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A combinatorial study of electrochemical anion intercalation into graphite

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Abstract

Dual-ion batteries are considered to be an emerging viable energy storage technology owing to their safety, high power capability, low cost, and scalability. Intercalation of anions into a graphite positive electrode provides high operating voltage and improved energy density to such dual-ion batteries. In this work, we have performed a combinatorial study of graphite intercalation compounds considering four anions, namely hexafluorophosphate (PF_6^-), perchlorate (ClO_4^-), bis(fluorosulfonyl)imide (FSI^-), and bis(trifluoromethanesulfonyl)imide (TFSI^-), via first-principles calculations. The structural properties and energetics of the intercalation compounds are compared based on different sizes, geometries, and the physical and chemical properties of the intercalated anions. The staging mechanism of anion intercalation into graphite and the specific capacities, and voltage profiles of the intercalated compounds are investigated. A comparison regarding battery electrochemistry is also done with available experimental observations. Our calculated intercalation energies and voltage profiles show that the initial anion intercalation into graphite is less favorable than subsequent ones for all the anions considered in this study. Although the effect of the size of anions in a graphite cathode on various properties of the intercalated compounds is not as significant as the size of cations in a graphite anode, some distinction between the studied anions can still be made. Among the studied anions, the intercalation compounds based on PF_6^- are the most stable ones. These PF_6^- anions cause relatively small structural deformations of the graphite and have the highest oxidative ability, highest onset voltage, and highest diffusion barrier along the graphene sheets. The overall small diffusion barriers of the anions within graphite explain the high rate capability of dual-ion batteries.

Introduction

We are currently in an era of energy transition driven by renewable energy sources like solar, wind, hydropower, and biomass [1–5]. Increased sustainable electricity production has fostered demand for environmentally friendly and efficient energy storage technologies. Rechargeable batteries and supercapacitors are two main energy storage technologies [6–9], which store electrochemical and electrical energies, respectively. Among the rechargeable battery technologies, Li-ion battery (LIB) is the predominant one and is found in almost all portable electronic devices and electric vehicles [10, 11]. In spite of the high energy density (350 W h kg^{-1}) [12] and open-circuit voltage (3.6 V) [13], LIBs cannot keep up with the growing demand for energy in the market, particularly for large-scale grid storage, where intermittent energy from solar, wind, and ocean waves needs to be stored [14]. The burden on global Li resources, cost of transition metals, and safety concerns are also putting limits on the future use of conventional LIBs [15].

There has been a constant search for alternate storage technologies which can fulfill high performance criteria such as high energy and power density, long cycle life, high coulombic efficiency, and fast charging rate. The focus of battery research has also been shifted towards sustainability, less CO₂ release during battery production, and safety. Some of the new energy storage systems developed so far are Li-S, Li-Si alloy, metal-air, all-solid-state, and dual-ion batteries (DIBs) [16–19]. Among these, DIBs are emerging as a potential alternative to LIBs in grid-based storage, where battery volume is not a primary issue [20]. Other advantages of DIBs such as safety, long cycle life, scalability, and large power range make them a promising technology [21–24]. DIBs are non-rocking-chair type batteries, i.e. cations and anions simultaneously get stored in electrodes during charging and are released back into the electrolyte during discharging. The electrolyte concentration keeps changing during the charge-discharge process. Therefore, in practice, the power density and specific capacity of an electrochemical cell depends on the type and concentration of the electrolyte as well. A special type of DIB in which both the cathode and the anode are made up of graphite is referred to as a dual-graphite battery (DGB) [20, 21, 25]. Being redox-amphoteric in nature, graphite acts as a donor-type electrode (anode) for metal ion intercalation (Li⁺, Na⁺) at low redox potentials and as an acceptor-type electrode (cathode) for anion intercalation (PF₆[−], BF₄[−], FSI[−], AlCl₄[−]) at high redox potentials [25, 26].

The quest for high energy density and long cyclability of batteries often faces challenges, for example volume change of the electrode material due to the insertion and extraction of ions [27]. During anion intercalation, there is a huge volume expansion in graphite cathodes (approx. 130% for PF₆C₁₈) compared to in graphite anodes of LIBs (approx. 10% for LiC₆) [28]. The strain induced in graphite cathodes due to the insertion and extraction of anions can lead to reduced specific capacity, electrode fracture, or exfoliation of the graphite, as well as unbinding of the current collector. There are several binders, such as alginate (Alg), sodium carboxymethyl cellulose, and polyvinylidene difluoride, that are used to prevent such structural deformation of the graphite cathodes [29, 30]. Additionally, the formation of a protective cathode-electrolyte interface can prevent solvent co-intercalation and therefore reduce graphite exfoliation, which in turn enhances cycling stability [31].

To improve the electrochemical properties of a DIB, an in-depth understanding of the staging mechanism of intercalant incorporation into graphite is important. Cation intercalation in graphite negative electrodes of conventional LIBs has been extensively studied [32–35]. Recently, anion intercalation in graphite positive electrodes has also been studied for various anions, both experimentally and theoretically [25, 26, 36–43]. Although previous theoretical studies have provided a firm base for the present intercalation studies, it is somewhat difficult to compare results from studies performed by different research groups [44, 45]. The reasons for such differences are the employment of different computational approaches and the use of different system sizes (which is an issue unique to these intercalation compounds). Hence, a unified approach is needed in order to compare various anions with regard to their graphite intercalation properties. Similarity in computational methodologies and analysis techniques provide ease in comparing the structural, energetic, and electrochemical properties of the graphite intercalation compounds (GICs).

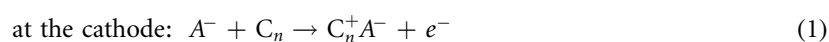
In this study, we have considered four anions, namely ClO₄[−], PF₆[−], FSI[−], and TFSI[−], with varied sizes, geometries, and conformations as intercalants in a graphite cathode. A systematic study of intercalation stages has been performed based on first-principles calculations. The effects of anion size and chemical nature on various properties of the intercalation compounds, such as volume change of the graphite cathode upon anion intercalation, stability of the intercalation compounds, and their electrochemical characteristics in different stages of intercalation, are discussed. Since ionic mobility within the electrode material is very important to assess the rate capability of a battery, detailed diffusion pathways and barriers of anions within graphite have been investigated. Furthermore, a qualitative as well as quantitative estimation of the ability of anions to oxidize the graphite cathode has been conducted. Among the studied anions, PF₆[−] performs better in terms of oxidizing the graphite cathode, but it diffuses slower than other anions. The combinatorial study of anion intercalation into graphite based on similar computational approaches enables better understanding for selecting electrolyte salts, which may be single- or multi-anion, and would improve the energy density and cycling stability of DIBs.

Computational details

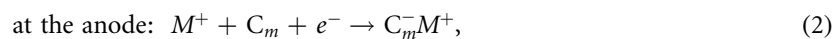
First-principles-based density functional theory (DFT) calculations were performed using the projector augmented wave method [46, 47], as implemented in the Vienna Ab initio Simulation Package (VASP) [48]. Exchange and correlations effects are described within the generalized gradient approximation (GGA), as parameterized by the Perdew–Burke–Ernzerhof (PBE) exchange–correlation functional [49]. Grimme’s DFT-D3 correction scheme [50] was used to include the effect of weak van der Waals (vdW) interactions between the graphene layers. A cutoff energy of 400 eV was used for the plane wave basis set. Electronic degrees of freedom were allowed to relax until a convergence criteria of 10^{−5} eV was met, and the atomic geometries were

considered to be converged when the residual forces were smaller than 0.01 eV/Å. Monkhorst–Pack Gamma-centered k-point grids [51] were used for different supercell sizes (see table S1 of the supplementary data available online at stacks.iop.org/MRX/8/085502/mmedia). We first optimized a pristine graphite AB-stacked unit cell using various exchange-correlation functionals with dispersion corrections. The optimized bulk lattice parameters, as obtained from PBE-GGA with DFT-D3, are 2.465 Å and 3.355 Å, corresponding to the in-plane lattice constant and interlayer distance, respectively. These calculated values closely match the experimental results [52]. We have considered four anions as intercalants in this study, which are labeled as A^- (A^- : PF_6^- , ClO_4^- , FSI^- , and TFSI^-). The GICs are modeled by inserting neutral molecules (A : PF_6 , ClO_4 , FSI , and TFSI) into the graphite host lattice. The climbing image nudged elastic band method (CI-NEB) [53] was used to study the kinetics of ion diffusion within the graphene layers. We also carried out Bader charge analyses [54, 55] to quantitatively estimate the amount of charge transfer between the anions and the graphite host. It has been observed by us and also shown in the works of others that the use of different unit cells to represent graphite host lattices (as reference systems) leads to different specific capacities and voltages [36, 43, 56]. Hence, we explicitly mention the size of the reference system in the relevant section of this manuscript. In most of the GICs studied here, we have used AB graphite stacking. In cases in which AA stacking is equally stable as AB, we have considered the former in order to minimize the computational load.

In DIBs, cations and anions from the electrolyte get reversibly intercalated into the electrodes during charging. The cathode (positive electrode) gets oxidized and the anode (negative electrode) gets reduced during charging. The half-cell reactions involved in a DIB (here a DGB) are



and



where A represents PF_6 , ClO_4 , FSI , or TFSI and M represents typically an alkali metal cation (Li, K). The intercalation compounds are represented as $C_n A$ and $C_m M$, where C_n and C_m represent graphite.

In GICs, the distance between adjacent graphene layers hosting the intercalated ions is referred to as the gallery height. This is an important parameter for assessing the amount of volume expansion of the electrode as a result of ion intercalation. If N is the number of graphene layers in the unit cell, the average gallery height can be calculated as

$$\text{avg. gallery height} = \frac{1}{N}(\text{total height of a GIC unit cell}), \quad (3)$$

whereas the volume expansion in a GIC corresponds to

$$\% \text{volume expansion} = \frac{\text{avg. gallery height} - \text{interlayer distance in pristine graphite}}{\text{interlayer distance in pristine graphite}} \times 100. \quad (4)$$

The stability of a GIC is estimated by the intercalation energy, which is calculated by the following expression

$$E_{\text{int}} = \frac{1}{x}(E[C_n A_x] - E[C_n] - xE[A]), \quad (5)$$

where $E[C_n A_x]$, $E[C_n]$, and $E[A]$ are the total energy of the intercalated compound, bulk graphite, and isolated neutral molecule, respectively, and x is the number of ions intercalated.

The equilibrium cell voltage of an electrochemical cell is determined by the difference in ion chemical potential at the cathode and anode [57]:

$$V = -\frac{\mu_A^{\text{cathode}} - \mu_M^{\text{anode}}}{zF}, \quad (6)$$

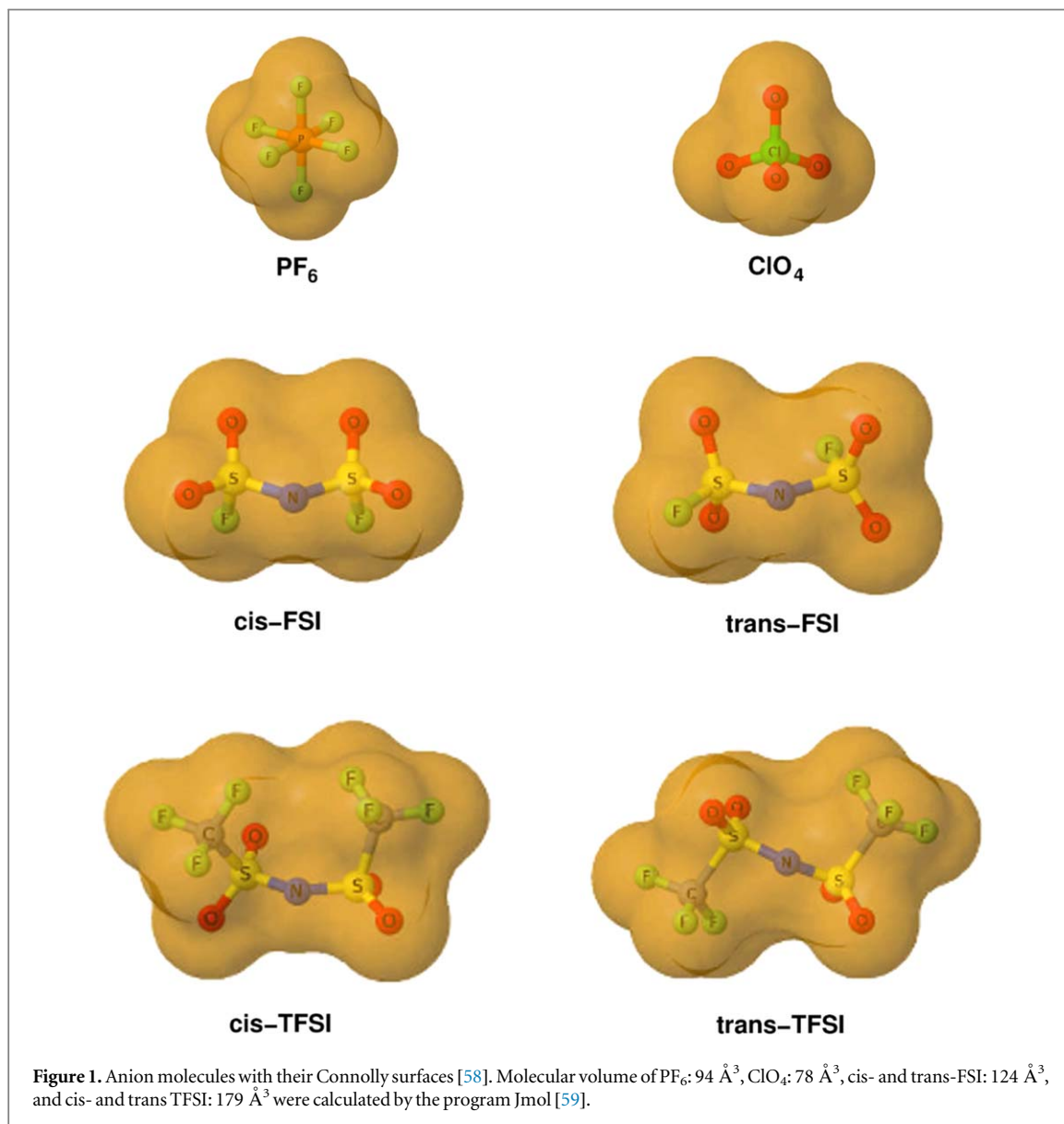
where z is the amount of charge transferred during the redox reaction and F is Faraday's constant (96485 C mol⁻¹). For a half-cell reaction as in (1), μ_M^{anode} is assumed to be zero. The average voltage for a finite number of ions transported can be written in terms of free energy change (ΔG_r) of the intercalation process, i.e.

$$\bar{V} = -\frac{\Delta G_r}{zF}. \quad (7)$$

At the DFT level of theory, the entropic and volumetric contributions to the reaction free energy are neglected and ΔG_r is approximated as ΔE_r , where ΔE_r is the total energy change for the intercalation process [57]. Under these approximations, the average voltage of an intercalation process is computed as

$$\bar{V} = -\frac{E[C_n A_x] - E[C_n] - (x)E[A]}{xe}, \quad (8)$$

where $E[C_n A_x]$, $E[C_n]$, and $E[A]$ are DFT total energies as defined earlier.



The gravimetric specific capacity of an electrode is defined as the amount of charge stored per unit molecular weight of the electrode material. It is given as

$$C = \frac{n \times x \times F}{3.6 \times M_w}, \quad (9)$$

where n is the number of electrons travelled through the external circuit per ion, x is the number of ions intercalated, and M_w is the molecular weight (in g mol⁻¹) of the host electrode.

The interaction between the host electrode and guest ions is studied by the change in the charge density distribution upon ion storage in an electrode. The difference in the electron density between the graphite host and the anion upon intercalation is given as

$$\Delta\rho = \rho(C_nA) - \rho(C_n) - \rho(A), \quad (10)$$

where $\rho(C_nA)$, $\rho(C_n)$, and $\rho(A)$ are electron density of the GIC, graphite, and the anion, respectively.

Results and discussion

Structural characteristics of GICs

In this study, we have compared the stability and structural and electrochemical characteristics of four anion-GICs. The anions considered in this study differ in their sizes, compositions, and geometries. While ClO₄⁻ is tetrahedral, PF₆⁻ is octahedral. FSI⁻ and TFSI⁻ are linear and exist in cis and trans conformations. These anions along with their conformers (where applicable) are shown in figure 1.

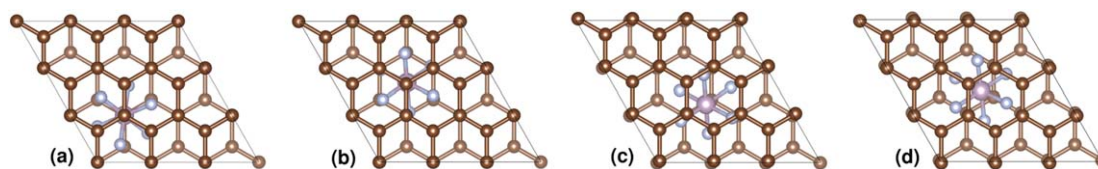


Figure 2. Optimized geometries of PF_6 at four intercalation sites within the AB-stacked graphite unit cell. (a) ontop (b) hollow, (c) bridge1, and (d) bridge2. P, F, and C atoms are represented as violet, purple, and brown spheres, respectively.

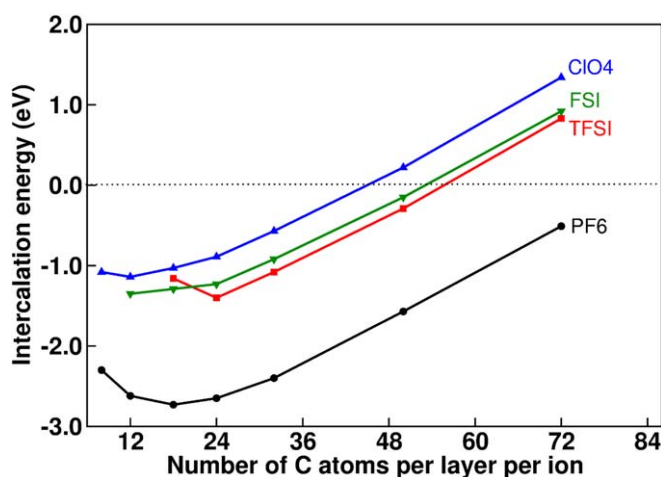


Figure 3. Intercalation energy per anion with respect to number of C atoms per graphene layer.

The geometries of isolated molecules were optimized by placing each molecule in a large cubic box of length 20 Å. In the case of the FSI and TFSI ions, two types of structural conformations were observed, viz C1 conformer (cis) and C2 conformer (trans) [60, 61]. It is possible that an intercalation/de-intercalation process can change the molecular geometries, particularly for larger ions like FSI and TFSI. We calculated bond lengths, angles, and dihedral angles of the conformers of FSI and TFSI in their solid crystal structures (which exist with an alkali metal cation) in their isolated states (before intercalation) and after intercalation into graphite. These details are tabulated in supplementary table S2. It can be inferred from the energy comparison of both conformers that the C2 conformer is slightly more stable than the C1 conformer for FSI and that C1 is more stable than C2 for TFSI. Owing to the small energy difference, it is possible that these conformers coexist in equilibrium during intercalation/de-intercalation as they do in their liquid state [61]. For further studies, we have considered the C2 (trans) conformer for FSI and C1 (cis) conformer for TFSI as the intercalant structures.

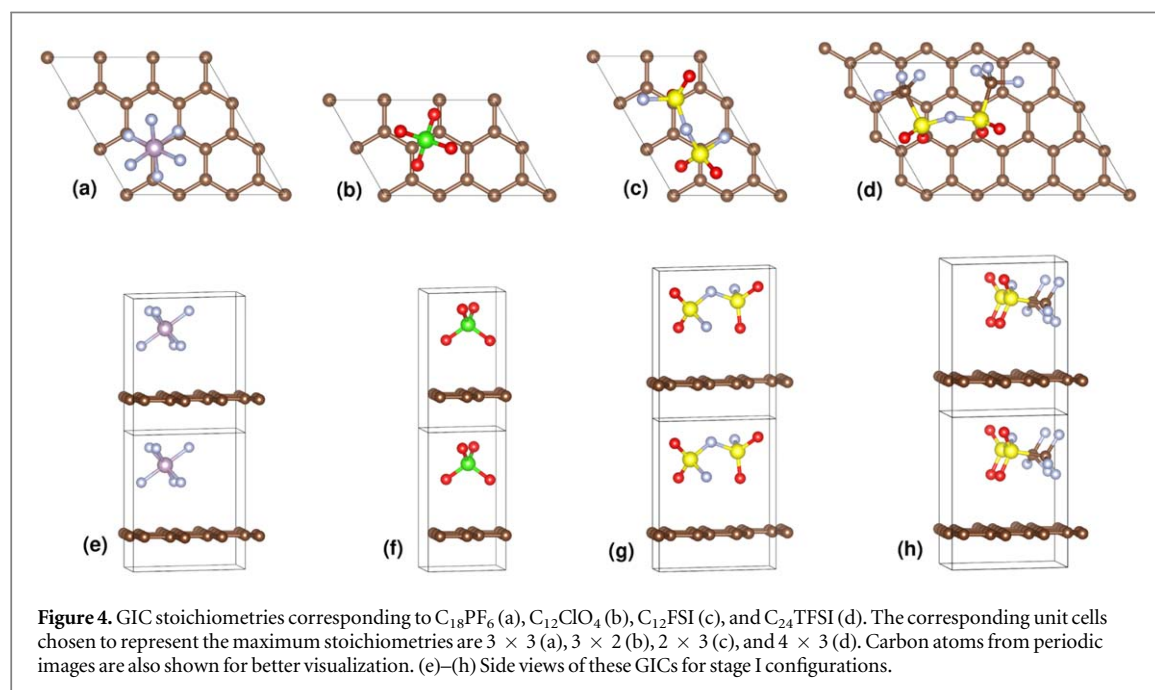
Intercalation sites

First, we have compared the energetics of four possible intercalation sites for the anions. These sites are labeled ontop, hollow, bridge1, and bridge2, and they are shown in figure 2 (for PF_6 -GIC as an example). It was found that all the considered intercalation sites are almost equally probable for a particular anion. To be precise, ontop is the most favorable site for PF_6 and FSI, hollow is the most favorable site for TFSI, and bridge1 is for ClO_4 , respectively.

Stoichiometry of GICs

A graphite intercalation compound is represented as C_nA , where A is the intercalant and n is the number of carbon atoms per graphene layer and intercalant. This number is directly related to the specific capacity and energy density of a particular ion-electrode pair. We estimated this number by varying the number of C atoms per graphene layer and anion. The calculated intercalation energies as a function of n for all the anions are shown in figure 3. It is to be noted that we have considered the energy per C atom of primitive bulk graphite as a reference and scaled this number according to number of C atoms in the GICs. Furthermore, AA-stacked graphite unit cells are considered in their stage I GIC configurations.

From the graph in figure 3, it can be seen that the optimum ratio of number of C atoms to the anion are 18, 12, 12, and 24 for PF_6 , ClO_4 , FSI, and TFSI, respectively. Our estimated stoichiometries for the GICs match with previous theoretical estimations [36, 45]. Note that experimentally observed stoichiometries for GICs may be



slightly different. For example, our experimental measurements show that the stoichiometries for PF_6 -GIC and FSI-GIC are $C_{23}PF_6$ and $C_{23}FSI$, respectively. Stoichiometry for TFSI-GIC is estimated to be $C_{26-27}TFSI$ [37, 62]. There can be many factors responsible for the difference between experimental estimations and theoretical predictions such as electrolyte salt concentration, type of solvent, and solvent co-intercalation, to name a few [37]. Furthermore, the maximum theoretical capacities for PF_6^- , ClO_4^- , FSI-, and TFSI-GICs are 124, 186, 186, and 93 $mAh\ g^{-1}$, respectively, as obtained from our fully intercalated stage I models. These values set an upper bound for the maximum capacities. In figure 4, the unit cells corresponding to the obtained GIC stoichiometries are shown.

Further, if a rough estimate of a sphere's radius is made from the calculated molecular volume of each ion (see figure 1), and considering the fact that FSI and TFSI ions are linear, the obtained stoichiometries for the respective GICs seem reasonable.

Figure 3 also shows that when anion concentration is low (higher number of C atoms per anion), it is difficult for the anions to get intercalated into graphite (positive or less negative intercalation energy). As anion concentration increases (fewer C atoms per anion), intercalation becomes more favorable up to a certain number of C atoms (stoichiometry as stated above). It can also be seen that out of the four anions considered here, PF_6 forms the most stable GIC and that the GICs of FSI, TFSI, and ClO_4 are almost equally stable with one another.

Volume expansion of electrode and its mechanical stability

A unique feature of a graphite electrode is that it exists in various staged phases with the intercalated ions [63]. This happens as a result of a balance between vdW forces (acting between graphene layers) and coulombic forces (acting between graphene layers and the intercalants). For illustration purposes, different stages of anion intercalation in graphite are depicted in supplementary figure S1. Based on the maximum stoichiometries obtained in section, we constructed models for stage I, II, III, and IV GICs. Since AB stacking is found to be slightly more stable than AA for all the stages, we have chosen the former to build these models. The models for PF_6 -GICs are $C_{36}(PF_6)_2$, $C_{36}(PF_6)_1$, $C_{108}(PF_6)_2$, and $C_{72}(PF_6)_1$ for stage I, II, III, and IV, respectively. For TFSI, the models are $C_{48}(TFSI)_2$, $C_{48}(TFSI)_1$, $C_{144}(TFSI)_2$, and $C_{96}(TFSI)_1$. The models for FSI and ClO_4 are $C_{24}(A)_2$, $C_{24}(A)_1$, $C_{72}(A)_2$, and $C_{48}(A)_1$, where A is FSI or ClO_4 . In table 1, the calculated gallery heights of the GICs are listed along with the reference values from experiments. It is to be noted that the gallery height for a particular intercalant would be the same in different stages. As can be seen from table 1, the larger the size of the intercalant, the larger the gallery height. Given that the size of these anions (intercalants) is smaller than the gallery heights in the corresponding GICs, fast and smooth diffusion of these anions along planes of graphite is expected. This will be reflected in our diffusion studies discussed later. For comparison, the interlayer distance of pristine graphite is 3.35 Å and reported gallery heights of LiC_6 and KC_8 are 3.7 and 5.4 Å, respectively [36].

To prevent electrode fracture and to have a long cycling stability, there should be minimum structural deformation of the electrode when it stores ions during charging and releases them during discharging. Using

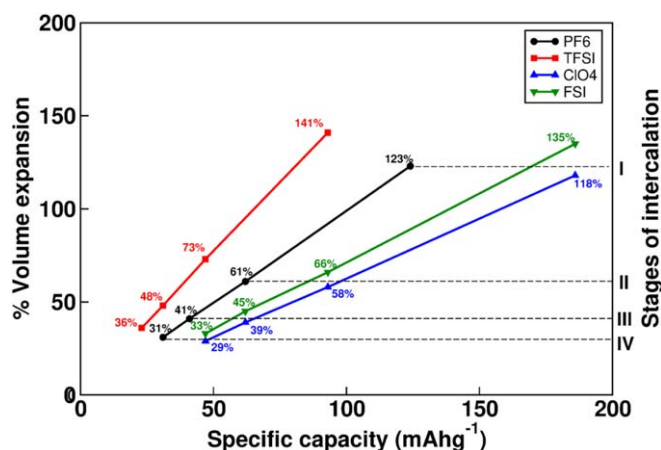


Figure 5. Percentage volume expansion of the graphite cathode as a result of anion intercalation versus specific capacity. Stage indices for PF₆-GIC are highlighted on the right side of the y-axis.

Table 1. Gallery height (in Å) for GICs considered in this study.

Intercalant	Gallery height (Å)	
	Present work	Experiments
ClO ₄ -GIC	7.29	7.34 [64]
PF ₆ -GIC	7.47	7.75 [37]
FSI-GIC	7.83	7.85 [38]
TFSI-GIC	8.12	8.21 [65]

(4), we calculated the amount of volume change in the graphite cathode as a function of increasing anion concentration (increasing specific capacity). The percentage of volume change in the graphite cathode during anion intercalation is shown in figure 5.

In figure 5, low specific capacity corresponds to a GIC with high stage index. As more anions get intercalated, the specific capacity increases and the stage index of the GIC becomes lower. As expected, TFSI-GICs have the largest volume expansion (141% in stage I intercalation) owing to the large size of TFSI. They are followed by the GICs of FSI, PF₆, and ClO₄, sequentially. Experimental percentage volume expansions reported for stage I TFSI, FSI, PF₆, and ClO₄ are 140%, 134%, 130%, and 118%, respectively [37, 38, 64, 65].

Stability of GICs in different stages

We also calculated the intercalation energies of GICs in various intercalation stages using the models mentioned in section. In table 2, the intercalation energies and the corresponding theoretical specific capacities at each stage are listed. As stated earlier, the reference graphite structure affects the intercalation energy and capacity values, therefore it is important to specify that in these stage models, we have used the total energy per C atom of primitive bulk graphite and scaled this number for the GICs.

As can be seen from table 2, the stability order of the anion GICs is PF₆ > TFSI ≥ FSI > ClO₄. There is only a marginal difference in the intercalation energy values for a given anion in the different stages. However, it appears that stage II and III are the dominant stages. In reality, a dominant stage depends on experimental conditions such as temperature, the number of discharge cycles, cut-off voltage, electrolyte salt concentration, and electrolyte-electrode combination. It is worth comparing our trend in the intercalation energies with previous theoretical work. Zhou *et al* [36] have obtained similar intercalation energy values for PF₆- and TFSI-GICs (shown in parentheses in table 2), but they found that the GIC with high stage index is more stable than the GIC with low stage index. The reason for this difference might lie in their choice of graphite stacking for the anion intercalation. While they had considered AA or AB stacking flexibly depending on whichever minimized the number of graphene layers needed for the intercalation, we strictly considered AB stacking for our stage models.

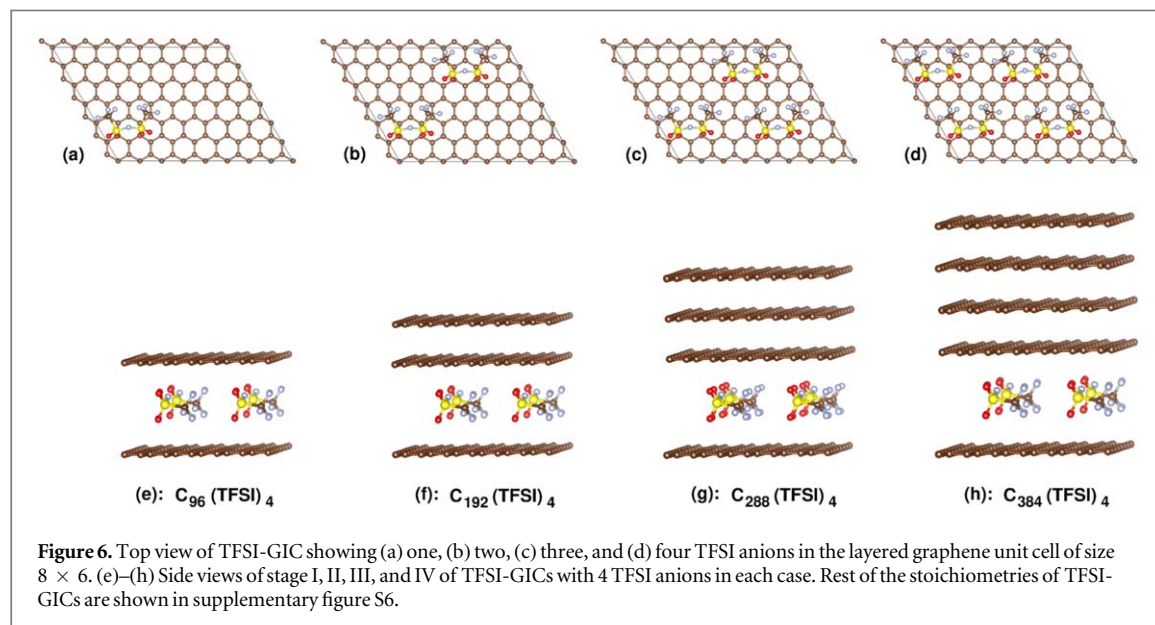


Table 2. Intercalation energy per intercalant E_{int} (eV) and theoretical specific capacity C (mAh g⁻¹) for various anion-GICs at different stages of intercalation^a.

Intercalant	Stage I		Stage II		Stage III		Stage IV	
	E_{int}	C	E_{int}	C	E_{int}	C	E_{int}	C
PF ₆	-2.73 (-2.87)	124.0	-2.94 (-3.04)	62.0	-2.93 (-3.07)	41.3	-2.83 (-3.07)	31.0
ClO ₄	-1.16	186.1	-1.21	93.0	-1.20	62.0	-1.18	46.5
FSI	-1.35	186.1	-1.44	93.0	-1.41	62.0	-1.39	46.5
TFSI	-1.40 (-1.33)	93.0	-1.47 (-1.47)	46.5	-1.48 (-2.08)	31.0	-1.41 (-2.10)	23.2

^a Intercalation energy values from previous theoretical work [36] are shown in parentheses for PF₆- and TFSI-GICs.

Electrochemical properties of GICs

So far, we have studied the structural properties and energetics of GICs in different stages of intercalation corresponding to the maximum capacity in each stage (using the models represented in section). In order to investigate the stability and electrochemical properties of GICs during the intercalation process, we have built supercell models for GICs such that in each stage, a maximum of four intercalants can be accommodated in one supercell. In order to compensate the computational time requirements, we considered AA stacking of the graphene layers for this analysis. The supercell models to represent different stages are as follows. For PF₆-GIC: C₇₂(PF₆)_n for stage I, C₁₄₄(PF₆)_n for stage II, C₂₁₆(PF₆)_n for stage III, and C₂₈₈(PF₆)_n for stage IV. For FSI-GIC: C₄₈(FSI)_n for stage I, C₉₆(FSI)_n for stage II, C₁₄₄(FSI)_n for stage III, and C₁₉₂(FSI)_n for stage IV. For TFSI-GIC: C₉₆(TFSI)_n for stage I, C₁₉₂(TFSI)_n for stage II, C₂₈₈(TFSI)_n for stage III, and C₃₈₄(TFSI)_n for stage IV; where $n = 1, 2, 3$, and 4. We did not investigate electrochemical properties of ClO₄-GICs, since our experimental observations showed that ClO₄ has a huge difference between charge and discharge capacities and also causes oxidation of the electrolyte. The experimental charge-discharge profile of LiClO₄ is shown in supplementary figure S2, and the experimental details are described in supplementary section S1. In figure 6, the top and side views of TFSI-GIC supercells are shown highlighting four intercalant sites (hollow for TFSI). The same scheme is adopted for PF₆ and FSI-GICs (see supplementary figures S3 and S4).

In table 3, intercalation energies for PF₆-, TFSI-, and FSI-GICs for different stages along with the difference in intercalation energies between n^{th} and $n^{\text{th}}-1$ intercalant are tabulated. Here, supercells of these GICs consisting of four AA-stacked graphene layers of size 6×6 , 8×6 , and 4×6 , respectively, are considered as references. From the calculated intercalation energies, we observe that the PF₆-GICs are the most stable ones, as observed in our previous stage models (table 2). The trend in the intercalation energies is such that in each stage, the first intercalation in graphite is the least favorable. This is because of the presence of vdW attraction between graphene layers. In order to accommodate the first intercalant, graphene layers have to be expanded, which

Table 3. Intercalation energy per intercalant E_{int} (eV) and difference in intercalation energy for n^{th} intercalant with respect to the preceding intercalation ($n^{\text{th}}-1$) (ΔE_{int}) for PF₆-, TFSI-, and FSI-GIC in different stages of intercalation; n represents the number of intercalants in each stage.

Stages	Number of intercalants	PF ₆ -GIC		TFSI-GIC		FSI-GIC	
		E_{int}	ΔE_{int}	E_{int}	ΔE_{int}	E_{int}	ΔE_{int}
Stage I	1	−1.60	0.0	0.54	0.00	−0.97	0.00
	2	−2.71	−1.11	−1.11	−1.65	−1.57	−0.60
	3	−2.94	−0.23	−1.60	−0.49	−1.62	−0.05
	4	−2.86	0.08	−1.74	−0.14	−1.50	0.12
Stage II	1	−1.86	0.00	0.20	0.00	−1.28	0.00
	2	−2.97	−1.11	−1.38	−1.58	−1.89	−0.61
	3	−3.25	−0.28	−1.88	−0.50	−2.00	−0.11
	4	−3.34	−0.09	−2.09	−0.21	−1.73	0.27
Stage III	1	−2.18	0.00	−0.18	0.00	−1.48	0.00
	2	−3.16	−0.98	−1.62	−1.44	−2.40	−0.92
	3	−3.37	−0.21	−2.04	−0.42	−2.27	0.13
	4	−3.40	−0.03	−2.59	−0.55	−1.83	0.44
Stage IV	1	−2.46	0.00	−0.60	0.00	−1.63	0.00
	2	−3.27	−0.81	−1.77	−1.17	−2.70	−1.07
	3	−3.42	−0.15	−2.12	−0.35	−2.45	0.25
	4	−3.41	0.01	−2.90	−0.78	−1.86	0.59

requires energy. Once the layers are expanded, subsequent intercalations become easier. Such a process is termed as the activation of the graphite host electrode, where the first intercalation of anions in the graphite galleries activates subsequent intercalations. As compared to PF₆, TFSI requires greater activation of graphite owing to its larger size. This is evident from the respective difference in intercalation energy (ΔE_{int}) between the first and second intercalation in all stages for PF₆ and TFSI. The ΔE_{int} value for the second intercalation of TFSI is higher in magnitude than that of PF₆. This kind of activation behavior of graphite for the initial intercalation has been observed in experiments as well as in previous theoretical studies [30, 36, 42, 45].

The trend in intercalation energies shows that the intercalation of ions into the graphite host electrode follows the staging mechanism. Once the graphite host gallery is expanded at a particular stage, further incoming ions prefer to get accommodated into the expanded gallery rather than intercalating into another gallery. This suggests that the repulsion between the ions in the same host gallery is smaller than the vdW attractions between graphene layers. At sufficiently high ion concentration, every graphite host gallery would be occupied, which would result in increased repulsion between the intercalants in adjacent graphite galleries and would make the corresponding GICs less stable. This effect can be seen from the decrease in intercalation energy values of the GICs in going from stage IV towards stage I. From table 3, it can also be seen that for PF₆, the magnitude of ΔE_{int} in the same stage decreases as more ions are inserted into the same graphite gallery and ultimately goes to zero for the 4th intercalation. This indicates that there is not much gain in stability in PF₆-GICs after the 3rd intercalation. For TFSI, ΔE_{int} values follow the same trend as for PF₆ for stages I and II, but the gain in stability is higher than that for PF₆. Particularly for stages III and IV, the ΔE_{int} value for the 4th TFSI intercalation increases, indicating that four TFSI molecules in a 8×6 graphite host lattice is the most stable stoichiometry for TFSI-GIC (C₂₄TFSI). In stages I and II, a 4th TFSI intercalation does not help give extra stability because of increased repulsion between TFSI intercalants in adjacent graphite galleries.

In the case of FSI-GICs, as studied by a 4×6 supercell model, the energy required to expand the graphite galleries is intermediate to that required for those of PF₆ and TFSI. This clearly indicates the size effect of the intercalants on the graphite activation upon first intercalation. The general trend of decrease in intercalation energies in going from stage IV towards stage I can also be seen in FSI-GICs. Within a particular stage, the gain in stability upon second intercalation is significant (magnitude of ΔE_{int}). Further increase in FSI concentration hardly leads to more stable GICs. In fact, it decreases the stability of FSI-GIC when four FSI ions are intercalated. This indicates that although the maximum stoichiometry for FSI-GIC obtained in our work is C₁₂FSI, a large voltage would be needed to insert the FSI ions required to achieve the reported stoichiometry. In other words, at low electrolyte concentration, the stoichiometry for FSI-GIC should be in the range C₁₈–C₂₄. It should also be noted that there is only a marginal difference in intercalation energies for FSI-GICs of 12, 18, and 24 C atoms per FSI molecule, as shown in figure 3. In fact, our experimentally estimated GIC stoichiometries for FSI and PF₆ ions are C₂₃FSI and C₂₃PF₆, respectively, for 2M LiFSI and 2M LiPF₆ in ethyl methyl carbonate (EMC). In supplementary figures S4 and S5, the optimized GICs of FSI on a 4×6 and on a 6×6 graphene unit cell in stage I configuration are shown.

We have computed the average voltage as defined in (8) for DIBs based on PF_6 , FSI, and TFSI anions. Since in DIBs, the electrolyte also acts as an active medium where ions are present in solvated form, some energy is required to separate the ions from the solvent so that they can intercalate in the electrode. Therefore, a cell voltage in DIBs depends upon the desolvation energy along with the intercalation energy. Here, we have not explicitly calculated the solvation/desolvation energy of the ions in the solvent medium, as has been done in other works [36, 45]. It is known that computational studies can reproduce the voltage profiles of experiments although the absolute values can differ. We have plotted the average voltages with some rigid shift [66, 67] for PF_6 , TFSI, and FSI ions as a function of specific capacities (figure 7).

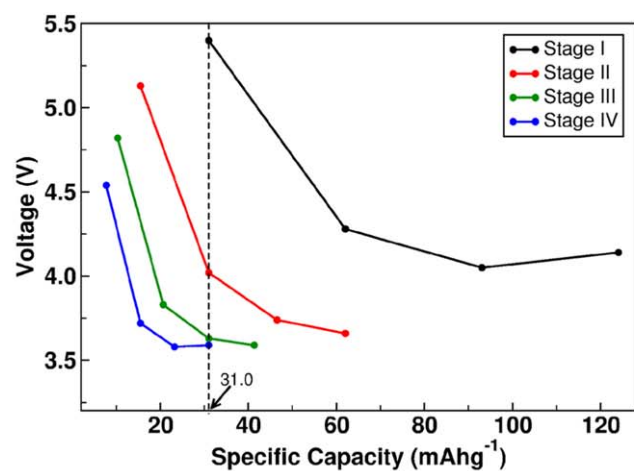
As can be seen from the voltage plots of PF_6 - and TFSI-GICs, the initial intercalation of anions in every stage requires high voltage. This indicates that some energy is required to expand the graphite host gallery. The voltage range of subsequent intercalations are narrower than that of the first intercalation. At the same capacity (ion concentration), higher voltages would be needed to achieve a stage with a low index, as highlighted by vertical dashed lines in figures 7(a) and (b). This means that at a particular concentration, the intercalants prefer to be intercalated into the same graphite host gallery, since expanding another graphite host gallery would cost energy. Furthermore, at the same specific capacity, the change in voltage in going from stage IV to III to II is lower than in going from stage II to I. This might be because of increased repulsion between anions in the adjacent intercalated layers in stage I. For the FSI-GIC stoichiometries, the voltage plots look different from those of PF_6 - and TFSI-GICs. Assuming that the present FSI-GIC represents a highly concentrated salt of FSI in the electrolyte, some conclusions can be made from its voltage plots (figure 7(c)). It is clear that in the case of FSI, initial intercalation would require a higher voltage at each stage. Forcing more FSI ions would initially not require much greater voltage, but after a certain capacity, further forcing ions into the same layer at a given stage would require higher voltage. Furthermore, at a particular capacity, mixed stages can be observed, as shown at a value of 46.5 mAh g^{-1} . Similar to the case with PF_6 and TFSI ions, the transition from stage II to I in FSI intercalation requires higher voltage.

Onset voltage is defined as the calculated voltage when only one ion is intercalated into the electrode. It is presumed that the larger the ion, the higher would be its onset voltage [68]. For alkali metal cations, it has been observed that a larger cation (K^+) has a higher onset voltage than a smaller one (Li^+) [56]. But in the case of anion intercalation, this trend is reversed [56, 68]. The experimental onset voltage reported for LiPF_6 is 4.4 V, and for LiTFSI , it is 4.1 V [56]. In another experiment, FSI is reported to have higher onset voltage (4.53 V versus Li^+/Li) than TFSI (4.44 V versus Li^+/Li) [68]. This indicates that the size of an anion does not have the same effect on onset voltage as the size of a cation. Our calculated onset voltages for PF_6 , FSI, and TFSI are 4.51, 4.27, and 4.25 V, respectively. The probable explanation for the higher onset voltage for the smaller anion may lie in the solvation of anions in the electrolyte medium. Zhou *et al* [56] have calculated the solvation energies of LiPF_6 and LiTFSI in various dielectric mediums. The reported values for LiPF_6 and LiTFSI in low dielectric medium of strength 5 are -6.07 eV and -5.79 eV , respectively. Thus, more energy is needed to desolvate the smaller anion from the solvent medium, which results in higher onset voltage.

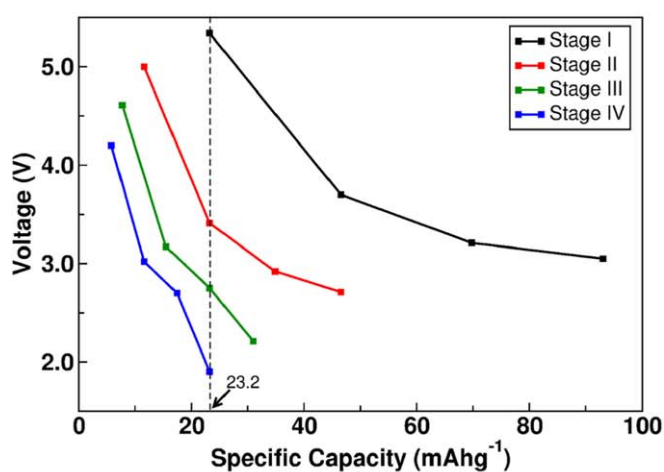
In figure 8, calculated voltage profiles at each stage as a function of fraction of ion in the corresponding GIC formula unit (C_nA) are shown. The experimental voltage profiles are shown in the insets of figure 8. Our experimental measurements show that the voltage windows of 2M LiPF_6 and 2M LiFSI in EMC are 2.5–5.2 V versus Li^+/Li , and 2.5–5.1 V versus Li^+/Li , respectively. The experimental intercalation/de-intercalation voltage window for TFSI in ionic liquid-based electrolyte is 4.37–5.20 V versus Li^+/Li [69–71]. Our calculated voltage profiles agree with the experimental profiles. The step-wise increase in voltage as a function of ion concentration indicates the existence of different staged phases in GICs. Although in experiment one or many stages can coexist simultaneously, the voltage nevertheless increases in going from high stage index towards low stage index (increasing charge storage capacity).

Diffusion dynamics of anions

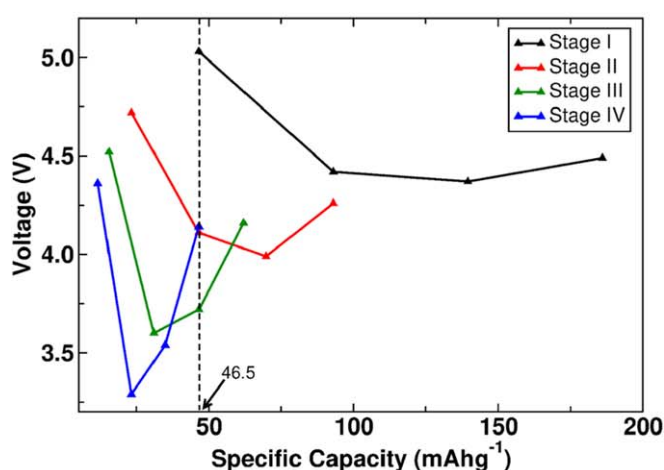
Along with high energy density and cycling stability, ultrafast charging is also a desirable characteristic of a DIB. The rate of charging/discharging of an electrochemical cell depends on how fast the guest ions can travel through the electrolyte and the electrode material. An ideal electrode should have sufficient electrical conductivity as well as allow fast diffusion of intercalated ions (ionic conductivity). For this purpose, it is imperative to study the diffusion dynamics and pathways of the ions intercalated between graphene layers. Here, we have investigated two-dimensional diffusion (parallel to graphene plane) of anions in their intercalation compounds. All of the diffusion studies have been carried out using AB-stacked graphene layers. We have calculated the barriers for anion diffusion along two prominent crystal directions, [100] and [110] (see supplementary figure S7). In table 4, we have listed some energy barriers for the diffusion paths of the anions. Stage I GICs are mainly considered in these diffusion studies. But for some cases, we have also investigated the pathways and barriers in stage II GICs. From table 4, it can be seen that all anions considered in this study diffuse



(a)



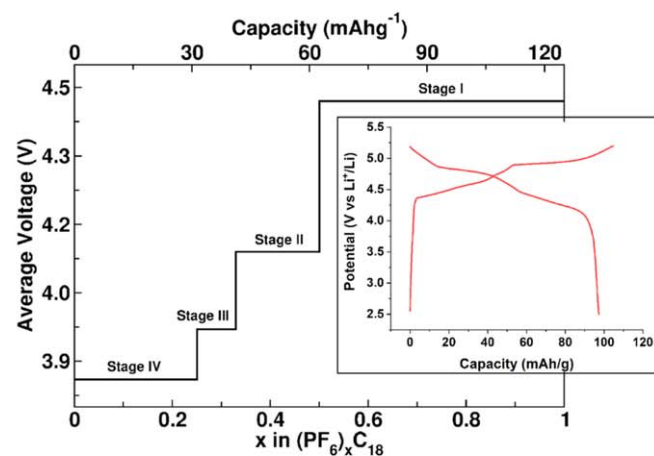
(b)



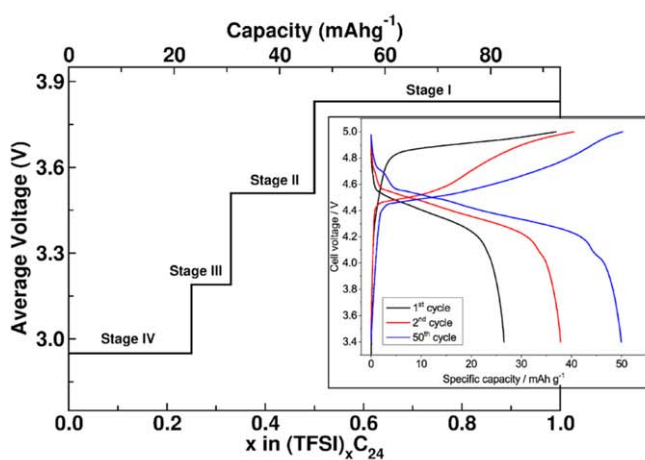
(c)

Figure 7. Average voltages of PF₆-GIC (a), TFSI-GIC (b), and FSI-GIC (c) as a function of specific capacity in different stages. Vertical dashed lines aid comparison of voltages between stages at a particular capacity value.

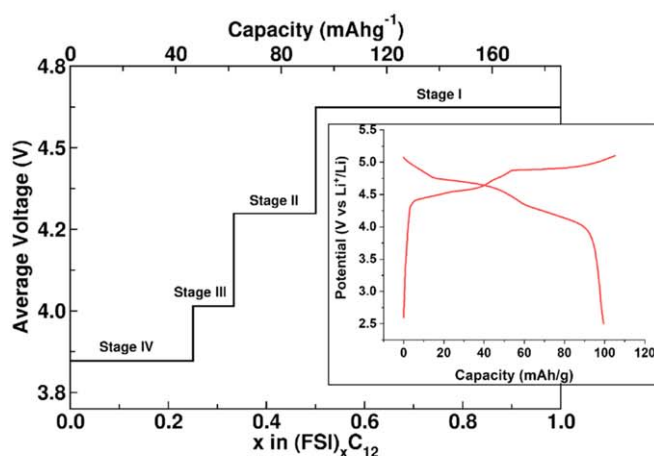
very fast along the planes of graphene. Our calculated diffusion barriers match those of previous theoretical works, where the barrier for PF₆ was reported to be around 0.15 eV [45] and that of TFSI was reported to be around 0.035 eV [43]. Small differences between our calculated barriers and those of previous works can be



(a)



(b)



(c)

Figure 8. Voltage profiles for PF_6^- (a), TFSI^- (b), and FSI^- GICs (c). Experimental voltage profiles are shown in the insets.

attributed to different unit cells, stages, and graphite stackings. Another important anion for dual-ion batteries is AlCl_4^- . Previous studies have shown that AlCl_4^- ions migrate with a barrier ranging between 0.023 and 0.089 eV [72, 73]. The low diffusion barriers of the anions might be a result of huge gallery height in anion-GICs compared to the size of these anions. An important difference between these anion-GICs and cation-GICs (e.g. of LiC_6 , NaC_6 , KC_8) is that unlike the cation-GICs, there is no significant effect of anion size on their diffusion

Table 4. Diffusion energy barriers (in eV) of anions along various diffusion paths along [100] and [110] directions.

Anion	Energy barrier (eV)	
	Stage I	Stage II
PF ₆ [ontop to ontop]	0.170[100] 0.150[110]	0.093[100]
ClO ₄ [hollow to hollow]	0.013[100] 0.030[110]	0.018[100]
FSI[ontop to ontop]	0.035[100]	0.023[110]
TFSI[hollow to hollow]	0.011[100]	0.020[100]

barriers. In cation-GICs, the barrier for diffusion decreases with increase in the size of the cation (Li: 0.55, Na = 0.27, K = 0.15 eV [32, 74]). Furthermore, strong covalent interactions between graphitic carbon and cations result in higher diffusion barriers than those for anions. The low diffusion barriers of anions in graphite electrodes and the non-rocking-chair character of DIBs make them potential candidates for ultrafast-charging batteries.

In some GICs, the diffusion barrier in stage II is lower than in stage I, while in others, there is not much change. The difference in diffusion barrier in different stages of intercalation may have some implications for the performance of the battery [30], but this fact needs to be investigated further.

Charge transfer

The relative charge transfer between the host material and the guest ion establishes the degree of stability of an intercalated structure. Using (10), we have calculated the charge density deformation upon anion intercalation in graphite. The isosurfaces of charge density deformation observed in stage II GICs for all the considered anions are shown in figure 9. These charge density difference plots show that the charge is transferred from carbon atoms of the graphite to the intercalated anions and that the anion intercalation is a charging process.

We also carried out Bader charge analysis [54, 55] to quantify the amount of charge transfer between the anions and graphite. In table 5, partial charges on the constituent elements of anions in their isolated states and in their corresponding GICs are listed. In the case of PF₆-GIC, the partial charge on each F atom increases from -0.83 |e| (in its isolated state) to -0.99 |e| (in the GIC), which is equal to a total of -0.96 |e| units of charge per PF₆ anion accepted from the graphite host. In the case of ClO₄-GIC, one ClO₄ molecule accepts -0.68 |e| units of charge from the graphite host. In the case of FSI-GIC, the N atoms of FSI mainly accept the electrons from the host. In total, one FSI molecule accepts -0.24 |e| electronic charge. For TFSI-GIC, a lot of charge redistribution happens within the TFSI molecule upon intercalation. Here, the partial electronic charge on N and O atoms of the TFSI increases. Simultaneously, partial charge on S and C atoms of the TFSI decreases. Overall, upon intercalation in the graphite host lattice, a TFSI molecule gains a net charge of -0.54 |e|.

In anion-GICs, geometry and the size of the anions greatly affect the interaction between graphite and the intercalant. In the case of PF₆-GIC, F atoms lie in the center of the hexagonal rings of graphene both above and below the PF₆ ion (figure 4(a)). This results in maximum interaction between F and C atoms, resulting in a maximum amount of charge transfer between them. This interaction between PF₆ and graphite is the reason why PF₆-GIC has the highest stability out of the GICs studied here. Although the charge transfer between ClO₄ and graphite is higher than that for FSI and for TFSI, the tetrahedral geometry of ClO₄ might account for the lower stability of the ClO₄-GIC. Charge transfer between imide ions (TFSI and FSI) and graphite is lower than that for PF₆ and for ClO₄. This might be because of the huge gallery height in these GICs. Nevertheless, TFSI accepts more charge from the graphite than FSI. It has been shown that the O atoms of the TFSI act as sites for electrochemical reduction [43]. We also found that the four O atoms of TFSI accept more charge than the N, S, and F. Overall, Bader charge analysis has provided meaningful insights into the elemental charge transfer between a graphite host and the intercalated anions.

Discussion

In this section, we have summarized and compared various structural, electronic and electrochemical properties of anion-GICs studied in this work. We have tabulated various calculated properties for these GICs in table 6. The stability order of anion-GICs based on calculated intercalation energies is as follows: PF₆-GIC > TFSI-GIC ≥ FSI-GIC > ClO₄-GIC.

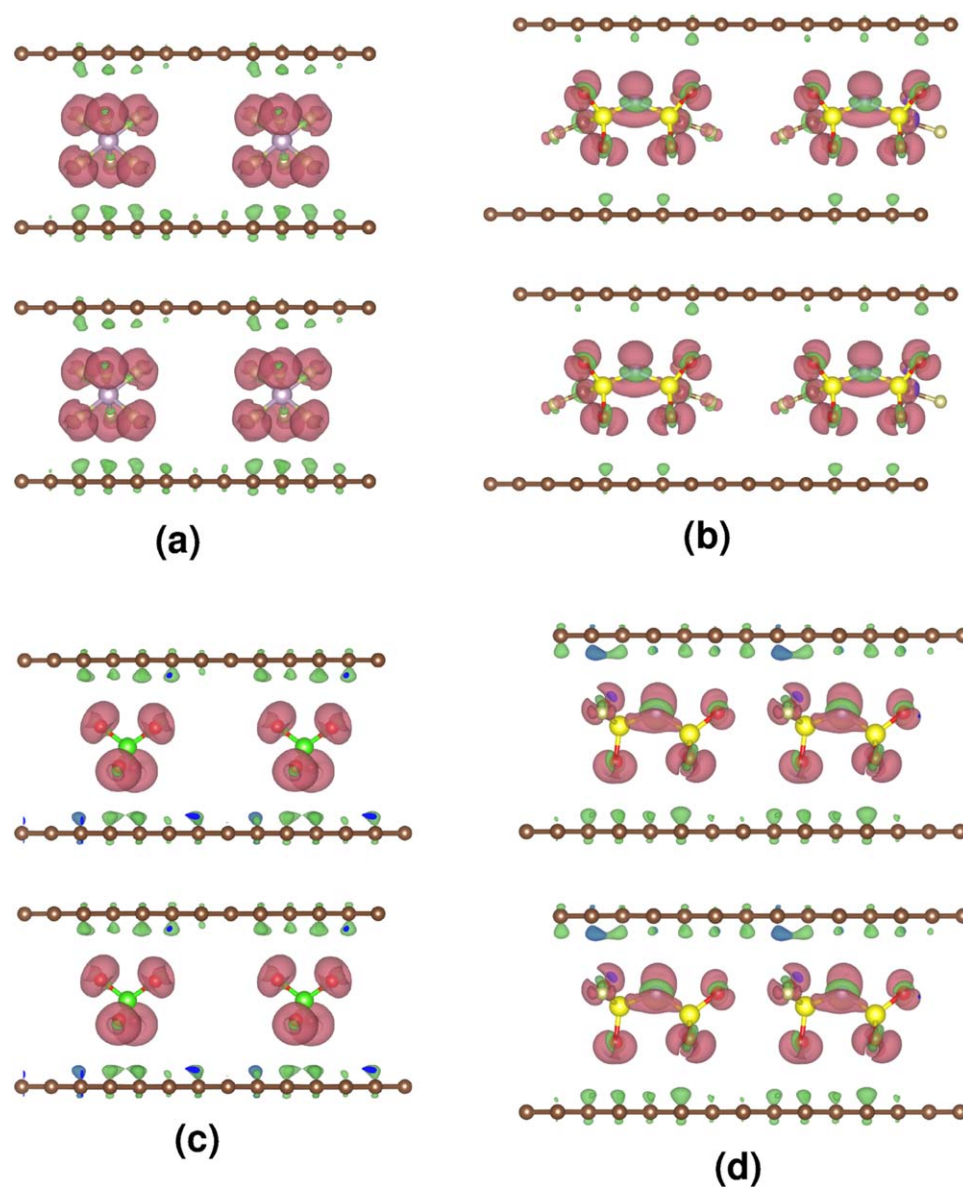


Figure 9. Isosurfaces of charge accumulation (maroon) and charge depletion (green) in (a) PF_6^- , (b) TFSI^- , (c) ClO_4^- , and (d) FSI-GICs in stage II. Isovalue is taken as $0.0027 \text{ e bohr}^{-3}$. All C, N, O, F, P, S, and Cl atoms are represented by brown, light blue, red, dull yellow, purple, yellow, and green spheres, respectively.

Table 5. Pauling's electronegativity (χ) and valence (z) and partial (δ) charges on the corresponding elements in the isolated anions, as well as in their corresponding GICs.

	C	N	O	F	P	S	Cl
χ	2.55	3.04	3.44	3.98	2.19	2.58	3.16
z	4.00	5.00	6.00	7.00	5.00	6.00	7.00
$\delta(\text{PF}_6^-)$				-0.83	+5.00		
$\delta(\text{ClO}_4^-)$			-1.75				+7.00
$\delta(\text{FSI})$		-2.68	-1.82	-1.00		+6.00	
$\delta(\text{TFSI})$	+2.73 ^a	-2.72	-1.82	-0.92		+5.03	
$\delta(\text{PF}_6\text{-GIC})$	+0.04			-0.99	+5.00		
$\delta(\text{ClO}_4\text{-GIC})$	+0.04		-1.92				+7.00
$\delta(\text{FSI-GIC})$	+0.04	-2.92	-1.82	-1.02		+6.00	
$\delta(\text{TFSI-GIC})$	+0.04(+2.61 ^a)	-2.98	-1.95	-0.92		+5.07	

^a C atoms in TFSI ion.

Table 6. Calculated stoichiometry, molecular volume ($\text{\AA}^3$), maximum specific capacity (mAh g^{-1}), gallery height ($\text{\AA}$), charge transfer from graphite to the anions (in units of $|e|$), onset voltage (V), and diffusion barrier (eV) of anions in the studied GICs.

Anion	Stoichiometry	Volume	Capacity	d	Charge transfer	Onset voltage	Barrier
PF_6	C_{18}PF_6	94	124	7.47	$-0.96 e $	4.51	0.09–0.17
ClO_4	$\text{C}_{12}\text{ClO}_4$	78	186	7.29	$-0.68 e $		0.01–0.03
FSI	C_{12}FSI	124	186	7.83	$-0.24 e $	4.27	0.02–0.03
TFSI	C_{24}TFSI	179	93	8.12	$-0.54 e $	4.25	0.01–0.02

Unlike the case with cations, anion intercalation in graphite is not much affected by the size of the various anions. However, we discuss the possible effects of anion size on the properties of anion-GICs. Although the gallery height in anion-GICs is huge when compared to the size of these anions, the trend is still the larger the anion, the higher the gallery height. The size of the anions directly affects the activation of the graphite host upon initial intercalation. A larger anion requires greater activation of graphite than a smaller one. Anion size also affects the onset voltage but in reverse order, that is, the larger the anion, the lower the onset voltage. This is in contrast to cation-GICs, where a larger cation has a higher onset voltage than a smaller cation. In the case of anion-GICs, solvation of anions in the electrolyte solvent contributes towards cell voltage, while in cation-GICs, cation solvation does not contribute significantly towards the overall cell voltage [56]. Therefore, anion size does not have the same effect on electrochemical properties that cation size has [56, 68]. This minimizes the effect of anion size on the chemical potentials of the electrodes.

Another property which is unaffected by the size of the anions is their diffusion in graphite. All the anions studied here would have trouble-free diffusion through the graphite electrode. The reason for low diffusion barriers for all the anions considered in this study, irrespective of their sizes, is the huge expansion of graphite host layers upon anion intercalation. Among the studied anions, PF_6 has the highest diffusion barrier (0.15–0.17 eV). One important requirement of a DIB is to have minimum structural deformation during its operation. Anion intercalation causes larger volume expansion (hence structural deformation) in graphite cathode as compared to cation intercalation in graphite anode (123% in PF_6C_{18} versus 10% in LiC_6). Such huge volume expansion in graphite cathode because of larger anions size affects the stability in DIBs. Smaller anions would cause less volume expansion, which can give more structural stability to the electrochemical cell. Out of the stable anions (PF_6 , FSI, and TFSI), PF_6 would form DIBs with the least volume expansion and hence least probability of graphite exfoliation. However, if using reasonable binders (Alg), the problem of volume expansion in graphite cathodes might not be a limiting factor in the development of DIBs [30].

The inherent chemical nature and geometry of the anion affect the amount of charge transfer between graphite and the anion. Among the stable GICs, the charge transfer is highest for PF_6 -GIC, followed by TFSI and then FSI-GIC. This indicates the higher oxidative ability of PF_6 followed by TFSI and FSI. The comparison between the oxidative ability of TFSI and FSI has also been reported experimentally [68]. First-principles studies on the combination of more than one anion would also be interesting.

Conclusions and future outlook

Graphite-based DIBs are promising alternatives to LIBs for large-scale energy storage applications. In this study, DFT calculations including dispersion corrections are performed to investigate anion intercalation in graphite positive electrodes. We have built theoretical models to understand the staging mechanism of anion intercalation and to obtain electrochemical properties such as specific capacities and average voltages during intercalation. We have explored various structural, electronic, dynamical, and electrochemical characteristics of GICs considering the four anions (PF_6^- , ClO_4^- , FSI^- , and TFSI^-). We found that stability of anion-GICs follows the order: $\text{PF}_6\text{-GIC} > \text{TFSI-GIC} \geq \text{FSI-GIC} > \text{ClO}_4\text{-GIC}$. The effect of staging on the stability of GICs is less than that of the type of the anion. Because of graphite gallery expansion upon anion intercalation, the diffusion of anions in graphite is very fast. This fast diffusion of anions in graphite could be one of the factors responsible for the high power capabilities of DIBs. The amounts of charge transfer from carbon atoms of graphite to the anions indicate that the anion intercalation in graphite is a charging process. Among the studied anions, PF_6^- seems to have the highest oxidative capability. Voltage profiles of the stable GICs show that the initial intercalation of the anions in graphite is difficult but that the voltage range for subsequent intercalations is narrower. Furthermore, the average voltage of GICs increases in going from stage IV to stage I intercalation.

We also found that the anion size affects the activation of the graphite host, maximum theoretical capacity, and mechanical stability of the electrode but its effect on diffusion through graphene layers is marginal. Moreover, unlike the case with cations, the solvation energy of the anions in the electrolyte affects the

electrochemical properties of a battery. Hence, an electrolyte which is, among other factors, stable (should not get decomposed within the working potentials of cathode and anode) and suitable (should have high dielectric constant and low viscosity) is very important for achieving reversible intercalation of ions into the electrodes. Although graphite is the most-used material for electrodes in DIBs, its limited charge storage capacity with respect to anions and solvent co-intercalation pose limitations to its commercial use. Therefore, to be applied as cathode materials in DIBs, further modification of graphite electrodes by doping, the storage of multivalent anions, and alternate cathode materials such as metal organic frameworks or porous carbon need to be explored. Graphite-like cathode materials having optimum interlayer distance should be sought. Such host materials would easily accommodate large anions without much structural deformation. Although the experimentally observed discharge capacities and energy densities of DIBs have been low compared to those of LIBs, advancements in these environment-friendly, low cost, and safe battery technologies are underway.

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Data availability statement

The data generated and/or analysed during the current study are not publicly available for legal/ethical reasons but are available from the corresponding author on reasonable request.

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