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Organic Cation (DMPI) Intercalated Graphite Anode for High Voltage Next Generation Dual-Ion Battery

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Abstract

Developing advanced energy storage systems to address the intermittency of renewable energy sources is crucial for meeting the ever-increasing energy demands. Among post lithium-ion battery systems, dual-ion batteries (DIBs) have shown bright prospects in developing low-cost and safe batteries with good electrochemical performance. Herein we have modelled for the first time, organic cation intercalated graphite systems. Imidazolium based ionic liquid, 2,3-dimethyl-1-propyl imidazolium chloride (DMPI-Cl) with AlCl₃ salt has been implemented as an electrolyte. Using first principles calculations, we have performed DMPI cation intercalation into the graphite anode based on different plausible staging mechanisms. The intercalation energy characteristics indicate favourable intercalation of the DMPI into graphite following staging mechanism, which has been further confirmed by simulated X-ray diffraction study. Higher cell voltage (3.7-4.6 V range) comparable to lithium-ion battery along with maximum capacity of 62 mAh/g has been achieved. The charge transfer analysis presents a +0.87 |e| charge transfer from DMPI to graphite indicating DMPI cation intercalation into graphite during the charging process. Moreover, the metallic character of DMPI cation intercalated graphite system and diffusion barrier as low as 0.2 eV suggests a constant electronic conductivity and better rate performance, respectively. Furthermore, we have explained the reason behind inapplicability of 1-ethyl-3-methyl imidazolium (EMI) cation as organic cation for dual-graphite battery and hence highlight the need to explore alternative ionic liquids. These results provide clear understanding of DMPI cation intercalation into graphite anode and could
be helpful in fabricating dual graphite electrode-based DIBs with better electrochemical performance compared to conventional DIBs using metal anodes.

**Keywords:**
Dual-ion batteries, Graphite, DMPI, Staging, Intercalation, Simulated XRD, Dual-graphite batteries, Voltage.

1. Introduction

Increasing utilization of renewable energy sources, like wind, hydroelectric and solar power is essential today for a sustainable economy. Due to the nature of volatility, randomness, and intermittency in such energy sources, they cannot be directly deployed for uninterrupted power supply. As a result, development of highly efficient energy storage and conversion systems is required to assist with the widespread usage of portable electronic devices in daily life.¹ Various types of rechargeable metal-ion batteries have been developed in the recent past such as Li-ion²–⁴, Na-ion⁵–⁷, Mg-ion⁸,⁹ Zn-ion¹⁰,¹¹ and Al-ion¹²,¹³ batteries. Among them, lithium-ion batteries (LIBs) have profoundly dominated the energy storage market due to their high output voltage and gravimetric capacity.²,⁴ However, using expensive transitional metal oxide as cathode material and less abundant Li metal as anode, may not be sustainable for large-scale application of LIBs in future.¹⁴,¹⁵ Moreover, the safety issues and thermal runaway events are major concerns that have not been completely resolved.¹⁶ Altogether, the high cost and the safety issues are not as an ideal choice of green energy storage in LIBs. Hence, new materials like graphite are being explored to develop better performance low-cost batteries. Owing to its redox-amphoteric nature and layered structure, the graphite can be reduced as well as oxidized by electrochemical reaction with proper cation/anion uptake and release. Thus, dual graphite batteries can be conceptualized, also called dual-ion batteries (DIBs) where both graphite anode
and cathode are involved in intercalation/deintercalation of cation and anion, respectively
during the charge/discharge cycle of battery.\textsuperscript{17–20} In 1989, McCullough \textit{et al.}
first reported a DIB using graphite as both the cathode and anode along with the nonaqueous electrolyte of 
ClO$_4$\textsuperscript{-}.\textsuperscript{21} The graphite-based DIBs are considered as promising alternative rechargeable
batteries because they have high working voltage (4.5 V), better safety and lower cost
compared to the conventional LIBs.\textsuperscript{22–25} In DIBs, the working principle is different from the
rocking chair mechanism as in LIBs. Here, the cations and anions are both reversibly
intercalated in graphite anode and cathode simultaneously in charging process, while the ions
are deintercalated from the graphite back to the electrolyte during the discharging process.\textsuperscript{26,27}
Commonly used DIBs have lithium salts (like LiPF$_6$, LiTFSI) with organic solvents (ethylene
carbonate, ethyl methyl carbonate) as an electrolyte which faces several fatal problems like, (i)
electrolyte decomposition at a high working voltage (> 4.5 V).\textsuperscript{28} (ii) graphite exfoliation due
to solvent co-intercalation along with ion intercalation,\textsuperscript{28} (iii) active battery material loss due
to solid-electrolyte interphase (SEI) formation.\textsuperscript{29} Hence, compatible electrolytes and electrodes
are required to reduce the exfoliation of graphite and replace the lithium metal. Carlin \textit{et al.}
have presented the room temperature ionic liquids (RTILs) as a better alternative to replace the
conventional volatile organic solvents.\textsuperscript{30}

Ionic liquids (ILs) are low melting point salts and have emerged as an important part in
electrochemistry to design new classes of electrolytes. ILs show several encouraging properties
for electrochemical applications such as low vapour pressure, broad range of electrochemical
window, and higher ionic conductivity.\textsuperscript{31–33} Special feature of using ILs as electrolytes is that
the electrochemical reaction is mainly driven due to their high oxidative and reductive stability
and thus possess a large electrochemical stability window.\textsuperscript{34–36} Several recent studies have
considered DIBs involving IL electrolytes and revealed that the organic cations of the ILs such
as 1-ethyl-3-methyl imidazolium cation (EMI$^+$), N-butyl-N-methyl pyrrolidinium (BMP$^+$) can
be intercalated into the graphite anode. The broad range of electrochemical window stability of ILs allow for high cut-off charging voltage (4.0-5.0 V). Carlin and co-workers, have also studied ILs composed of cations like 1-ethyl-3-methyl imidazolium (EMI\(^+\)) and 2,3-dimethyl-1-propyl imidazolium (DMPI\(^+\)) and anions such as CF\(_3\)SO\(_3\), AlCl\(_4\), C\(_6\)H\(_5\)CO\(_2\), PF\(_6\) and BF\(_4\) as electrolytes in dual ion battery. Our previous reports have shown AlCl\(_4\) anion along with different ILs based organic cation (imidazolium, pyrrolidinium) can be used as electrolytes in Al DIBs. Using organic cations as charge carriers have the added advantage of preventing unwanted co-intercalation of solvents into the graphite anode (as in case of LiPF\(_6\)) as well as diminished chances of solvent decomposition at high charging voltage.

Consequently, apart from the intercalation mechanism, there is a lack of clear molecular level understanding of intercalation capacity and intercalated species for organic cation intercalation in graphite-like anodes. In this study, we have computationally modelled for the first time, organic cation intercalated graphite anode system successfully. We have chosen imidazolium-based IL, 2,3-dimethyl-1-propyl imidazolium chloride (DMPI-Cl) with AlCl\(_3\) at 1:1 molar ratio as electrolyte. We have investigated the intercalation mechanism by considering the staging manner of DMPI cation intercalation into the graphite anode. First principles calculations are performed for a systematic study of the structure, stability, electronic properties, and theoretical capacity along with average voltage of DMPI cation intercalated graphite electrode. Furthermore, we have also investigated the diffusion pathways of DMPI cation in graphite system. Along with this, we have also explained why EMI\(^+\) cannot be used as organic cation for dual-graphite battery research, although EMI based IL electrolytes are extensively used in the battery technology. On the basis of the obtained theoretical insights, we believe that organic cation intercalated graphitic anodes could be utilised in DIBs to achieve better electrochemical features compared to DIBs using metal anodes, and our study would motivate further developments in cheaper dual graphite battery technology.
2. Computational Details

The first principles calculations have been performed using the Vienna Ab initio Simulation Package (VASP).\textsuperscript{43,44} All geometry optimizations and respective calculations have been performed using generalized gradient approximation of Perdew-Burke-Ernzerhof (GGA-PBE) functional.\textsuperscript{45} The projected augmented wave (PAW) method is used for treating interaction between the ions core and valence electron.\textsuperscript{46} An energy cut off of 470 eV has been implemented. During the structural optimization, the Brillouin zone has been sampled with $\Gamma$ centered k-point grid of $11 \times 11 \times 5$ for the unit cell and $2 \times 2 \times 1$ for the considered supercells. All structures have been optimized with an energy criterion of $10^{-5}$ eV/Å and force criterion of $\leq 0.01$ eV/Å for all the atoms to obtain full relaxation between the atomic and lattice positions. DFT-D3 approach has also been considered for van der Waals corrections in our calculations.\textsuperscript{47} We have modelled four different stages for both DMPI cation and AlCl\textsubscript{4} anion intercalation process, where the $6 \times 6 \times 2$ supercell of graphite containing 288 carbon atoms for stage-1, stage-2 and stage-4 systems and $6 \times 6 \times 3$ supercell containing 432 carbon atoms has been chosen for the stage-3 calculation with the same concentration of both cations and anions. The density of states (DOS) calculations has been performed for a $4 \times 4 \times 1$ supercell with a $\Gamma$ centered k-point mesh of $9 \times 9 \times 1$. The Bader charge analysis has been performed using the Henkelman program to determine the quantitative charge transfer upon intercalation of DMPI cation into graphite layers.\textsuperscript{48–50} The Ab Initio Molecular Dynamics (AIMD) simulations have been performed with NVT ensemble for a broad temperature range of 300-600 K for 5 picosecond (ps) timescale. Nosé-Hoover thermostat\textsuperscript{51} with a Nosé mass parameter of 0.01 has been implemented to control the temperature fluctuations. The activation barriers for DMPI cation diffusion pathways have been calculated using the climbing image nudged elastic band method (CI-NEB).\textsuperscript{52} The minimum energy paths (MEPs) are initialized by considering six image structures between fully optimized initial and final geometries with an
energy convergence criterion of $10^{-3}$ eV. During the charging process, the net electron obtained from the external circuit (with very small-time lag) induces the intercalation of DMPI cation which subsequently transfers its charge thereby reducing graphite. The reverse phenomenon is occurring for AlCl$_4$ anion transferring charge to consequently oxidise graphite cathode. This time lag is very short compared to the time required to reach thermodynamic equilibrium of DMPI-graphite system. Hence, in our DFT study we have considered a neutral system of both DMPI-graphite and AlCl$_4$-graphite as we carry out our calculations in equilibrium condition. Such consideration of neutral systems has yielded electrochemical performance results comparable to experimental reports in past.\textsuperscript{27,54} The zero-point energy (ZPE) corrections have also been included for diffusion barrier calculation using the formula, $ZPE = \sum_i h \nu_i / 2$, where $h$ is the Planck’s constant and $\nu_i$ is the vibrational frequency. The ZPE is calculated by considering the degrees of freedom of intercalated DMPI into graphite system.

3. Results and Discussion

3.1. Structural Changes and Stable Binding Sites

\textbf{Scheme 1}. Considered intercalant cation, 2,3-dimethyl-1-propyl imidazolium (DMPI) with labelled atoms. Here, blue, cyan, magenta, and brown colours indicate N, C, H, and graphite layers carbon atoms, respectively.
In DIBs, the cations (DMPI in our case, Scheme 1) and anions are reversibly intercalated/deintercalated from the cathode and anode in charging/discharging process, respectively. Hence, it is important to study the structural changes upon intercalation. We have chosen two possibilities of DMPI cation intercalation in the graphite layer, where one is oriented perpendicular to the graphite layers and the other is parallel to the graphite layers (Figure 1a, b).

Figure 1. DMPI intercalated structures: (a) Perpendicular orientation, and (b) Parallel orientation. Optimized structures of DMPI intercalated system; (c) S1 (Top), (d) S2 (Bridge 1), (e) S3 (Bridge 2), (f) S4 (Hollow). Here, brown, blue, cyan, and magenta colours represent graphite layer, N, C, H of DMPI cation, respectively.

Owing to the strong van der Waals interaction between imidazolium ring and graphite layers, the parallel orientation of DMPI cation into graphite layer is found to be stable. The perpendicular orientation shifts to parallel upon relaxation with dispersion correction. However, without vdW correction the perpendicular orientation is retained which proves that the extensive interactions between π-stacked graphite and parallel orientation (imidazole ring) of DMPI is responsible for this configuration being more stable. We have further investigated
the structural distortions such as change in bond length and bond angle obtained due to the anisotropic van der Waals interaction between layered graphite and DMPI cation. Upon intercalation of DMPI, the $\angle$C2-N3-C bond angle decreases from 124° to 118°, and the $\angle$C2-N1-C decreases from 126° to 121°. Similarly, bond length changes are also observed in intercalated DMPI, where bond lengths of N1-C, N3-C and C2-C change to 1.43, 1.41 and 1.58 Å from 1.47, 1.34 and 1.48 Å in free DMPI, respectively. The alkyl group variance between DMPI and EMI can be labelled as, extra methyl and propyl groups are present in the C2 and N1 position for DMPI, respectively, compare to the EMI. In our earlier report we have studied the effect of alkyl group variation in N1 position of imidazolium ring. But a fundamental understanding is required in the effect of addition of methyl group in the C2 position of the imidazolium ring. So, with respect to C2 position of DMPI, we have arranged four possible sites of binding in graphite layers, (i) S1 (Top), (ii) S2 (Bridge 1), (iii) S3 (Bridge 2) and (iv) S4 (Hollow) as shown in Figure 1c-f. In the S1 (Top) site, the C2 of DMPI occupies the top position of a C atom of graphite. In the S2 (Bridge 1) site, the C2 occupies the bridging position between two non-bonded carbon atoms, whereas in the S3 site (Bridge 2), it occupies the bridging position of the C-C bond. Similarly, for the S4 (Hollow) site C2 occupies the centre of hexagons ($C_6$) of the graphite layer. Our relative energy calculations in Table S1 show that the hollow site with respect to C2 position is most stable for DMPI cation binding into the graphite layers. Particularly, hollow and top site have a very small (0.009 eV) relative energy difference. Hence, there is a high possibility of the equilibrium existence of both hollow and top sites. We have carried out AIMD simulations to verify the thermal stability of DMPI cation intercalated graphite system as well as equilibrium existence of both hollow and top binding sites. Upon AIMD simulation at 300 K for 5 ps, we have observed that while AB stacking of graphite layers are unaltered, the intercalated DMPI cation shifts from most stable site (Hollow) to second most stable (Top) site of binding as shown in Figure S1. Owing to the very small
energy difference (~0.009 eV), these structures can change the adsorption sites at the expense of thermal energy \((3/2 k_B T = 0.03 \text{ eV})\), where \(k_B\) and \(T\) are the Boltzmann’s constant and temperature, respectively. As the calculated relative energies are less than the DFT intrinsic error, therefore all binding sites are equally accessible and DMPI can keep on changing binding sites. These has also been observed during the AIMD simulation as shown in Figure S2. For the sites B1 and B2, relative energies are 0.04 and 0.05 eV, respectively which are higher than thermal energy (0.03 eV). Upon further simulation of DMPI bonded at the most stable hollow site of graphene at 300-600 K, the system was found to be stable (Figure S3). The bond lengths and bond angles of DMPI cation do not change significantly, although position and orientation of the DMPI does fluctuate a little. Hence, from the simulation study we could confirm that these two sites (Hollow and Top) are equally stable, and we have considered hollow site for our further studies.

### 3.2. Model System

In the DIBs, graphite intercalation compounds (GICs) are formed between the graphite layer and intercalant species.\(^{53}\) The formation of GICs follows a systematic staging mechanism of intercalant insertion based on various competing interactions among the intercalate and intercalant. The van der Waals interaction between the parallely stacked graphite layers needs to be overcome by the incoming DMPI cations. Again, the intercalated DMPI cations may experience intermolecular repulsive forces among themselves. Hence, the intercalation phenomena can proceed by maintaining a balance among these competing forces.\(^{54-57}\) Consequently, different stages of intercalation can be considered to occur during charging/discharging process, which has been observed experimentally,\(^{55,58}\) as well as theoretically.\(^{54,56}\) The staging features can be represented by the stage index, which stands for the number of unintercalated graphene layer present between the intercalated layers. The stage-n system resembles to the “n” number of graphene sheet or “n-1” empty host galleries present
between two intercalating layers. For instance, stage-1 GICs correspond to intercalation happening after every graphene layer, while in stage-2, intercalation will happen after a gap of two empty layers. In this manner, different stages are expected in DIBs during intercalation of DMPI cations into graphite. Hence, we have chosen the four most favourable intercalation stages for the same DMPI cation concentration. For that we have modelled the $6 \times 6 \times 2$ supercell of graphite containing 288 carbon atoms for stage1, stage-2 and stage-4 systems and their corresponding relative energies have been compared as shown in Figure 2. The stage-2 configuration is observed to be most stable for DMPI cation intercalation, followed by stage-4 and stage-1 for same concentration of DMPI cations. The energy required to overcome the repulsive forces between intercalant species is less than the energy required to overcome the van der Waals forces between graphite layers required for gallery height opening for intercalation. Hence, the DMPI intercalation favours stage-2 rather than stage-1. The stage-4 is less stable than stage-2, which may be due to the van der Waals repulsion among long carbon chain of four DMPI cations intercalated into a single graphene layer rather than two DMPI intercalated in two separate layers as in stage-2. Upon increasing the number of DMPI cations intercalating to 8, the relative energy difference between stage-1 and stage-2 intercalation decreases, (Figure S4) thus indicating that stage-1 would be more stable compared to other stages for higher concentration of DMPI cation. Owing to different supercell size of stage-3, the result is not comparable to other stages. However, the DMPI intercalation mechanism is followed during charging, same deintercalation mechanism is followed at the time of discharging process. Overall, from the theoretical stability calculation, we could describe the formation of different DMPI cation intercalated stages.
**Figure 2.** Systematic representation of (a) pristine graphite and the staging mechanism of DMPI cation intercalation (b) stage-4, (c) stage-2 and (d) stage-1. R.E is in eV units. Here, brown, blue, cyan and magenta colours represent graphite layer, N, C, H of DMPI cation, respectively.

Furthermore, we have considered the maximum possible intercalation in our supercells for each stage. A $6 \times 6 \times 3$ supercell containing 432 carbon atoms has been chosen for the stage-3 calculation. In the case of stage-1, 288 carbon containing graphite system can intercalate a maximum of 16 DMPI cations to give a stable GIC, which can be represented by the formula unit $[C_{288}(DMPI)_{16}]$. Other lower stoichiometry of DMPI has been chosen such as 4, 8 and 12 per 288 carbon atoms of graphite, maintaining the criteria of stage-1 characteristics. Thus, the generalised formula unit would be $[C_{288}(DMPI)_{n}]$ where $n$ values are 4, 8, 12, and 16 for stage-1. Similarly, for the other stages formula units have been considered such as, $n = 2, 4, 6, $ and 8 for stage-2; and $n = 1, 2, 3, $ and 4 for stage-4. For stage-3, the formula unit would be $[C_{432}(DMPI)_{n}]$ where, $n = 2, 4, 6, $ and 8 of DMPI. All optimised structures have been provided in supplementary information (Figure S5-S8). Overall, from the different considered stoichiometries, we have tried to get an idea about the maximum storage capacity of these systems and compared our results with experimental reports to investigate more about the staging mechanism followed by DMPI cation intercalation in graphite.25
Figure 3. Schematic representation of all optimised structure of the four different DMPI cation intercalated systems, (a) stage-1, (b) stage-2, (c) stage-3 and (d) stage-4; where, \( I_c \) and \( d_i \) are periodic repeating distance and intercalant gallery height, respectively and brown, blue, cyan, and magenta colours represent graphite layer, N, C, H of DMPI cation, respectively.

3.3. Binding Energy

Binding energy is a good criterion to investigate about the stability of intercalated graphite systems. We have calculated the binding energy for various numbers of DMPI intercalation into graphite following different staging mechanisms, using the following equation.

\[
E_{\text{Binding}} = \frac{E_{[(\text{DMPI}),C_m]} - E_{C_m} - xE_{\text{DMPI}}}{x}
\]

(1)

where, \( x \) is the number of DMPI cations, \( E_{[(\text{DMPI}),C_m]} \), \( E_{C_m} \) and \( E_{\text{DMPI}} \) are the total energies of DMPI intercalated graphite system, bulk graphite system and single DMPI cation, respectively. Hence, more negative binding energy value indicates the more feasible intercalation of DMPI cation into the graphite system as shown in Table 1. At a low concentration of DMPI cations (4 DMPI), intercalation into graphite is less favourable for every stage with lower binding energy (~2.5 eV) compared to intercalation at higher concentrations. This low binding energy may be due to the activation barrier which needs to be overcome during gallery height opening against the interplanar van der Waals interactions among graphite layers. Further DMPI cation
intercalation into the already opened galleries becomes more feasible in case of each stage with higher calculated binding energies. This phenomenon is also reported in several experimental studies on DIBs, where the experimental coulombic efficiency is very poor in the first few cycles.\textsuperscript{25,27} Moreover, binding energy ($\sim$ -3.5 eV) of DMPI cation intercalation is found to be higher than the anion ($\text{AlCl}_4^-$: -1.5 eV; $\text{PF}_6^-$: -2.9 eV) binding in graphite, which can be possible due to the $\pi$-$\pi$ interaction between DMPI imidazolium ring and the graphite layers.\textsuperscript{54,55} However upon approaching maximum DMPI cation intercalation the binding energy again decreases for each stage, which could be due to the electrostatic repulsion between neighbouring DMPI cations in the same gallery. As the binding energy value is still negative, the effective repulsive forces between cations must be less than the attractive forces due to intercalation. In an experimental report by Lv \textit{et al.}, higher cut-off working voltage has been considered to maintain the better coulombic efficiency, which could be due to our calculated high binding energies (2.4-4.5 eV) for DMPI cation intercalation in graphite anode for all the possible stages.\textsuperscript{25} Additionally, we have also tried to address the advantage of using DMPI rather than EMI for intercalation into graphitic anode for dual graphite batteries. We have calculated the binding energy of EMI cation intercalated graphite layers. Our calculated low binding energy (+0.007 eV for stage-1) for EMI cation intercalation validates the infeasibility of using EMI with graphite anode, which has been reported experimentally.\textsuperscript{59} Hence, very poor electrochemical performance is observed which can be ascribed to the lack of alkyl substituents in the C2 position of the imidazolium ring of EMI cation. The imidazolium cations with proton in the C2 position are less stable inside the graphite layers. This observation can be explained by applying natural bond orbital (NBO) charge calculation \textsuperscript{60}, where the C2 carbon of DMPI has an almost double charge (0.493 |e|) than C2 carbon (0.288 |e|) of EMI (Figure S9). So, the resultant interaction of DMPI-graphite is more compared to the EMI-graphite. This is also reflected in the experimental XRD studies, where any characteristic peak is absent for EMI-
graphite system. Overall, from binding energy calculations, we can conclude that the DMPI cation has fair binding strength which is essential in DIBs, and graphite can be used as a potential anode.

Table 1. Binding Energy per DMPI cation (eV) and Interlayer Distance (Å) for All the Stages with Different Concentration.

| Stages | No. of DMPI cations | Binding Energy (eV) | Interlayer Distance (Å) |
|--------|---------------------|---------------------|-------------------------|
| 1      | 4                   | -2.48               | 6.92                    |
|        | 8                   | -3.58               | 7.14                    |
|        | 12                  | -3.90               | 7.16                    |
|        | 16                  | -3.59               | 7.54                    |
| 2      | 2                   | -2.51               | 5.23                    |
|        | 4                   | -3.99               | 5.30                    |
|        | 6                   | -4.01               | 5.39                    |
|        | 8                   | -3.80               | 5.53                    |
| 3      | 2                   | -2.45               | 4.64                    |
|        | 4                   | -4.04               | 4.61                    |
|        | 6                   | -4.26               | 4.71                    |
|        | 8                   | -3.76               | 5.03                    |
| 4      | 1                   | -2.64               | 4.37                    |
|        | 2                   | -4.17               | 4.39                    |
|        | 3                   | -4.54               | 4.38                    |
|        | 4                   | -3.90               | 4.47                    |

3.4. Staging Mechanism and XRD Analysis

To relate the staging mechanism actually occur during DMPI intercalation into graphite, we have simulated XRD patterns for our optimised intercalated systems. We have compared our simulated XRD patterns with the experimental results. We notice that the graphite structure gets deformed upon intercalation of the DMPI cations along with increase in the interlayer spacing. As the gallery height (3.35 Å) of graphite is less than the DMPI cation size (4.6 Å), the graphite interlayer spacing increases in the very first intercalation step. After the
intercalation of DMPI cation, the average gallery height expansion in graphite is found to be 115%, which is comparable to reports of various anion intercalation in graphite.\textsuperscript{54,55} The average interlayer distance can be calculated by the formula,

\[
\text{Average interlayer distance} = \frac{\text{total height of the stage} - n \times \text{having } n-1 \text{ galleries or } n \text{ graphite layers}}{n-1 \text{ galleries or } n \text{ graphite layers}}
\]

The average interlayer distance for all the stages has been included in Table 1. The distance between two layers of DMPI intercalated graphite \textit{i.e.}, the intercalant gallery height (d\textsubscript{i}) remains similar (~7.1-7.6 Å) for all the stages which are comparable with the experimental report (7.16 Å) for DMPI intercalation.\textsuperscript{59} Our simulated XRD pattern of DMPI intercalated system for all the stages (n =1-4) as shown in Figure 4, helps to understand the structural changes in graphite system. The XRD patterns suggest the structural changes in graphite upon intercalation with characteristic shifting of (002) peak of graphite. To index the stage number (n) of the GICs, two characteristics peaks are observed, such as (00n +1) and (00n + 2) planes along the stacking direction upon the XRD analysis. The \(d\textsubscript{00n+1}\) represents the spacing between adjacent layers. The intercalant gallery height (d\textsubscript{i}), gallery expansion (\(\Delta d\)) and periodic repeating distance (I\textsubscript{c}) of a particular stage index ‘n’ are calculated using the d-spacing values as, \(I\textsubscript{c} = d\textsubscript{i} + (n - 1) \times 3.35 = \Delta d + n \times 3.35 = (n + 1) \times d\textsubscript{00n+1} \); similarly for \(d\textsubscript{00n+2}\), \(I\textsubscript{c} = (n + 2) \times d\textsubscript{00n+2} \); where \(\Delta d = d\textsubscript{i} - 3.35\) and 3.35 Å is the interlayer distance between two consecutive graphite layers.\textsuperscript{52} In the case of pristine graphite an intense peak is found at 2\(\theta\) = 26.5° belonging to its (002) plane generally.\textsuperscript{12} For our simulated XRD pattern, we can identify such a peak at 26.16° for the pristine system which shifts to 25.88°, 25.18°, 25.75° and 24.96° for stage-1, stage-2, stage-3 and stage-4 intercalation, respectively as shown in Figure 4. As the distortion and lateral displacement in graphite layer stacking increases with increase in DMPI intercalation, other intense peaks belonging to various planes can also be identified at lower ranges of 2\(\theta\) in the XRD plot as represented in Figure S10. In the previous report of
experimental DMPI intercalation by Lv et al., the (002) peak of the system found to shift from $2\theta = 26.4^\circ$ for pristine graphite to $2\theta = 26.0^\circ$ for GIC. Consequentially, from our XRD plots we can suggest that the stage-1 intercalation ($2\theta = 25.88^\circ$) of DMPI cation in graphite occurs predominantly (Figure S4), which also agrees with an experimental study by Sutto et al.\textsuperscript{59}

**Figure 4.** Schematic diagram of simulated XRD pattern of pristine graphite and different stages of DMPI intercalated systems where $2\theta$ ranges in $22^\circ - 34^\circ$.

### 3.5. Electrochemical Properties

In this section, we have discussed the electrochemical performance of a DIB with dual-graphite electrodes, where DMPI cations are paired with the AlCl\textsubscript{4} anions. Upon charging, the DMPI cations and AlCl\textsubscript{4} anions are expected to undergo intercalation into graphite anode and cathode,
respectively, while during discharging both the ions are expected to diffuse back to the electrolyte. Hence to investigate the electrochemical properties of DMPI with graphite anode, it is necessary to also include the AlCl\(_4^-\) anion intercalation into graphite cathode.

### 3.5.1. AlCl\(_4^-\) Intercalation into Graphite Cathode

Anion intercalation phenomena for layered structure like graphite electrode has been well studied both theoretically and experimentally.\(^{54,12}\) Our previous study has also established the exact staging mechanism pathway for AlCl\(_4^-\) anion intercalation into the graphite cathode.\(^{54}\) Motivated by those studies, we have modelled four stages (n = 1-4) for AlCl\(_4^-\) anion intercalation keeping the concentration of AlCl\(_4^-\) anion fixed. From our relative energy calculations, we could confirm that in the initial period of charging process, stage-4 AlCl\(_4^-\) intercalation is more favourable (Figure S11). From our simulated XRD data, we could identify (005) and (006) planes at 2\(\theta\) = 23.32° and 28.07° with the d-spacing of 3.81 and 3.17 Å, respectively. For experimental diffraction patterns, 2\(\theta\) values are obtained at 23.7° and 28.5° with the d-spacing of 3.77 and 3.15 Å which are comparable with our simulated patterns.\(^{12}\)

### 3.5.2. Voltage Calculations

The open circuit voltage (OCV) is one of the most important parameters in deciding a suitable battery which stands for the output voltage of a battery at full intercalation capacity or at full charge in other words. As in DIB system, the IL electrolytes (DMPI-AlCl\(_4^-\)) behave not only as a charge carrier but also as the active material towards electrochemical activity. The OCV depends upon both cathode and anode reactions of the DIB system. The discharge voltage can be calculated from the following cathodic and anodic reaction,

\[
\text{Cathode reaction: } C_n(AlCl_4)_y + e^- \leftrightarrow C_n + yAlCl_4^- \\
(2)
\]

\[
\text{Anode reaction: } C_m(DMPI)_x \leftrightarrow C_m + xDMI^+ + e^- \\
(3)
\]
Overall:  \[ C_m(DMPI)_x + C_n(AlCl_4)_y \leftrightarrow x(DMPI)^+ + yAlCl_4^- + C_m + C_n \]  

where, \( x \) and \( y \) are the number of DMPI cations and AlCl\(_4\) anions, respectively. \( C_m \) and \( C_n \) are graphite anode and graphite cathode, respectively. From the above reaction it is evident that the reaction mechanism of the DIB also includes contribution from electrolyte medium.

The cell voltage (V) can be calculated from the Nernst equation, \( V = \frac{-\Delta G_{cell}}{zF} \); where, \( z \) and \( F \) are the number of electrons transferred and Faraday constant, respectively, while \( \Delta G_{cell} \) is the change in Gibbs free energy during the chemical reactions.

\[ \Delta G_{cell} = \Delta H_{cell} - T\Delta S_{cell}; \quad \Delta G_{cell} = \Delta E_{cell} + P\Delta V_{cell} - T\Delta S_{cell} \]

As our calculations are performed at 0 K temperature, so the change in volume (\( \Delta V_{cell} \)) and entropy (\( \Delta S_{cell} \)) of the reactions are negligible. Thus, the Gibbs free energy change only depends upon the change of internal energy (\( \Delta E_{cell} \)).

Therefore, the internal energy change of the overall reaction would be,

\[ \Delta E_{cell} = \{xE_{DMPI}^+ + yE_{AlCl_4^-} + E_{C_m} + E_{C_n}\} - \{E_{[C_n(AlCl_4^-)_y]} + E_{[C_m(DMPI^+)_x]}\} \]

where, \( E_{[C_n(AlCl_4^-)_y]} \), \( E_{[C_m(DMPI^+)_x]} \), \( E_{AlCl_4^-} \) and \( E_{DMPI^+} \) are the total energy of AlCl\(_4\) intercalated graphite system and DMPI intercalated graphite system, AlCl\(_4\) and DMPI fragments, respectively. \( E_{C_m} \) and \( E_{C_n} \) are total energy of the graphite system. \( E_{AlCl_4^-} \) and \( E_{DMPI^+} \) are calculated by the optimizing of AlCl\(_4\) anions and DMPI cations as a molecular species due to the nonavailability of their crystal structure.

Then the average voltage would be,

\[ V = \left( \frac{\{E_{[C_n(AlCl_4^-)_y]} + E_{[C_m(DMPI^+)_x]}\} - \{xE_{DMPI}^+ + yE_{AlCl_4^-} + E_{C_m} + E_{C_n}\}}{z} \right) \]
To understand the exact mechanism of intercalation in a DMPI-AlCl$_4$ DIB, we have considered the different staging intercalation behaviour of both cations and anions at initial and final periods of the charging process. Therefore, based on our model we have considered all combinations of staging behaviour possible upon intercalating four cations and anions into graphite anode and cathode to replicate the initial charging environment, which is presented in Table 2. The highest calculated voltage is 5.25 V, which is obtained from the combination of stage-2 DMPI - stage-4 AlCl$_4$ intercalated system. Experimental evidence suggests that the voltage plateaux range within 3.1-4.3 V with cut-off charging voltage at 4.4 V indicating that the discharging voltage would remain lower than 4.4 V. However, our observation and literature suggest that stage-4 intercalation in case of AlCl$_4$ is more feasible compared to the other stages during the initial charging process. The combination of stage-3 DMPI - stage-4 AlCl$_4$ and stage-4 DMPI - stage-4 AlCl$_4$ yields voltage of 5.23 and 5.16 V, respectively, which are also higher than the considered cut-off voltage in experimental report. Interestingly, the combination of stage-1 DMPI - stage-4 AlCl$_4$ voltage values gives an output voltage of 3.74 V, which matches with the experimental voltage range 3.1-4.3 V. In addition, our calculated results and experimental evidence supports that stage-1 formation of DMPI is more feasible than other stages. Thus we propose that during initial charging process, the stage-1 DMPI - stage-4 AlCl$_4$ intercalation occurs. However, when the charging process approaches completion, both DMPI and AlCl$_4$ ions are expected to follow stage-1 type of intercalation into graphite system. Considering the combination of stage-1 DMPI - stage-1 AlCl$_4$ results in OCV of 4.6 V for maximum intercalation (16 cations and anions) at both the electrodes, which is comparable with the upper limit of reported experimental voltage.

Table 2. Calculated theoretical voltage (V) with different stages of DMPI cations and AlCl$_4$ anions.
Furthermore, we have calculated the gravimetric capacity (C) for our considered DIB system. The gravimetric capacity of both cathode and anode can be calculated using the following equation:\(^5^4\)

\[
C_{\text{cathode}} = C_{\text{anode}} = \frac{nxF}{M_f}
\]  

(7)

where, \(n\) is the number of electrons transferred per formula unit, \(x\) is the number of ions intercalated, \(F\) is the Faraday constant, \(M_f\) is the mass of formula unit, and \(C_{\text{cathode}}\) and \(C_{\text{anode}}\) are the capacity of the cathode and anode, respectively. The total cell capacity (\(C_{\text{total}}\)) can be expressed as a combination of the individual capacity of both cathode and anode.\(^6^3\)

\[
C_{\text{total}} = \frac{1}{C_{\text{anode}}} + \frac{1}{C_{\text{cathode}}} + \frac{1}{C_M}
\]  

(8)

Where, \(1/C_M\) is the specific mass of the other cell components such as electrolyte, separator, and current collector. \(1/C_M\) varies significantly with cell to cell design process, so the contribution of \(1/C_M\) in total theoretical cell capacity is neglected. Therefore the theoretical cell capacity can be given by,

\[
C_{\text{total}} = \frac{C_{\text{anode}} \times C_{\text{cathode}}}{C_{\text{anode}} + C_{\text{cathode}}}
\]  

(9)

Our calculated gravimetric capacity for the early stage of the charging process (four number of intercalated ions) is 15 mAh/g which reaches a maximum capacity of 62 mAh/g upon full
intercalation (sixteen number of ions). In the experimentally produced DMPI-AlCl\textsubscript{4} DIB, initial gravimetric capacity was reported to be 27 mAh/g which could further be increased up to 82 mAh/g at higher current density with subsequent loss in coulombic efficiency of the cell.\textsuperscript{25} During the initial charging process by considering four ions intercalation, as the DMPI cations follow stage-1 and AlCl\textsubscript{4} anions follow the stage-4 intercalation, a partial gravimetric capacity of 15 mAh/g is calculated. In a fully charged system considering sixteen ions intercalation, both DMPI and AlCl\textsubscript{4} ions follow the stage-1 intercalation, resulting in maximum capacity of 62 mAh/g. Based on our theoretical insights and available experimental observations, we believe that graphite-like layered materials can be further explored as anode material for intercalating large size organic cations in order to achieve higher output voltages (~4.6 V) compared to batteries based on intercalation of AlCl\textsubscript{4}– ions only (~2.0 V).\textsuperscript{12,54} Moreover, we have calculated volume expansion for DMPI intercalation in graphite to be ~115%. So, the expansion due to DMPI intercalation is less compared to AlCl\textsubscript{4} intercalation in graphite system (150-160%).\textsuperscript{54} However, the reported cycle life values (1000 cycles) are less for DMPI-graphite system which could be due to the strong interaction between DMPI and graphite, hindering repeated intercalation/deintercalation cycle. Along with this, we have also tried to provide rationale for the experimentally observed self-discharge nature of the DMPI-AlCl\textsubscript{4} DIB with the help of free energy calculation of the cell reactions. The cathodic reaction for AlCl\textsubscript{4} intercalation into graphite cathode (reaction 2) is well established in DIBs studies and AlCl\textsubscript{4} anions are not known to actively participate in the self-discharge process. The anodic reaction of DMPI intercalation into graphite is calculated to have a reaction free energy of +0.08 eV, which is much lower than that of cathodic reaction (+5.6 eV). Thus, in a bias free discharging environment, DMPI deintercalation is expected to occur much spontaneously compared to AlCl\textsubscript{4} deintercalation. This partiality in spontaneity of the individual cell reactions may be the
reason for the DMPI-AlCl$_4$ battery experiencing self-discharge process which needs to be further investigated.

### 3.6. Electronic Properties

We have studied the electronic structure circumstance of the DMPI cation intercalated graphite system to understand the nature of interaction between DMPI cation and graphite host, as organic cation intercalation is less common compared to the anion intercalation into layered graphitic structure. During charging, the electron flows from cathode to anode through the external circuit which allows the adsorption/intercalation of cations and anions into the anode and cathode material, respectively. Similarly, during discharge, the reverse phenomena happen as electron flows from anode to cathode thus providing electricity. Hence, constant electronic conductivity of the electrodes during charge/discharge cycle is essential in a battery. The electronic conductivity can be interpreted from the DOS plots on the basis of nature of the Fermi region. Figure 5a represents the total DOS (TDOS) and projected DOS (PDOS) for the DMPI intercalated graphite system. Graphite is known to show good in-plane electronic conductivity because of presence of the $p_z$ electronic states at the Fermi and no interplane conductivity as s, $p_x$ and $p_y$ electronic states are far from the Fermi. In comparison with DOS plot of well-known pristine graphite system, in our DOS plot of cation intercalated graphite, the Fermi level is shifted towards the conduction band due to the charge transfer from DMPI to graphite. Hence, the electronic conductivity is maintained as shown by the presence of electronic states at the Fermi in Figure 5a. The DMPI-graphite system is found to be metallic in nature due to overlapping between 2p orbital of imidazolium ring of cation containing C and N atom with the 2p orbital of graphite C atoms. The shifting of the Fermi level towards the conduction band indicates the reduction of graphite layers which satisfies the criteria for selection of a suitable DIBs anode material.
The qualitative charge transfer between DMPI cation and graphite layers can be illustrated by plotting charge density difference (CDD) of the systems before and after intercalation. Thus, CDD can be calculated from the following equation,

\[ \rho_{\text{CDD}} = \rho_{\text{total}} - \sum_i \rho_{\text{fragments}} \]  

(10)

Where, \( \rho_{\text{total}} \) is the total charge density of the DMPI-graphite system and \( \rho_{\text{fragments}} \) is the charge density of the individual fragments. The CDD plot has been shown in Figure 5b, where yellow colour represents the charge density accumulation and cyan colour represents the charge density depletion. From the CDD plot, we can infer that charge from the loosely bounded \( \pi \)-electron cloud of the DMPI imidazolium ring is transferred to the graphite layers. Furthermore, the C2 containing methyl group of the DMPI also transfers less amount of charge to the graphite layers. The charge transferred from the propyl chain of the DMPI cation is less because of tightly bounded \( \sigma \)-electron of the C-C and C-H bonds. Overall, net charge is gained by the graphite layers and lost by the DMPI cation, thus indicating partial ionic interaction between them. To justify this qualitative explanation, we have determined the quantitative charge transfer using the Bader charge analysis. Quantitatively, 0.87 |e| charge transfer is found to occur from DMPI to graphite layer which signifies the electrochemical reduction of graphite and DMPI being cationic, during the charging process. Overall from the DOS and CDD study, we can conclude that the graphite can also be used as an anode material for DMPI cation intercalation along with as a cathode material for AlCl₄ anion intercalation thus behaving as an amphoteric electrode material for dual graphite battery technology.¹⁷,¹⁹,²⁰
Figure 5. (a) TDOS and PDOS of the DMPI cation intercalated graphite. The Fermi level is set to zero. (b) Isosurface (0.0008 |e|Å⁻³) for the CDD plot of DMPI intercalated system, where yellow colour indicates the electron density accumulation and cyan colour indicates electron density depletion.

3.7. Diffusion Pathway of DMPI Cation

The fast charge/discharge rate of DIB can be explained from the diffusion barriers of DMPI cation in the graphite layers. The diffusion barrier has a high impact on the battery performance, where the charging/discharging rate can be determined by the mobility of DMPI cations on the AB stacked plane of the graphite layers. Hence, trouble-free diffusion and high mobility of DMPI cations is a prerequisite for developing a dual graphite battery with a fast charge/discharge rate. To determine the diffusion barriers of the DMPI cation within graphite lattice using the CI-NEB method, we have considered four minimum energy pathways (MEPs) of diffusion initiating from the most stable site (Hollow) of DMPI cation to next most stable binding site (Hollow) on the AB stacked graphite in Figure 6a. The MEPs have been shown in the Figure 6b and the structural energy profile diagram have been displayed in Figure S12. For diffusion of DMPI cation along path-1, a minimum energy barrier of 0.2 eV is obtained. Similarly, for path-2, path-3, and path-4 the diffusion barrier is calculated to be 0.35, 0.36, and 0.44 eV, respectively.
Our calculated diffusion energy barrier values are very much comparable with the various reported alkali metal cation intercalated graphite systems such as for Li or Na (0.2-0.4 eV). Therefore, our diffusion studies indicate that the organic DMPI cation intercalated anode can be used for high performance DIB with high discharge voltage, low diffusion barrier, and high electronic conductivity.

Figure 6. Schematic representation of the four diffusion barriers pathway, (a) Nearest possible most stable site of the hollow in AB stacking, where green, red, yellow and orange colour arrows indicate the path-1, path-2, path-3 and path-4, respectively. (b) Energy profile diagram of four diffusion process, where path-1, path-2, path-3 and path-4 energy barriers are 0.2 eV, 0.35 eV, 0.36 eV and 0.44 eV, respectively.

4. Conclusion and Outlook

In this work, we have carried out a systematic computational investigation of organic cation (DMPI) intercalation into the graphite anode for the first time. Based on the dispersion-corrected density functional theory calculations, we have investigated the staging mechanism of DMPI cation intercalation, charge transfer mechanism from the graphite anode, diffusion barrier, and electrochemical properties like voltage and specific capacity. Here, we have modelled four different stages (stage-1, stage-2, stage-3, and stage-4) of DMPI cation
intercalated graphite system to investigate the staging mechanism and electrochemical properties. To verify the stability, we have calculated the binding energy of the DMPI cation intercalated graphite system, where DMPI cation prefers to intercalate parallel over the perpendicular orientation into AB stacked graphite plane due to $\pi-\pi$ interaction of aromatic imidazolium cation with graphite hexagonal rings. Further, we have validated the thermal stability of the DMPI cation intercalation at stable hollow site of AB stacked graphite using AIMD simulations. We also report the existence of thermal equilibrium between the hollow and top site of DMPI intercalation. Upon intercalation of DMPI cation, interlayer spacing of graphite is found to increase from 3.34 Å to 7.2 Å which facilitates trouble-free diffusion of DMPI cation through graphite layers. Our calculated diffusion barriers support this fact, and we observe a quite small barrier of 0.2 eV for DMPI cation diffusion inside graphite. Our calculated total energy values for different stages of DMPI cation intercalation follow the stability trend as: stage-2 < stage-4 < stage-1 during the initial charging process. However, later stages of DMPI intercalation into graphite are expected to follow stage-1 type intercalation mechanism as is evident by the decrease in relative energy of stage-1 compared to other stages with increase in concentration of DMPI cations. Our simulated XRD patterns for stage-1 DMPI cations intercalation process and stage-4 AlCl$_4$ anion intercalation process match with the experimental XRD patterns of the electrodes during charging process, thus validating the staging mechanism proposed by us. Our calculated average voltages for early and later periods of intercalation (3.7 V and 4.6 V) are in good agreement with the experimental range (3.1-4.3 V). These results signify the importance of using graphite anodes for organic cation intercalation along with AlCl$_4$ anion intercalation in cathodes to achieve better electrochemical performance compared to DIBs using metal anodes along with AlCl$_4$ intercalated graphitic cathodes. The metallic character of graphite before and after DMPI cation intercalation obtained from DOS plots confirm the constant electronic conductivity of graphite anode. The
CDD and quantitative Bader charge analysis suggest +0.87 |e| charge transfer occurring from the DMPI cation imidazolium ring to the host graphite carbon atoms, thus indicating the electrochemical reduction of graphite during the charging process. Additionally, we have addressed the reason behind the self-discharge nature of DMPI-AlCl₄ graphite DIBs. Some of the shortcomings of the dual-ion batteries are electrolyte decomposition and exfoliation of the electrode materials. There is minimal scope of electrolyte decomposition occurring at our calculated output voltage of 3.7 V as it is lower than the experimentally determined cut-off voltage (4.4 V). Exfoliation can result in the loss of crystallinity of the electrode. Exfoliation can occur (1) due to lack of proper synchronization of volume expansion and contraction of electrode upon charging and discharging process, (2) all ions are not fully deintercalated in discharge process. As the volume expansion is limited for DMPI intercalated graphite system, hence the exfoliation can occur from presence of DMPI cation inside the graphite layer in discharge process due to high binding energy between DMPI cation and graphite. However, experimental data showing the presence of DMPI cation inside graphite in discharge state is not available and hence, further experimental investigation is required. Overall, this article provides an in-depth understanding of the interaction between DMPI cation and graphite and help in explaining the different staging mechanisms in both cation and anion to obtain the precise electrochemical properties such as voltage and storage capacity for DMPI-AlCl₄ graphite DIBs. We believe these findings will motivate further exploration of various organic cations which can be suitably intercalated into anodes and coupled with AlCl₄ intercalated graphite cathodes to design high performance dual ion batteries at par with lithium-ion battery technology.

5. Electronic Supplementary Information

The supplementary information file contents are, relative energies of the different binding site, details of molecular dynamics analysis at different temperature, comparative study of stage-1
and stage-2 with varying DMPI ions, pictorial representation of all four stages, NBO charge analysis of DMPI and EMI cations, XRD pattern of the DMPI intercalated graphite anode, stability study of different stages of AlCl₄ intercalated graphite cathode, and NEB diffusion barriers.

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