BCN monolayer for high capacity Al-based dual-ion batteries†

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Recent advances in the field of Al dual-ion batteries have put forward a major challenge of developing a novel and advanced cathode material that can provide high specific capacity, besides maintaining a constant high voltage. In this context, significant research has been carried out to identify new electrochemical energy storage materials, which suggest the applicability of low dimensional materials as an excellent choice due to their high surface-to-volume ratio. Herein, we perform first principles calculations to investigate the BCN monolayer as a suitable cathode material for Al dual-ion batteries. AlCl₄ has been found to reversibly adsorb on the BCN monolayer with a significant charge transfer of 0.9 |e| from BCN to AlCl₄, indicating the oxidation of BCN monolayer during the charging process. Moreover, the BCN monolayer shows excellent structural stability on systematically increasing the concentration of adsorbed AlCl₄, and could provide an open circuit voltage of 1.8 V (average voltage is 1.43 V) with a high specific capacity of 316.9 mA h g⁻¹ at the maximum concentration of AlCl₄ adsorption. The adsorption of AlCl₄ also enables good electronic conductivity. Diffusion energy calculations reveal a minimum energy barrier of 0.12 eV for the migration of AlCl₄ within BCN, ensuring similar low dimensional materials to improve the performance of Al dual-ion batteries.

1. Introduction

With the continuously increasing energy demand, secondary batteries have been widely used as energy conversion and storage units in devices, ranging from portable electronics to heavy electronic vehicles.¹ ² Li-ion batteries and lead-acid batteries, being the most commercialized batteries, are quite efficient but have certain limitations in terms of safety, abundance and manufacturing cost.³ ⁶ In this context, multivalent metal ion (Mg, Zn, Al) batteries can be a better choice due to their high abundance, low cost and high volumetric capacity.⁸ ¹⁵ Amongst the recently developed batteries, Al batteries have garnered interest due to the higher abundance (third most abundant metal in earth’s crust), high gravimetric (3 A h g⁻¹) and volumetric capacity (8.04 A h cm⁻³) compared to other metal ions.¹² ¹⁵ However, these merits are due to the anodic part and there is an essential need to look out for materials to improve the cathodic part, which can provide suitable electrochemical properties. Lin et al. assembled an Al battery having Al metal as an anode and three dimensional graphite foam as a cathode in an ionic liquid electrolyte of [EMIm]Cl/AlCl₃ (molar ratio 1 : 1.3) whose working mechanism involves the reversible intercalation/deintercalation of AlCl₄ on the cathode side during the charging/discharging process.¹⁶ ¹⁷ Simultaneously, the electrochemical deposition/dissolution of Al takes place at the anodic part during charging/discharging. This cell provides a good discharge voltage of 2 V with a specific capacity of 70 mA h g⁻¹ and an ultrahigh charge–discharge rate. Since then, different forms of graphite and conducting polymers have been utilized as cathode materials for Al batteries.¹³ ¹⁸ ²² Similarly, theoretical studies have also been carried out for carbonaceous cathode materials, such as BC₃, CₓN and G/h-BN.²³ ²₅ Among various investigated cathode materials, low dimensional materials have shown improved results in terms of storage capacity, voltage, and cyclic stability.²² ²₆ ²₉ Importantly, two-dimensional materials have attracted special interest due to their high surface-volume ratio, mechanical flexibility, cycle life and thermal stability.³₀ ³₁ Thus, for the improvement of the electrochemical properties.
of Al dual-ion batteries, there is a need to look out for other low-dimensional cathode materials. One such potential candidate is the 2D hexagonal graphenic BCN monolayer, recently synthesized by Beniwal and co-workers using bis-BN cyclohexane (B₂C₂N₂H₂) as a precursor for the epitaxial growth of the BCN monolayer on an Ir(111) substrate under ultrahigh vacuum. Graphene and hBN were also previously synthesized on Ir(111) and Rh(111) substrates. The authors further predict that due to strong intermolecular bonding between the atoms in the monolayer, free-standing monolayers can be obtained by exfoliation. In previous studies, we have observed that BC₃ gives lower capacity with higher voltage for bulk systems, while CₓN delivers higher capacity with lower voltage compared to graphite. BCN is isoelectronic in nature to graphene, but has both electron-deficient B and electron-rich N atoms, which may provide a unique adsorption environment for AlCl₄. BCN is semiconducting in nature with a bandgap (1.50 eV) that is intermediate between graphene and h-BN. Apart from these features, BCN shows higher directional anisotropy than graphene, suggesting a lower barrier for ion diffusion. Moreover, BCN has a smaller Young’s modulus value and higher flexibility than graphene, which justifies its mechanical stability. All of these properties suggest that the BCN monolayer may be a potential electrode material candidate.

In this work, we have theoretically investigated the electrochemical properties of BCN as a cathode material for Al dual-ion batteries using density functional theory (DFT). We have considered a configuration of the BCN monolayer containing equal proportions of B, C and N atoms, and studied the adsorption behavior and nature of interaction of AlCl₄ on the BCN monolayer. The electronic properties have been determined through density of states (DOS) calculation of pristine BCN and AlCl₄-adsorbed BCN. The electrochemical properties have been examined by subjecting the monolayer to step-by-step AlCl₄ adsorption. The diffusion characteristics were also carried out and overall, our results point towards the aptness of the BCN monolayer as an Al dual-ion battery cathode.

2. Computational details

The first principles calculations were carried out using the projector-augmented wave (PAW) method, as implemented in the Vienna Ab Initio Simulation Package (VASP). The generalized gradient approximation of Perdew–Burke–Ernzerhof (GGA-PBE) was used for describing the exchange–correlation potential, along with a plane-wave cut-off energy of 470 eV. All structures were fully optimized until the total energy convergence criteria of 10⁻⁵ eV were met, and the Hellmann–Feynman forces on all atoms were less than 0.01 eV Å⁻¹. A Γ-centered k-point grid of 9 × 17 × 1 was used for the unit cell optimization, while a 5 × 5 × 1 Γ-centered k-point grid was used for the 2 × 4 × 1 supercell optimization. To avoid all periodic interactions, a vacuum of 20 Å was considered along the z-direction. The DFT-D3 approach was used to include van der Waals interactions and dispersion energy corrections.

To calculate the diffusion energy barrier for the AlCl₄ molecule across the BCN monolayer, the climbing image nudged elastic band (CI-NEB) method was used by considering six intermediate images between the fully optimized initial and final structural geometry with the energy convergence criteria of 10⁻⁴ eV for each image. Bader charge analysis was performed by means of the Henkelman program, using the near grid algorithm refine edge method to understand the extent of charge transfer from BCN to AlCl₄. DOS calculations were performed using a Γ-centered k-point grid of 15 × 15 × 3 for the BCN monolayer and AlCl₄-adsorbed BCN monolayer. To examine the thermal stability of the 2 × 4 × 1 BCN monolayer, we performed ab initio molecular dynamics (AIMD) simulations using the Nosé thermostat model. A k-point grid of 5 × 5 × 1 was considered to perform the simulation at 300 and 400 K, as the batteries were expected to work using room temperature ionic liquid electrolyte for 10 picoseconds (ps) with a time step of 1 femtosecond (fs).

The overall cell reaction for the adsorption of x number of AlCl₄ molecules on the BCN monolayer can be written as:

\[
\frac{3}{x}[\text{AlCl}_4]_x \text{BCN} + 4[\text{EMI}^+ \text{AlCl}_4^-] + \text{Al} \leftrightarrow \frac{3}{x}[\text{BCN}] + 4[\text{EMI}^+ \text{Al}_2\text{Cl}_7^-]
\]

The cell voltage can be calculated by the Nernst equation,

\[
V = \frac{-\Delta G_{\text{cell}}}{zF}
\]

where \(\Delta G_{\text{cell}}\) is the change in Gibbs free energy of the cell reaction, z is the total number of electrons involved in the cell reaction, and F stands for the Faraday constant. \(\Delta G\) for a reaction is given as

\[
\Delta G_{\text{cell}} = \Delta E_{\text{cell}} + PAV_{\text{cell}} - T\Delta S_{\text{cell}}
\]

At 0 K temperature, the contribution of the volume effect \(V_{\text{cell}}\) and entropy \(S_{\text{cell}}\) can be neglected. Hence, \(\Delta G_{\text{cell}}\) can be approximated to the change in internal energy \(\Delta E_{\text{cell}}\). This change in the internal energy for the overall cell can be calculated by eqn (4).

\[
\Delta E_{\text{cell}} = \left\{ \frac{3}{x}E_{\text{BCN}} + 4E_{[\text{EMI}^+ \text{AlCl}_4^-]} \right\} - \left\{ \frac{3}{x}E_{[\text{AlCl}_4]_x \text{BCN}} + 4E_{[\text{EMI}^+ \text{Al}_2\text{Cl}_7^-]} + E_{\text{Al}} \right\}
\]

where \(E_{\text{BCN}}\) is the total energy of the BCN system, while \(E_{[\text{AlCl}_4]_x \text{BCN}}\), \(E_{[\text{EMI}^+ \text{Al}_2\text{Cl}_7^-]}\), and \(E_{[\text{EMI}^+ \text{AlCl}_4^-]}\) are the total energies of the AlCl₄-absorbed BCN system, EMI⁺Al₂Cl₇⁻ and EMI⁺AlCl₄⁻, respectively. \(E_{\text{Al}}\) is the energy per Al atom in its bulk. \(E_{[\text{EMI}^+ \text{Al}_2\text{Cl}_7^-]}\) and \(E_{[\text{EMI}^+ \text{AlCl}_4^-]}\) were calculated by optimizing EMI⁺Al₂Cl₇⁻ and EMI⁺AlCl₄⁻ as ion pairs in a box due to the unavailability of their crystal structures. The solvent effect was not considered in our calculation, as it has been reported that the difference between the solvation energies of AlCl₄⁻ and Al₂Cl₇⁻ is very small (∼0.1 eV) in such cases.

Therefore, the voltage \(V\) for the system can be calculated by using eqn (5),
where \( z \) is the electronic charge. However, the specific capacity (\( C \)) can be calculated by using eqn (6),

\[
C = \frac{zxF}{M_f}
\]

where \( z \) is the number of electrons transferred per formula unit, \( x \) is the number of \( \text{AlCl}_4^- \) adsorbed on the BCN monolayer, \( F \) is the Faraday constant and \( M_f \) is the mass of the BCN formula unit.

3. Results and discussion

3.1. Structural stability of BCN

Fig. 1a–c show the three most commonly studied configurations of BCN, which contain B, C and N atoms in the same stoichiometric ratio of 1:1:1, with the arrangement of atoms and the connectivity between them being different. They are made up of different hexagonal units, as configuration (a) consists of a \( \text{B}_2\text{C}_2\text{N}_2 \) unit, while (b) is composed of \( \text{B}_4\text{C}_2\text{N}_2, \text{B}_2\text{C}_3\text{N}, \text{BC}_3\text{N}_2, \) and \( \text{B}_5\text{N}_3 \) units, and (c) is made up of \( \text{B}_2\text{C}_2\text{N}_2, \text{B}_5\text{N}_3, \text{B}_4\text{C}_3, \) and \( \text{C}_6\text{N}_3 \) units. Among all three configurations, (a) was found to be relatively most stable energetically, followed by (b) and (c). The monolayer configurations (a) and (b) have B–C, B–N, C–N and C–C connecting bonds, while (c) does not have any C–C bonds. Upon comparing the bond lengths, we found that the C–C bonds were shortest with a bond length of 1.38 Å, followed by C–N, B–N and B–C with bond lengths of 1.40 Å, 1.45 Å, and 1.54 Å, respectively. This explains the lower stability of monolayer (c) with respect to (a) and (b), as it does not have strong C–C bonds. In contrast, monolayer (a) has the maximum number of C–C bonds, and is thus found to be the most stable. This is consistent with a previous theoretical study stating that the most stable BCN structures tend to maximize the number of B–N and C–C bonds. The higher stability of configuration (a) was also previously reported on the basis of the computed electronic energy and relative cohesive energy. Our cohesive energy calculations yielded a value of –8.38 eV per atom for the BCN unit cell of configuration (a), which is comparable to our calculated value of graphene (–8.9 eV). The reported value for graphene is around –8.1 eV. Thus, the monolayer once formed will not spontaneously decompose into individual atoms.

Henceforth, we have adopted configuration (a) of the BCN monolayer to construct a 2 × 4 × 1 supercell, as presented in Fig. 1d for investigating the suitability of BCN as a cathode material. To start with, we have examined the thermal stability of the 2 × 4 × 1 monolayer. The effect of temperature on the phase stability was analyzed at 300 and 400 K. There is no appreciable energy change throughout the simulation for both cases, as shown in Fig. S1a and b (ESI†). Furthermore, we present the snapshots of the final structure after simulation in Fig. S1d and e (ESI†), which do not show much deviation from the initial structure. The graphene-like lattice structure is also retained at the end of simulation. Hence, we can consider our BCN monolayer supercell to be thermally stable.

3.2. Adsorption properties of AlCl₄

During the charging of the Al dual-ion battery, the AlCl₄ intercalates/adsorbs into the cathode material. Hence, in order to study the adsorption properties of AlCl₄, both planar and tetrahedral configurations of AlCl₄ have been considered for adsorption on the BCN monolayer. However, AlCl₄ prefers the tetrahedral geometry after the adsorption on the BCN monolayer, as reported earlier for other carbonaceous cathodes. To identify the most stable site, all available possibilities were considered, as shown in Fig. 1d for a 2 × 4 × 1 supercell. Nine stable adsorption sites could be identified, which comprise the three top sites (B top, C top and N top), four bridge sites (B–C bridge, B–N bridge, C–N bridge and C–C bridge) and two hollow sites (C–B–N–C–B–N and C–C–B–N–B–N rings). The optimized structures of AlCl₄ adsorption at these sites are also represented in Fig. S2 (ESI†). The relative adsorption energies of these sites are given in Table S1 (ESI†). The adsorption energies (\( E_{\text{adsorption}} \)) corresponding to these sites have been calculated by using eqn (7).

\[
E_{\text{adsorption}} = (E_{\text{BCN}}+\text{AlCl}_4) - (E_{\text{BCN}} - E_{\text{AlCl}_4})
\]

where \( E_{\text{BCN}}+\text{AlCl}_4 \) and \( E_{\text{BCN}} \) are the total energies of the BCN system with and without AlCl₄, respectively, while \( E_{\text{AlCl}_4} \) is the total energy of one AlCl₄ molecule. Hence, a more negative value of adsorption energy signifies the more stable adsorption of AlCl₄ on that site. As a result, the AlCl₄ adsorption is found to be most stable (–2.36 eV) at Site 8, which corresponds to the hollow site surrounded by the C–C–B–N–B–N ring, as illustrated in Fig. 1d. The average distance of Al of AlCl₄ from BCN monolayer on its adsorption at the hollow site surrounded by C–C–B–N–B–N ring is also least (3.85 Å) among all the sites, as represented in Table S1 (ESI†). The distance between AlCl₄ and the monolayer can be justified by the absence of any overlap between the electron clouds of the monolayer and AlCl₄ anion, as the interaction can be thought of as predominantly anion–π type. This has been the case in the previously reported adsorption of AlCl₄ in few-layered graphene, where the distance between C and Cl was also found to be more than 3 Å, as the Cl atoms have an ionic radii of 1.67 Å and the overall size of AlCl₄ is estimated to be 6.09 Å. The adsorption of AlCl₄ occurs in such a way that the three Cl atoms facing towards the monolayer tend to stabilize closer to the B atoms of the monolayer. This may be due to the possibility of interaction between the lone pairs of Cl and vacant p orbital of the B atoms. As a result, the AlCl₄ molecule undergoes a slight deformation as the three Al–Cl bonds facing towards the BCN monolayer get...
The adsorption of $\text{Al}_2\text{Cl}_7$ on the BCN monolayer was also investigated and the adsorption energy was calculated to be $-2.77$ eV, which is much more favourable than the $\text{AlCl}_4$ adsorption ($-2.36$ eV). This is expected due to the presence of a higher number of electronegative Cl atoms in the $\text{Al}_2\text{Cl}_7$ anion, which can induce a higher charge transfer from the monolayer. However, despite being energetically favourable, there is less probability of $\text{Al}_2\text{Cl}_7$ adsorption during the charge/discharge cycle of the battery. Firstly, it is reported that for a 1:1 ratio of [EMIm]Cl : AlCl$_3$, only AlCl$_4$ exists and the ratio must be 1:1.3, indicating that the AlCl$_3$ concentration should be higher to generate $\text{Al}_2\text{Cl}_7$ in the electrolyte.$^{55}$ Thus, the concentration of the $\text{Al}_2\text{Cl}_7$ ions is much less compared to $\text{AlCl}_4$. Second, during the charging of the battery by application of an external potential through the circuit, when AlCl$_4$ intercalation takes place on the cathodic part, $\text{Al}_2\text{Cl}_7$ must undergo simultaneous reduction to generate Al and $\text{AlCl}_4$.

$$4\text{Al}_2\text{Cl}_7^- + 3e^- \rightleftharpoons \text{Al} + 7\text{AlCl}_4^- \text{ (Anode)}$$

$$\text{C}_n + \text{AlCl}_4^- \rightleftharpoons \text{C}_n[\text{AlCl}_4] + e^- \text{ (Cathode)}$$

As a result, there is less chance that low concentrations of $\text{Al}_2\text{Cl}_7$ achieved by keeping the ratio greater than 1:1, can engage in binding with the cathode material. Based on the very low probability of $\text{Al}_2\text{Cl}_7$ being available for binding at the cathodic part, the voltage equation (eqn (5)) was derived, considering only $\text{AlCl}_4$ intercalation.

Next, to identify the nature of interaction between the adsorbed $\text{AlCl}_4$ and BCN monolayer, the charge density difference (CDD) was evaluated using eqn (8):

$$\rho_{\text{CDD}} = \rho_{\text{total}} - \sum_i \rho_{\text{fragments}}$$

where $\rho_{\text{total}}$ is the total charge density of the $\text{AlCl}_4$-absorbed BCN system, and $\rho_{\text{fragments}}$ is the charge density of the individual fragments from the system. The charge density of the individual fragments ($\rho_{\text{fragments}}$) was calculated using the pseudo structure in which the individual fragment retained the same structure as that in the system, while the remaining fragments were deleted. The CDD plot of the $\text{AlCl}_4$-absorbed BCN system at the most stable site is depicted in Fig. 2. The nature of interaction was found to be ionic. On adsorption, there is an accumulation of
electronic charge on each chlorine atom of AlCl$_4$, while depletion of electronic charge can be detected on the BCN monolayer atoms close to the adsorbed AlCl$_4$. As a result, the oxidation of the BCN monolayer cathode (along with simultaneous reduction of AlCl$_4$) during the charging mechanism can be concluded. Moreover, the charge depletion can be seen to occur from the C and N atoms, and not B atoms among the atoms surrounding the adsorption site due to the difference in electron density among them. Bader charge analysis of the system also shows that AlCl$_4$ accepts a net electronic charge of 0.9 $|e|$ from the BCN monolayer upon adsorption, signifying the cathode oxidation during charging.

### 3.3. Electrochemical and electronic properties

To calculate the electrochemical properties (like voltage and specific storage capacity) for the BCN cathode material, the BCN monolayer was systematically subjected to adsorb different concentrations of AlCl$_4$. For the different concentrations of adsorbed AlCl$_4$, all possible configurations were considered to find out the most stable configurations, as represented in Fig. 3 and Fig. S3 (ESI†). The maximum number of AlCl$_4$ adsorbed on a $2 \times 4 \times 1$ BCN monolayer was found to be 14.

To investigate the variation in adsorption behavior of the BCN monolayer with increasing concentration of AlCl$_4$ adsorption, we calculated the adsorption energy for all cases, as presented in Table 1. As the concentration of AlCl$_4$ adsorbed on BCN increases, the adsorption energy per AlCl$_4$ molecule (as well as the charge transferred per AlCl$_4$ molecule) was found to decrease. This decrease in adsorption energy might be due to the increase in repulsive forces, as the number of adsorbed AlCl$_4$ molecule increases on the monolayer. The AlCl$_4$ molecules occupy the most stable hollow site surrounded by the C–C–B–N–B–N ring in the monolayer up to 12 AlCl$_4$ molecules. On further increasing the concentration, AlCl$_4$ molecules do not necessarily occupy the most stable site and instead try to maintain distance among themselves, as shown in Fig. 3d.

| Number of AlCl$_4$ adsorbed | Adsorption energy/AlCl$_4$ (eV) | Charge transfer to per AlCl$_4$ molecule ($|e|$) | Voltage (V) |
|-----------------------------|---------------------------------|-----------------------------------------------|-------------|
| 1                           | −2.36                           | −0.90                                         | 0.84        |
| 2                           | −2.21                           | −0.88                                         | 0.99        |
| 3                           | −2.05                           | −0.82                                         | 1.15        |
| 4                           | −1.95                           | −0.75                                         | 1.24        |
| 5                           | −1.85                           | −0.70                                         | 1.35        |
| 6                           | −1.79                           | −0.67                                         | 1.41        |
| 7                           | −1.74                           | −0.64                                         | 1.46        |
| 8                           | −1.70                           | −0.61                                         | 1.50        |
| 9                           | −1.63                           | −0.58                                         | 1.56        |
| 10                          | −1.59                           | −0.56                                         | 1.60        |
| 11                          | −1.55                           | −0.54                                         | 1.65        |
| 12                          | −1.52                           | −0.52                                         | 1.67        |
| 13                          | −1.46                           | −0.51                                         | 1.74        |
| 14                          | −1.38                           | −0.47                                         | 1.81        |

The maximum of 14 AlCl$_4$ molecules are adsorbed reversibly on a $2 \times 4 \times 1$ supercell of the BCN monolayer. Further adsorption of AlCl$_4$ results in dissociation into AlCl$_3$ and Cl, as shown in Fig. S4 (ESI†), which is not recommended for the reversible charging/discharging mechanism of a cathode material. However, the BCN monolayer was not found to show any kind of structural distortion on the adsorption of 14 AlCl$_4$ molecules, and remained stable to be used as cathode material.

We calculated the theoretical charging voltage using eqn (5) for the systematic adsorption of AlCl$_4$ molecules on the BCN

![Fig. 3](image-url) Side and top views of the most stable configurations of the AlCl$_4$-adsorbed BCN monolayer at different AlCl$_4$ concentrations: (a) (AlCl$_4$)$_2$BCN, (b) (AlCl$_4$)$_4$BCN, (c) (AlCl$_4$)$_6$BCN, and (d) (AlCl$_4$)$_{14}$BCN.
monolayer. From Table 1, it is evident that the voltage for the adsorption of the first AlCl₄ molecule is only 0.84 V, which continues to increase with increasing concentration of AlCl₄. Hence, the average voltage obtained is 1.43 V. This seems to be inversely proportional with the change in adsorption energy per AlCl₄, which is understandable from eqn (5). A more stable AlCl₄-adsorbed system will require a lower charging voltage. As the AlCl₄ concentration increases, the system gets destabilized due to the repulsion among the adsorbed anions, thus requiring a high charging voltage. The open circuit voltage for the maximum AlCl₄-adsorbed system is 1.8 V, which is comparatively lower than that experimentally reported for the graphite cathode (2 V). However, the theoretical specific capacity calculated by eqn (6) for the BCN monolayer at the maximum AlCl₄ adsorption is 316.9 mA h g⁻¹ BCN, which is much more than that experimentally reported for the graphite cathode (70 mA h g⁻¹). Hence, the BCN monolayer can be considered an attractive high specific capacity cathode material that is suitable for Al dual-ion batteries.

Furthermore, the electronic conductivity of a material also plays a crucial role in determining its suitability as a cathode material. We have plotted the total and partial density of states (DOS) of the pristine BCN and AlCl₄-adsorbed BCN system, as represented in Fig. 4. In previous reports, configurations (b) and (a) of BCN have been found to be semiconducting in nature with a band gap of 1.5 eV and 1.18 eV using the HSE06 density functional and PBE functional, respectively. The DOS plots of pristine BCN of configuration (a) show the material to be semiconducting in nature with a small bandgap of 1.18 eV. The states near the Fermi level are mainly occupied by the BCN (2p) states. However, the DOS picture completely changes on adsorption of AlCl₄ on the most stable site of the BCN monolayer. The Fermi level can be detected to shift towards the valence band compared to the pristine BCN DOS plot due to the charge transfer from BCN to AlCl₄, which destabilizes the valence band. As a result, the states are introduced at the Fermi level, as there is interaction between the p states of AlCl₄ and BCN. The band gap width was also observed to shrink with increasing concentration of AlCl₄ adsorption (1.09 eV, 1.04 eV and 1.02 eV for 7, 10 and 14 AlCl₄ adsorption, respectively), as represented in Fig. S5 (ESI†). Hence, the conductivity of the BCN monolayer may increase with AlCl₄ adsorption, and satisfies the criteria for electronic conductivity of the cathode material.

3.4. Diffusion properties
Another crucial factor that determines the performance of a battery is the charge/discharge rate of its cathode material.
The charge/discharge rate depends on the migration of the adsorbed species within the cathode system. Thus, we have calculated the diffusion barrier for AlCl₄ within similar adsorption sites of the BCN monolayer using the CI-NEB method. For this, a 2 × 4 × 1 supercell of the BCN monolayer has been considered. Site 8, which corresponds to the hollow site surrounded by C–C–B–N–B–N ring (as discussed earlier in Subsection 3.2), is taken as both the starting and the end point for AlCl₄ diffusion because of its least adsorption energy. There are three possible pathways (path A, path B and path C) for AlCl₄ diffusion, as illustrated in Fig. 5. The energy vs. reaction coordinate graph shows the anisotropic diffusion behavior, as path C is the most favorable path for AlCl₄ diffusion with a smaller diffusion barrier (0.12 eV) compared to that of path A and path B, as represented in Table 2. Hence, we try to examine the stability of the highest energy transition state for path C compared to that of path A and path B. This relative stability of the highest energy transition states can be explained based on their orientations, as represented in Fig. S6 (ESI†). While trying to find the most stable orientations of AlCl₄ adsorption, we saw the tendency of the three Cl atoms of the AlCl₄ molecule in remaining closer to the B atoms of the BCN monolayer. Along the same line of thought, we find that the Cl atoms of AlCl₄ for the most stable highest energy transition state (corresponding to path C) maintain a shorter average distance (3.47 Å) to their nearest B atom of the monolayer compared to the corresponding transition states of path A and B, as given in Table 2. Overall, we find that the diffusion barrier of the minimum energy pathway (0.12 eV) is lower than the diffusion barrier calculated for the graphene bilayer as the cathode (0.19 eV) in a previous report.⁵⁴ This demonstrates the ability of the BCN monolayer to allow trouble-free AlCl₄ diffusion.

### Conflicts of interest

There are no conflicts of interest to declare.

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