage 1 models. The top views and distance information of the stage 1 Li/K–GIC systems with four atom intercalants are shown in Figure S4c,d, respectively. As discussed in Section 2, for Na–GICs, we adopted the same stoichiometries as the K–GICs. As shown in Figure 3, the repulsion between the intercalated metal is less significant than that between the intercalated molecules. It is expected that the effects of the repulsive interaction on the anode side would be less significant than on the cathode side. As the intercalation of the molecules on the cathode side has much smaller concentrations than those of the metal atom intercalation on the anode side, the capacity of DIBs is determined by cathode intercalation. Our calculations set the theoretical upper bound of the specific capacities, which are in reasonable agreement with the experimentally reported specific capacity of 112 mA h g⁻¹ in the full graphite DIBs. On the other hand, the in-plane structural information will be helpful for setting the models of the staging structures.

The intercalation can cause the change of the stacking sequence of the graphene sheets in the graphite. In our previous work, we found that AB stacking is more favorable than AA stacking for the un-intercalated graphite. For M–GIC (M = Li, Na, and K), AA stacking is preferred. For the A–GICs (A = PF₆, BF₄, ClO₄, and AlCl₄), the two stackings are very close in energy. Based on the results, the following stacking sequences were considered to build the stage models: for the graphite without intercalation, we kept the AB stacking; for the metal atom intercalated sheets, we used AA stacking; and for the graphene sheets intercalating the large molecules, we can choose AA or AB stacking flexibly to reduce the number of graphene sheets needed. Based on the stage 1 unit cell stoichiometries, stages with higher indices were constructed by stacking more intercalated sheets, we used AA stacking; and for the graphene sheets intercalating the large molecules, we can choose AA or AB stacking flexibly to reduce the number of graphene sheets needed. Based on the stage 1 unit cell stoichiometries, stages with higher indices were constructed by stacking more intercalated graphene sheets. In summary, we have considered stage 1/2/3/4 for PF₆/BF₄/ClO₄/AlCl₄/GICs and stage 1/2/3 for Li/Na/K–GICs adopting the unit cell stoichiometries mentioned in Section 2.

3.1.2. Gallery Height. The gallery height d is the distance between two graphene sheets in GICs. The gallery expansion Δd was calculated by subtracting the inter-layer distance (3.5 Å) of the pristine graphite from the gallery height d. Table 1 lists the gallery heights for the GIC unit cells. For the same intercalant, the gallery height and the expansion have almost the same values at different stages of intercalation. However, different intercalants give slight differences in the gallery heights. Interestingly, the AlCl₄/TFSI–GICs have large gallery heights of over 8 Å, probably due to the bulky size of the AlCl₄ and TFSI molecules.
Table 1. Calculated Intercalant Gallery Height $d_i$ and Its Gallery Expansion $\Delta d$ of Various GIC Systems (Unit in Å)

| Intercalant | Stage 4 | Stage 3 | Stage 2 | Stage 1 |
|-------------|---------|---------|---------|---------|
| $PF_6$      | 7.5     | 4.0     | 7.5     | 4.0     |
| $BF_4$      | 7.1     | 3.6     | 7.1     | 3.6     |
| $ClO_4^-$   | 7.3     | 3.8     | 7.3     | 3.8     |
| $AlCl_4$    | 8.8     | 5.3     | 8.8     | 5.3     |
| $TFSI$      | 8.1     | 4.6     | 8.2     | 4.7     |
| $Li$        | 3.7     | 0.2     | 3.8     | 0.3     |
| $Na$        | 4.6     | 1.1     | 4.6     | 1.1     |
| $K$         | 5.4     | 1.9     | 5.4     | 1.9     |

Table 2. Formation Energies (eV) per Molecule Intercalant of the Stage 4, Stage 3, Stage 2, and Stage 1 GICs$^{42}$

| Stage model | $ClO_4^-\text{-GIC}$ | $AlCl_4^-\text{-GIC}$ | $TFSI^-\text{-GIC}$ | $BF_4^-\text{-GIC}$ | $PF_6^-\text{-GIC}$ |
|------------|----------------------|----------------------|----------------------|----------------------|----------------------|
| Stage 4    | $-1.24$              | $-1.53$              | $-2.10$              | $-2.76$              | $-3.07$              |
| Stage 3    | $-1.23$              | $-1.50$              | $-2.08$              | $-2.76$              | $-3.07$              |
| Stage 2    | $-1.20$              | $-1.47$              | $-1.47$              | $-2.73$              | $-3.04$              |
| Stage 1    | $-1.07$              | $-1.33$              | $-1.33$              | $-2.56$              | $-2.87$              |

$^42$The previous theoretical results on the $AlCl_4^-$-GIC$^{38}$ are also shown in parenthesis for comparison.

3.2. Stability of GICs. The stability of cathode GICs was examined by calculating the formation energy per intercalant,

$$E_f = \frac{E[C_m A] - nE[A]}{n}$$  

where $E[C_m A]$ and $E[A]$ are the energies of the anion molecule intercalated GICs, the pristine graphite and the neutral molecule $A$ with $m$ and $n$ denoting the numbers of carbon atoms and molecule intercalants, respectively. The stability of the anode GICs was also examined, using the bulk metal as the reference system. The formation energy is calculated by

$$E_f = \frac{E[C_m M] - nE[M] - E[C_m]}{n}$$

where $E[M]$ is the energy of the metal system per atom. The formation energy is negative for the GIC is thermodynamically stable compared to the states before intercalation (the pristine graphite and the neutral molecule or the metallic state). A more negative formation energy indicates a higher stability of the considered GIC, suggesting the intercalation process is more favorable.

Using the unit cell models of stage 1 ($C_{14}A$), stage 2 ($C_{16}A$), stage 3 ($C_{24}A$), and stage 4 ($C_{28}A$), where $A = PF_6^-, BF_4^-, ClO_4^-$, and $AlCl_4^-$ and stage 1 ($C_{24}$TFSI), stage 2 ($C_{48}$TFSI), stage 3 ($C_{72}$TFSI), and stage 4 ($C_{96}$TFSI) as stated in Section 2, the formation energies of $PF_6^-/BF_4^-/ClO_4^-/TFSI^-\text{-GICs}$ are shown in Table 2. The formation energies are all negative indicating that those GICs are favorable to form. The results of $AlCl_4^-$-GIC are comparable to the ones in the previous theoretical work as shown in the parenthesis. Among them, the $PF_6^-$-GIC has the highest stability, while the $ClO_4^-$-GIC is the least stable one. For the intercalant species effect on the stability of intercalated compound, different molecules show the following descending order: $PF_6^->BF_4^->TFSI^->AlCl_4^->ClO_4^-$. This order agrees well with our previous work on the extraction energy, which reported that $ClO_4^-$ is the most favorable intercalant for extraction or least favorable for intercalation.$^{43}$

Among these GICs, there is a similar trend over different stages: the system with a higher stage index (e.g., stage 4) has a higher stability than the one with a lower stage index (e.g., stage 1). This is expected as the GIC with a lower stage index, especially stage 1, contains a closer intercalated layers along the normal direction of the basal plane of the graphite. This leads to a stronger repulsion between the intercalants at different intercalated layers. However, compared to the effect of different molecule species, the staging effect shows a smaller significance. For $Li/Na/K$-GICs (Table 3), we compared their stability with the same intercalation densities. We found that $Li$-GICs show similar stability with respect to their respective reference states (the pristine graphite and the metallic state), whereas $Na$-GICs have slightly more positive formation energies, indicating its lower stability, thus a less favorable formation of the GICs. Our results on the stability trend of $Li/Na/K$-GICs agree well with the previous theoretical and experimental reports.$^{42,57,58}$ The previous theoretical work states that the instability of the $Na$-GIC comes from the induced strain of the graphite matrix.$^{42}$ Across different stages of intercalation of the same species, the stability shows little difference, suggesting that the stability is mainly determined by the intercalant species.

Above, we have compared the stability of the unit cell model of the GICs with various intercalants and at different stages. Here, we selected the $PF_6^-$-GIC as the representative example to examine the stability during the intercalation process, in which larger models are needed. We built supercells of the $2 \times 2 \times 1$ unit cell of the corresponding stage so that a maximum of four intercalants can be accommodated in the same intercalation layer. The four intercalant sites relative to the graphene sheets are illustrated by the top view picture, as shown in Figure 4a–d. Four stages with different intercalants, namely, stage 1 $C_{24}(PF_6)$, stage 2 $C_{48}(PF_6)$, stage 3 $C_{72}(PF_6)$, and stage 4 $C_{96}(PF_6)$ were constructed. The side-view pictures for stage 1, stage 2, stage 3, and stage 4 with one intercalant are depicted in Figure 4e–h to show the stacking sequences for the staging models. On the other hand, we used the $Li$-GIC supercells to study the stability during the intercalation process of stage 1 and stage 3. We adopted supercells of the $2 \times 2 \times 1$
unit cells, which have stoichiometries of $C_{24(Li)}$ for stage 1 Li-GICs and stoichiometries of $C_{72(Li)}$ for stage 3 Li-GICs.

By calculating the formation energies, we examined the stabilities of Li-GICs and PF$_6$-GICs with different stoichiometries but at the same stage as plotted in Figure 5a,b. For Li-GICs, although the formation energies are very close, the values increase as the number of intercalants increases, suggesting the continuing intercalation becomes less stable. However, for the PF$_6$-GIC, the initial intercalation is much less favorable than the subsequent intercalations. This can be explained by the expansion of the intercalated layer for the first intercalation to accommodate the molecules, which requires a larger energy.

Figure 4. Top views of the PF$_6$-GIC systems with (a) one, (b) two, (c) three, and (d) four intercalants with respect to the graphene sheets and side views of the (e) stage 1, (f) stage 2, (g) stage 3, and (h) stage 4 PF$_6$-GICs with one intercalant for each. Note that for (b–d), the periodic images of the molecules at the edges are also shown.

Figure 5. Formation energies per intercalant of the staging systems as a function of the weight fraction of (a) Li and (b) PF$_6$ intercalants.

Figure 6. Band structure plots for (a) stage 1 Li–GIC and (b) its graphite host without intercalant, and (c) stage 1 PF$_6$–GIC and (d) its graphite host without intercalant. The Fermi level is indicated by the dashed line at 0 eV.
After that, the subsequent intercalation becomes easier in the expanded gallery. This behavior has been found in the intercalation of the neutral species of other anions, such as the TFSI and AlCl4 intercalation as reported in previous works.\textsuperscript{38,59} The first intercalation requires a significantly larger energy because of the initial expansion of the graphene interlayers. The next intercalants are much easier to be accommodated in the expanded gallery until the interlayer is fully intercalated. This suggests that the intercalation process should follow the staging sequence rather than going through non-staging intercalation. Among the different stages of the PF6\textsuperscript{−}−GIC, the stability shows the following order: stage 4 > stage 3 > stage 2 > stage 1. This can be explained by the repulsion of the intercalants at different intercalated layers, which gets larger at stages with lower stage indices. Particularly, stage 1 shows significantly larger repulsion, which leads to the significantly lower stability of the GICs as discussed earlier in this section for the unit cell staging models.

The formation energies for the metal ion−GICs were calculated in reference to the pure metal and the unintercalated graphite. In the case of anion−GICs, the reference systems are the isolated molecule in vacuum and the unintercalated graphite. The isolated molecule is relatively less stable compared to the atom in the metal state. Thus, we obtained the more negative formation energies for the anion−GICs.

### 3.3. Electronic Structures of GICs

We examined the electronic band structures and DOS of the intercalated compounds using the unit cell staging models. To plot the band structure, three paths (\(\Gamma\rightarrow K\rightarrow M\rightarrow \Gamma\rightarrow A\rightarrow H\rightarrow L\rightarrow A\rightarrow K\rightarrow H\), and M→L) were selected to ensure that all symmetry points in the \(k\)-space were considered.

Figure 6 shows the band structure plot for the (a) stage 1 Li−GIC and (b) its graphite host and (c) stage 1 PF6−GIC and (d) its graphite host. The band structures of the other stages of the Li−GIC and PF6−GIC are shown in Figures S5 and S6, respectively. The valence band or the conduction band shifts as the stage changes (a lower index stage number indicates a higher intercalant concentration). In Figure 6, the graphite host has the same structure as the corresponding GIC with the intercalants taken away. The conduction band and the valence band have shifted down and up by around 1 eV for the Li−GIC and the PF6−GIC, respectively, compared to that of the pure graphite hosts. This change supports the fact that there has been charge transfer between the intercalant and the host graphite. During the intercalation process of charging, the Li intercalant gives its outermost electron to the graphite host forming a donating GIC, while the PF6 intercalant obtains an extra electron from the graphite, and thus it is called the accepting GIC.

To further examine the difference in the electronic structure due to intercalation of different species, the DOS results of several considered stage 1 GICs were also calculated as shown in Figure 7. As concluded from the band structure, we can also observe that the position of the valence and conduction bands are shifted down or up for the donating type GICs (such as C6Li, C8Na, and C8K) or the accepting type GICs (such as C18PF6, C18BF4, C24TFSI, C18AlCl4, and C18ClO4) respectively. Moreover, it is shown that the graphene sheets of the graphite dominate the states near the Fermi level for stage 1 C6Li, C18PF6, and M−L.
C14BF4 and C24TFSI. There is a larger contribution for C8Na and C8K from the intercalant, but the graphene sheets still dominate as shown in Figure 7b,c. On the contrary, the main contributor to the electron states near the Fermi level becomes the intercalant for C14AlCl4 and C14ClO4. Specifically, the Cl and O mainly contribute to the electron states near the Fermi level for stage 1 C14AlCl4 and C14ClO4 as clearly shown in Figure S8a,b. This variation in the electronic structure could be related to the lower stability of stage 1 AlCl4−GIC and ClO4−GIC as shown in Table 2 of Section 3.2. The difference in the extraction energy is related to the energy of the orbitals of the intercalants in the GICs. As discussed in our previous work, upon intercalation, the molecular species take electrons from the graphite framework to form the anions (e.g., AlCl4−, ClO4−, and PF6−). Based on our DOS results (Figure 7), the intercalated AlCl4− and ClO4− have a significant contribution near the Fermi level. For extraction from the graphite, the AlCl4− and ClO4− anions lose the electron more easily to form the neutral species. 

3.4. Voltage. We calculated and compared the voltages of the DIBs with the Li/Na/K salts involving the PF6−/BF4−/TFSI−/AlCl4−/ClO4− anions at different stages of the GICs using the unit cell stage models shown in Figures 2 and S3. The Li/Na/K metal was chosen as the anode here. Specifically, using the Li salt as an example, the voltage of the DIBs at a particular stage of the GIC can be obtained by

\[
V = \frac{E_{CA} + E_{Li} - E_{CA} - E_{Li^+} - E_K}{e}
\]

(3)

where \(e\) is the elementary charge, \(E_{CA}\), \(E_{CJ}\), and \(E_{Li}\) are the energies of the GIC at that stage, of the graphite, and of the metal Li (per atom), respectively. \(E_{Li}\) and \(E_{A}\) are the energies of the solvated cation Li+ and anion A−. For the calculation of the voltages at different stages in all the systems considered, the density functional theory (DFT) energies were calculated from the PWscf part of the Quantum Espresso package. The NWChem package was used to obtain the solvation energies of the ions, which are the differences between the total energies of the dissolved and undisolved ions. The same scheme was adopted for the calculation the intercalation energies and the average voltages for the LiPF6 salt cells.

The most common electrolyte solvent is the mixture of organic carbonates, in which the mixing of the linear carbonate with a low dielectric constant and the cyclic carbonate with a high dielectric constant results in a solvent with a moderate dielectric constant. Here, we used the dielectric constant of 50 for the COSMO solvation energy calculation. The calculated voltages are shown in Table 4. For all the stages considered, the voltage stays more or less constant until stage 1, which has a higher voltage than the other stages. This larger change is because each interlayer is fully occupied at stage 1, which leads to strong repulsion between the intercalants. The repulsion between the intercalants is significantly smaller beyond the nearest graphene interlayers. Moreover, the salts with the TFSI anion generally give a lower voltage. This is because of the low solvation energy of the TFSI anion and the solvation process mainly contributes to the voltage for different anions as concluded in our previous work. For different cation salts, the Na salt-based batteries have lower voltages than Li and K salt-based batteries by 0.3 V because of the larger energy difference between the Na metal state and the dissolved Na+. Specifically, this energy difference comes from several steps: (1) isolation of single atom from the metal; (2) ionization of the single atom; (3) solvation for dissolving the ion. We compared the energy differences of each step as shown in Table S2. We found that it is the moderate energy difference of each step of the Na case that gives the DIBs with the Na salt a lower voltage.

We have compared the effect of different stages and intercalant species on the voltage using the unit cell stage models. Here, we studied the intercalation energies and computed the average voltages using the \(2 \times 2 \times 1\) supercells of the PF6−-GIC with successive intercalation of 1 to 4 intercalants at each stage. Four stages with different numbers of intercalants, namely, stage 1 C14(PF6)−1−4, stage 2 C14(PF6)−1−4→3 C216(PF6)−1→4, and stage 4 C188(PF6)−1−4, corresponds to the specific capacity of up to 124 mA h g−1. We define the intercalation energy as the energy required to drive the intercalation process. It was calculated by the equation

\[
\Delta E = E_{CA} - E_{Li} - E_{CA_{m-1}} - E_{Li^+} - E_K
\]

(4)

where \(m\) is the intercalant number (\(m = 1, 2, 3, \) and 4) and \(E_{CA_m}\) is the total energy of the intercalated compound with \(m\) molecule intercalants. Therefore, \(E_{CA_m}\) represents the energy of the pure graphite, that is, \(E_{CA_m} = E_{CA}\). Here, \(A\) represents the PF6 molecule. The intercalation energies for the four intercalation processes at the same stage, including the first intercalation, second intercalation, third intercalation, and the fourth intercalation are shown in Figure 8. For each stage, the first intercalation requires a significantly larger intercalation energy (by around 2 eV) than the subsequent intercalations do. Also, the intercalation energy increases slightly with further intercalation of the subsequent intercalants. This is expected as the first intercalation needs a much larger energy to overcome the van der Waals interaction between the two neighboring graphene sheets. Once the gallery height expands, the subsequent intercalation becomes easier compared with the first intercalation. On the other hand, the continuing intercalation has to overcome the Coulomb repulsion between the intercalants in the same interlayer. The more the intercalants accommodated, the stronger the repulsion to overcome. This results in a higher intercalation energy. The same trend is observed for all the stages. Comparing the energies of different stages, there are differences between the total energies of the GICs at that stage, of the graphite, and of the metal Li (per atom), respectively. \(E_{Li}\) and \(E_{A}\) are the energies of the intercalated compound with \(m\) molecule intercalants. Therefore, \(E_{CA_m}\) represents the energy of the pure graphite, that is, \(E_{CA_m} = E_{CA}\). Here, \(A\) represents the PF6 molecule. 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The more the intercalants accommodated, the stronger the repulsion to overcome. This results in a higher intercalation energy. The same trend is observed for all the stages. Comparing the energies of different
stages, the intercalation energies among stage 4 to stage 2 are similar because of the weak repulsion between the intercalants beyond the nearest inter-graphene layers. However, the energy change from stage 2 to stage 1 is significantly larger because of the stronger repulsion between the intercalants in the nearest inter-graphene layers. This is also reflected in the voltage change at different stages discussed below.

The average voltage is computed by the equation

\[ V = \frac{E_{GIC} + mE_{Li} - E_{A} - mE_{Li^+} - mE_{A^+}}{me} \]

(5)

where A represents PF₆.

The average voltages of different stages with respect to the specific capacities are shown in Figure 9 and Table S3. The calculated voltage varies from 4 to 5.5 V, in good agreement with the experimental results.²⁴,⁶⁰ The voltage increases when changing from stage 4 to stage 1 for the same capacity such as 15.5, 31.0 and 62.0 mA h g⁻¹ indicated by the vertical dashed lines in Figure 9. This is due to the increasing Coulomb repulsion between the intercalants in different intercalated interlayers at the stage with a smaller index. However, the change from stage 2 to stage 1 is significantly larger than those from stage 4 to stage 3 to stage 2. This larger change is because every interlayer is fully occupied at stage 1, which leads to significantly stronger repulsion. The screening effect dominates only for stage 2/3/4. On the other hand, the high voltage at the beginning of each stage is because of the high intercalation energy for the first intercalation.

One should also note that the reason for the rising voltage during the charging process in cyclic voltammetry (CV) experiments can be multiple. In this work, we considered the stage feature and its relation to the voltage. Our calculations showed that significant voltage change only occurs between the transition from stage 2 to stage 1. Also, the changes for other stage transitions are small due to screening from the graphene layers. On the other hand, other factors such as crystal imperfection (defects, grain sizes), the charging rate, salt concentration, and electrolyte composition can play a role in determining the peaks of the CV curves. Further studies are needed to investigate the detailed mechanisms that lead to the voltage change.

4. CONCLUSIONS

The novel concept of the graphite-based dual-ion battery provides a good alternative for future energy storage with good environmental friendliness, low cost, and high voltage. In this class of batteries, GICs are the active materials in which the staging properties are closely related to the specific capacity and the voltage of the battery. Different types of intercalant candidates are also needed to be carefully examined. In this work, we studied the staging of the GICs and their corresponding DIBs in detail. These include their structural, electronic properties and the voltage profiles. The conclusions are summarized below:

(i) The in-plane structure of the intercalated layers was examined by energy comparison. The in-plane distance of the intercalants is closely related to the theoretical upper bound of the specific capacity, which can be determined from the in-plane distance limits. The calculated capacity was found to be in good agreement with the experimental reported specific capacity.

(ii) On the cathode side, we examined the stability of the GICs at different stages with different intercalant species. We found that the favorability of intercalation of the molecular intercalant into the graphite follows the descending of PF₆ > BF₄ > TFSI > AlCl₄ > ClO₄. On the anode side, we found that the Li-GICs and K-GICs are of similar stability but Na-GICs are less favorable to form. For both the cathode GICs and anode GICs, the staging shows less effects on the stability compared to the effects of the intercalant type. Among the different stoichiometries of a certain stage, the initial intercalation is the least favorable step because of a larger energy required to expand the graphene interlayer distance.

(iii) For the electronic structure, the electronic bands shift down and up compared to those of the graphite host for the stage 1 Li-GIC as the donor GIC and the PF₆-GIC as the acceptor GIC, respectively. Moreover, the contribution near the Fermi level varies for different GICs. For C₈Li, C₁₈PF₆, C₁₈BF₄ and C₂₄TFSI, the graphene sheets are the main contributor to those states. For C₈Na and C₈K, the contribution from the intercalants is larger but those states are still dominated by the graphene sheets. On the other hand, the contribution from the intercalants becomes significantly more dominant for C₁₈AlCl₄ and C₁₈ClO₄ which may be related to their lower stability.

(iv) For the voltage of the DIBs at different stages, it was found to increase from stage 4 to stage 1. The change from stage 2 to stage 1 is significantly larger than those from stage 4 to stage 3 to stage 2 because of the stronger repulsion between the intercalants at stage 1. The repulsion is significantly smaller beyond the nearest inter-graphene layers for stage 2/3/4 because of the screening effect.
dominates. For the salt species, the cells using the TFSI− anion salts or the Na+ cation salts have smaller voltages than other cells. We also considered multiple intercalations at the same stage. With the PF6 molecule as an example, we found that the first intercalation requires a significantly higher intercalation energy because of the initial expansion of the graphene interlayers, resulting in a higher voltage for this step. Although after first intercalation the overall average voltage gets smaller because of the significant energy drop, the subsequent intercalations need to overcome the repulsion from already intercalated intercalants. Thus, the intercalation energy gradually increases again.

■ ASSOCIATED CONTENT

† Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c01950.

k-point sampling grids for the calculated stage models, top views of different positions of the intercalant in the graphite, top views of the models with different in-plane distances, side views of the unit cell stage models illustrating the staging sequence, top views of the stage 1 structures, and electronic band structures of Li−GIC (PDF)

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Notes
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