BCN Monolayer for High Capacity Al based Dual-Ion Batteries

M.Sc. Thesis

By HARIOM SAINI



DISCIPLINE OF CHEMISTRY INDIAN INSTITUTE OF TECHNOLOGY INDORE JUNE 2020

BCN Monolayer for High Capacity Al based Dual-Ion Batteries

A THESIS

Submitted in partial fulfillment of the requirements for the award of the degree of Master of Science

> by HARIOM SAINI



DISCIPLINE OF CHEMISTRY INDIAN INSTITUTE OF TECHNOLOGY INDORE JUNE 2020



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CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled **BCN Monolayer for High Capacity Al based Dual-Ion Batteries** in the partial fulfillment of the requirements for the award of the degree of **MASTER OF SCIENCE** and submitted in the **DISCIPLINE OF CHEMISTRY, Indian Institute of Technology Indore**, is an authentic record of my own work carried out during the time period from July 2019 to June 2020 under the supervision of **Dr. Biswarup Pathak**, Associate Professor, Discipline of Chemistry, IIT Indore.

The matter presented in this thesis has not been submitted by me for the award of any other degree of this or any other institute.

Signature of the student with date (Hariom Saini)

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Signature of the Supervisor of M.Sc. thesis (with date) (Dr. Biswarup Pathak)

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V

Abstract

Recent advances in the field of Al based ion batteries have put forward a major challenge of developing a novel and advanced cathode material that can provide large storage capacities high specific capacity besides maintaining a constant high voltage. In this context, a noticeable 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 BCN monolayer as a suitable cathode material for Al based dual ion batteries. AlCl₄ has been found to reversibly adsorb on 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, BCN monolayer shows excellent structural stability on systematically increasing the concentration of adsorbed AlCl₄ and could provide a voltage of 1.8 V with a high specific capacity of 316.9 mAhg⁻¹ at maximum concentration of AlCl₄ adsorption. The adsorption of AlCl₄ also leads to the transition of BCN monolayer from semiconducting to metallic nature thus enabling constant electronic conductivity. Diffusion energy calculations reveal a minimum energy barrier of 0.10 eV for the migration of AlCl₄ within BCN ensuring a fast charge/discharge rate. All these findings suggest that BCN monolayer could be a potential cathode material for Al based dual ion batteries as well as motivates us to carry out further studies on similar low-dimensional materials to improve the performance of Al based dual ion batteries.

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Chapter 1 Introduction

With the continuously increasing energy demand, secondary batteries have been widely used as energy conversion and storage units in the devices ranging from portable electronics to heavy electronic vehicles [1,2]. Li-ion batteries and the lead-acid batteries being the most commercialized batteries are quite efficient but have certain drawbacks in terms of safety, abundance and manufacturing cost [3-7]. In this regard, multivalent metal ion (Mg, Zn, Al) batteries can be a better choice due to their high availability, low cost and high volumetric capacity [8-15]. Among all these recently developed batteries, Al batteries have garnered interest due to the higher abundance (third most abundant metal in earth's crust), high gravimetric (3 Ahg⁻¹) and volumetric capacity (8.04 Ahcm⁻³) compared to other metal ions [12-15]. However, all these merits are due to the anodic part and there is an essential need to look out for the materials to improve the cathodic part which can provide suitable electrochemical properties. Lin et al. assembled an Al-ion battery having aluminium metal as an anode and 3-D graphitic foam as a cathode. They have used [EMIm]Cl/AlCl₃ as an electrolyte in a molar ratio of 1:1.3. The working mechanism of that cell involves the reversible insertion/disinsertion of AlCl₄ molecule on the cathode side during charging/discharging process [16,17]. Simultaneously, electrochemical dissolution/deposition 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 mAhg⁻¹ and an ultrahigh charge-discharge rate. Since then, different forms of graphite and conducting polymers have been utilized as cathode material for Al batteries [13,18-22]. Similarly, theoretical studies have also been carried out for carbonaceous cathode materials such as BC₃, C₃N and G/h-BN [23-25]. Among various investigated cathode materials, low dimensional materials have revealed better results with regards to storage capacity, voltage, and cyclic stability [22,26-29]. Mainly two-dimensional materials have attracted special interest due to their high surface-volume ratio, mechanical flexibility, cycle life and thermal stability [30-33]. Thus, for the improvement of electrochemical properties of Al based dual ion batteries, there is a need to look out for other low-dimensional cathode materials. One such potential candidate is 2D hexagonal graphenic BCN monolayer, recently synthesized by Beniwal and co-workers. Bis-BN cyclohexane $(B_2C_2N_2H_{12})$ has been used to synthesize BCN monolayer on Ir (111) substrate under ultrahigh vacuum [34]. In previous studies we have observed that for bulk systems, BC₃ gives lower capacity with higher voltage while C₃N delivers higher capacity with lower voltage compared to graphite [23,24]. BCN is isoelectronic in nature to graphene and has both electron-deficient B and electron-rich N atoms which may provide a unique adsorption environment for AlCl₄. Previous studies show that BCN possesses a similar structure as that of graphene and is semiconducting in nature with a bandgap (1.50 eV) that is more than that of graphene and less than that of h-BN. Apart from these BCN shows higher directional anisotropy than graphene suggesting a lower barrier for ion diffusion [35]. Moreover, BCN has a smaller Young's modulus value and higher flexibility than graphene. All these properties suggest BCN monolayer as a potential electrode material candidate.

Here, by the means of DFT we have determined the electrochemical properties of BCN monolayer as a promising cathode for Al based dual ion batteries. Here, we have considered a configuration of BCN monolayer containing equal proportions of B, C and N atoms and studied the adsorption behaviour and nature of interaction of AlCl₄ on 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 step by step increasing the concentration of AlCl₄ on BCN monolayer. The charging and discharging rate have also been examined by studying the diffusion characteristics of AlCl₄ across

BCN monolayer and overall, our results point towards the aptness of BCN monolayer as Al based dual ion battery cathode.

Chapter 2

Computational methods

2.1. Computational methods and approximations

2.1.1. Schrödinger equation

During the latter part of 19th century, several experimental observations (e.g. photoelectric effect, black body radiation, discrete spectra emitted by excited atoms etc.) were reported which could not be explained based on classical theory. This led to the search for some other theory which was able to account for these experimental observations and hence origination of the concept of quantum mechanics takes place.

The quantum mechanics is basically set up on the concepts of the uncertainty principle, quantization of energy, dual behaviour of electron and the non-locality concept of the wave functions. In this context, quantum mechanical state of a system is given by a mathematical function Ψ (known as wavefunction) which depends on time and the positional coordinates of the particle of the system. In 1926, Schrödinger has proposed an equation for the description of the behavior of electron waves in atoms and molecules which could be expressed as

$$\hat{H}\psi = E\psi \tag{2.1}$$

In the above equation, \hat{H} represents the Hamiltonian operator whereas E represents total energy of the system. The above expression is known as the time independent Schrödinger equation.

While, time dependent Schrödinger equation is given as,

$$\hat{H}\psi = i\hbar\frac{d\psi}{dt} \tag{2.2}$$

Here, \hbar is given by $\frac{h}{2\pi}$, and h is planck's constant. This time dependent Schrödinger equation is the basis of most of the quantum chemical calculations. However, the given equation 2.2 can be easily solved for single

electron system (like H, He⁺, Li^{2+} etc.) but the solvation of the expression 2.2 is difficult for a many electrons system.

The Schrödinger equation for many electron systems is given as

$$\hat{H} \Psi(x_1, x_2, ..., x_n, r_1, r_2, ..., r_n) = E \Psi(x_1, x_2, ..., x_n, r_1, r_2, ..., r_n)$$
(2.3)

In the equation 2.3, $x_1, x_2, ..., x_n$ represent position coordinates of electrons and $r_1, r_2, ..., r_n$ represent position coordinates of the nucleus.

For many electron systems the Hamiltonian operator is given as follows

$$H = T_e + T_n + V_{ee} + V_{nm} + V_{ne}$$
(2.4)

Where T_e , T_n represents the total energy due to the motion of the electrons and nucleus, respectively, while V_{ee} , V_{nn} represents the coulombic interaction between electrons and nuclei, respectively, V_{ne} corresponds to the coulombic interactions between nucleus and electron. Hence, the extended Hamiltonian operator is given by equation 2.5.

$$H = -\frac{\hbar^2}{2m_e} \sum_{i=1}^{n} \nabla_i^2 - \frac{\hbar^2}{2} \sum_{I=1}^{m} \frac{\nabla_I^2}{m_I} + \sum_{i=1}^{n} \sum_{j>i}^{m} \frac{e^2}{r_{ij}} + \sum_{I=1}^{m} \sum_{J>I}^{m} \frac{z_I z_J e^2}{r_{IJ}} - \sum_{i=1}^{n} \sum_{I=1}^{m} \frac{z_I e^2}{r_{iI}} (2.5)$$

For many electron systems, the Schrödinger equation becomes very difficult to solve. As in many electron systems the exact equation can't be separated into the uncoupled equations. So, for solving this equation, some approximations are used which permits us to separate the function into uncoupled equations. The Born-Oppenheimer approximation is one of the principal approximation methods which reduces the difficulties in solving the equation 2.5 to a greater extent.

2.1.2. Born-Oppenheimer Approximation (BO Approximation)

The BO approximation is promising for describing the many body problem. It states that since the mass of the nucleus of an atom is 1836 times more than the mass of an electron and hence the nucleus of the atom can be considered stationary with respect to the electron. Therefore, the contribution of kinetic energy of the nucleus can be neglected in comparison to other terms and the coulombic interaction between nuclei can be considered as constant.

Hence, the Hamiltonian operator becomes

$$H = -\frac{\hbar^2}{2m_e} \sum_{i=1}^n \nabla_i^2 + \sum_{i=1}^n \sum_{j>i}^m \frac{e^2}{r_{ij}} - \sum_{i=1}^n \sum_{l=1}^m \frac{z_l e^2}{r_{il}}$$
(2.6)

Even after the application of BO approximation, the solution for the many electron systems wave function is computationally too expensive. Hence, further modification is required to obtain the solution more economically. Keeping this in view, other approximations like density functional theory (DFT) are very beneficial.

2.1.3. Density Functional Theory (DFT)

Schrödinger equation for many electron systems cannot be solved easily as for a system having n electrons there is 3n spatial coordinates for each electron. The inter-electronic forces also make the movement of each electron correlated. So, among the various quantum-mechanical theories designed to overcome these problems, DFT is the most used modelling method in computational and material science. As the name suggests DFT enables us to describe all the properties of the system by using electron density instead of using wave function. This electron density is a function of three positional coordinates only. Hence, the introduction of electron density reduces a problem involving 3n variables into a problem involving 3 variables making it more economical to solve. Thomas and Fermi were the first one to propose this scheme for non-interacting gaseous system. Later, it was proved by the theorem proposed by Hohenberg and Kohn.

2.1.3.1.Hohenberg-Kohn Theorems

P. Hohenberg and W. Kohn have proposed the two theorems which are known as the heart of DFT. They have proposed the following things in their theorems for the understanding of the DFT.

- 1. The ground state properties of the many electron systems can be calculated from the density of the of all the interacting electrons under the potential V_{ext} . Therefore, the ground state energy of the system in the Schrödinger's equation is the functional of the electron density n_0 .
- The second theorem says that the ground state electron density can be obtained by minimizing the energy by changing the electron density.

The Hohenberg and Kohn theorems suggest a method for minimizing energy by involving only electron density but is not capable of relating the kinetic energy with electron density. This problem has been solved by Kohn and Sham in 1965.

2.1.3.2. Kohn-Sham Equations

To understand the electron density functions clearly, Kohn and Sham have proposed a set of equations. For this the many body system is replaced by a fictious system of non-interacting electrons. They fractionized the total energy functional into the different parts as described in equation 2.7.

$$E[\rho(r)] = T_0[\rho(r)] + \frac{1}{2} \iint \frac{\rho(r)\rho(r)'drdr'}{|r-r'|} + \int V_{ext}(r)\rho(r)dr + E_{xc}[\rho(r)dr] + E_{II}$$
(2.7)

In the above equation, $T_0[\rho(r)]$ represents the energy due to the motion of the the electrons in a system having electron density ρ same as that of real system excluding electron-electron interactions. Second term in the equation 2.7, $\frac{1}{2} \iint \frac{\rho(r)\rho(r)'drdr'}{|r-r'|}$ represents the pure coulombic interaction between the electrons, third term $\int V_{ext}(r)\rho(r)dr$ is the interaction between core and valence electrons. The fourth term $E_{xc}[\rho(r)dr]$ is known as exchange-correlation energy which takes care of all the quantum interactions between electrons needed to be approximated. The last term E_{II} represents the nuclei-nuclei interactions. However, the above equation can be reduced in the following form

$$E[\{\Psi\}] = E_{known}[\{\Psi\}] + E_{xc}[\{\Psi\}]$$
(2.8)

Where, E_{known} is sum of the all the known parameters such as kinetic energy, potential energy and all the coulombic interactions which can be easily obtained. While, E_{xc} can only be solved by knowing the value of exchange-correlation potential. However, getting these values is very difficult.

2.1.3.3. Exchange-correlation functional

In equation (2.8), the unknown parameter is an exchange correlation functional, which is generally approximated by the Kohn-Sham equation. E_{xc} can be expressed as a sum of electron exchange and electron correlation as described as follows.

$$E_{xc} = E_x + E_c \tag{2.9}$$

Various local functional are used for approximating the exchange correlational energy. Some of the widely used approximations are given below.

2.1.3.4. Local Density Approximation (LDA)

The LDA is one of the important approaches to approximate exchange correlational energy. In this approach, the exchange correlational functional is considered from the homogeneous gas of the electron. Moreover, the exchange correlation functional in this approximation can be represented as follow:

$$E_{xc}^{LDA} = \int d^3 r \, n(\boldsymbol{r}) \, \mathcal{E}_{xc}^{hom}(n(\boldsymbol{r})) \tag{2.10}$$

Where, $\mathcal{E}_{xc}^{hom}(n(\mathbf{r}))$ is the average exchange correlation energy in the considered homogenous system (a system made of uniformly distributed electrons moving on a positive charge) with $n(\mathbf{r})$ as the homogeneous electron density.

If the contribution of exchange and correlational energy functional is considered separately, the exchange functional can be computed analytically however, the correlational energy lacks an analytical expression and depends on the homogeneous electron density which could be written as a sum of ρ_{α} and ρ_{β} (spin densities of the electron).

$$\rho = \rho_{\alpha} + \rho_{\beta} \tag{2.11}$$

LDA gives much better results than that of HF and is mainly used approach for the computation of stable ground state of solid materials. However, it is unable to determine crucial properties like bond dissociation energy, cohesive energy, adsorption energy and band gap of the semiconductor so precisely.

2.1.3.5. Generalized Gradient Approximation (GGA)

The GGA modifies the definition of the exchange correlational energy by including the gradient of electron density instead of electron density. Hence the exchange correlational energy functional is expressed as

$$E_{xc}^{GGA} = \int d^3 r n(\mathbf{r}) \, \mathcal{E}_{xc}^{GGA} \big(n(\mathbf{r}), \nabla n(\mathbf{r}) \big) \tag{2.12}$$

The GGA gives very precise results of the total energy as compared to that of LDA. One of the most commonly GGA approximation was formulated by Perdew, Burke and Ernzerhof (PBE) as follows

$$E_{x}^{PBE} = \int d^{3}r \, n(\boldsymbol{r}) \, \mathcal{E}_{x}^{PBE} \big(n(\boldsymbol{r}), s(\boldsymbol{r}) \big)$$
(2.13)

The PBE exchange energy expression is generated by multiplying LDA exchange by an enhancement factor F_x^{PBE} which depends on $s(\mathbf{r})$. Hence E^{PBE} could be written as follows

$$\mathcal{E}_{x}^{\text{PBE}}(n(\mathbf{r}), \mathbf{s}(\mathbf{r})) = \mathcal{E}_{x}^{\text{LDA}}(n(\mathbf{r})) * F_{x}^{\text{PBE}}(\mathbf{s}(\mathbf{r}))$$
(2.14)

2.1.4. Projector Augmented Wave Method (PAW)

Since the electronic wave functions of true materials have different behaviour in different regions. i.e. in bonding (or valence region) the oscillation of wave function is very smooth while for the electrons in cores the oscillation is very rapid. In general valence electrons are described by a plane wave basis set while, Core electrons could not be represented by the plane wave basis set due to their high computational cost. Hence this method uses the partial wave function to represents the electron in the augmented region. In PAW method, the highly oscillating wave function transforms to smoother form which depends on the linear transformation operator (T). The linear transformation operator transforms a wavefunction into pseudo wave function.

$$|\tilde{\Psi}_{n}\rangle = T|\Psi_{n}\rangle \tag{2.15}$$

Where $\widetilde{\Psi}_n$ represents the pseudo wave function. The wave functions $(|\Psi_n\rangle$ and $|\widetilde{\Psi}_n\rangle$) are expressed as a linear combination of partial waves for each augmentation regions as described below:

$$|\Psi_{n}\rangle = \sum_{i} c_{i} |\phi_{i}\rangle \qquad (2.16)$$

$$|\widetilde{\Psi}_{n}\rangle = \sum_{i} c_{i} |\widetilde{\phi}_{i}| \qquad (2.17)$$

The operator T is given by

$$T = 1 + \sum_{i} (|\phi_{n}\rangle - |\phi_{n}\rangle) \langle \tilde{p}_{i}| \qquad (2.18)$$

Where, $\langle \tilde{p}_i |$ is the projection function which is initiated from different practical schemes. In this context, pseudopotential helps to get rid from the problem of core and valence electrons. There are a variety of pseudopotentials which can transfer oscillating wave function to a smoother one. However, the PAW is combined with the ultra-soft pseudopotentials and augmented-planewave.

Herein, we have used the PAW method as given in the Vienna ab-initio simulation package (VASP).

2.1.5. Other computational tools

In this thesis work, several other computational tools have been used along with the VASP package to understand the properties of the solid materials, e.g. Bader charge analysis, CI-NEB etc. All of these have been discussed one after another for more detail.

2.1.5.1. Bader Charge Analysis

Richard Bader from the McMaster University developed most promising way of dividing molecules into atoms on the basis of the charge density. Here, zero-flux surfaces determine the partitioning electronic density of the materials. In this context, the zero-flux surfaces that the two-dimensional surface where the charge density is minimum along the perpendicular to the surface. This distribution of the charge density can be used for the understanding of the interaction and repulsion among atoms in the molecule and crystals. However, we have used the Henkelman group developed algorithm for the investigation of the Bader charge in this thesis. This algorithm is very fast for the charge density grid Bader analysis. This is presented for the decomposition of electronic charge density into atomic contributions.

2.1.5.2 Climbing Image Nudged Elastic Band method (CI-NEB)

NEB is a method for finding the minimum energy path (MEP) between the reactant and product of a reaction by finding the saddle points. NEB is widely accepted for estimating transition rates where a harmonic approximation of transition state theory (hTST) is used. In NEB method, MEP is obtained by generating and optimizing a set of images between a range of 4-20 between the initial and the final geometry. The images generated is identical to the initial and final structure of the system. In order to maintain the continuity of the path a spring is attached between the

images which resembles the elastic band. For finding the saddle point it is necessary to distribute the forces into parallel and perpendicular to the tangent drawn at a point on the spring. The projection of force is such that the spring force does not affect the true forces acting on the image. It also ensures that the true forces do not affect the position of each image. This kind of force projection is referred as nudging.

2.2. Computational Details

The first principal calculations are carried out using the projector augmented wave (PAW) method as given in the Vienna Ab initio Simulation Package (VASP) [36-39]. The exchange-correlation potential is given by using the generalized gradient approximation of Perdew-Burke-Ernzerhof (GGA-PBE) [40]. A kinetic energy cutoff of 470 eV has been used for all the optimization. The convergence criteria for total energy and force is set to 10^{-5} eV and 0.01 eV/Å for the complete optimization of all the structures. A $9 \times 17 \times 1$ Γ -centered k-point grid has been used for the unit cell optimization while a $5 \times 5 \times 1$ Γ -centered k-point grid is used for the $2 \times 4 \times 1$ supercell optimization. To avoid all the periodic interactions a vacuum of 20 Å is given along the z axes. The DFT-D3 approach is used to account for van der Waals interaction and dispersion energy corrections [41]. To compute the diffusion energy barrier for AlCl₄ molecule across BCN monolayer, the climbing image nudged elastic band (CI-NEB) method has been used by adding six intermediate images among the completely optimized initial and final structural geometry. The convergence criteria for energy is set to be 10^{-4} eV for each image [42]. To calculate the extent of charge transfer from BCN to AlCl₄, Bader charge analysis has been performed by using the near grid algorithm refine edge method as developed by Henkelman [43-46]. To understand the electronic conductivity of BCN monolayer and AlCl₄ adsorbed BCN, DOS calculations are performed using a Γ -centered k-point grid of $15 \times 15 \times 3$ for the BCN monolayer and AlCl₄ adsorbed BCN monolayer.

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

$$\frac{3}{x} \left[(AlCl_4)_x BCN \right] + 4 \left[EMI^+ AlCl_4^- \right] + Al \leftrightarrow \frac{3}{x} \left[BCN \right] + 4 \left[EMI^+ Al_2 Cl_7^- \right] (2.19)$$

The cell voltage is calculated with the help of Nernst equation,

$$V = -\frac{\Delta G_{cell}}{zF} \tag{2.20}$$

where F stands for Faraday constant, Z represents the total number of electrons involved in the overall cell reaction and ΔG_{cell} represents the change in Gibbs free energy of the cell reaction. ΔG for a reaction is given as

$$\Delta G_{cell} = \Delta E_{cell} + P \Delta V_{cell} - T \Delta S_{cell}$$
(2.21)

At 0 K temperature, we have considered the participation of change in entropy of cell (S_{cell}) and the change in volume of cell (V_{cell}) to be negligible. Hence, we can say that the change in Gibbs free energy of the cell (ΔG_{cell}) is equal to the change in the internal energy (ΔE_{cell}) [47]. This change in the internal energy for the overall cell can be calculated by using following Equation.

$$\Delta E_{cell} = \{\frac{3}{x} E_{BCN} + 4E_{[EMI^+Al_2Cl_7^-]}\} - \{\frac{3}{x} E_{[(AlCl_4)_x BCN]} + 4E_{[EMI^+AlCl_4^-]} + E_{Al}(2.22)\}$$

where, E_{BCN} represents the total energy of the BCN system while $E_{[EMI^+Al_2Cl_7^-]}$, $E_{[(AlCl_4)_xBCN]}$, $E_{[EMI^+AlCl_4^-]}$ represent the total energies of $EMI^+Al_2Cl_7^-$, AlCl₄ absorbed BCN monolayer and $EMI^+AlCl_4^-$, respectively. While, E_{Al} is the total energy per atom in Al bulk phase. Since the crystal structures of $EMI^+Al_2Cl_7^-$ and $EMI^+AlCl_4^-$ are not available so we have calculated the total energy of $EMI^+Al_2Cl_7^-$ and $EMI^+AlCl_4^-$ by relaxing the $EMI^+Al_2Cl_7^-$ and $EMI^+AlCl_4^-$ as ion pairs in a box. In our calculations the solvent effect has not been considered as it has been reported that there is a negligible difference of ≈ 0.1 eV between the solvation energies of $AlCl_4^-$ and $Al_2Cl_7^-$ [48].

Hence, by using equation 2.20, 2.21 and 2.22 we can conclude that the voltage (V) for the cell can be determined with the help of the following Equation

$$V = \frac{\left(\left\{\frac{3}{x}E_{[(AlCl_{4})_{x}BCN]} + 4E_{[EMI^{+}AlCl_{4}^{-}]} + E_{Al}\right\} - \left\{\frac{3}{x}E_{BCN} + 4E_{[EMI^{+}Al_{2}Cl_{7}^{-}]}\right\}\right)}{z} \quad (2.23)$$

where, z represents the number of electrons involved in the overall cell reaction. While, the following expression is used to determine the specific capacity (C) of the cell

$$C = \frac{nxF}{M_f} \tag{2.24}$$

where, n represents the total number of electrons transferred per BCN formula unit, x represents the amount of $AlCl_4^-$ adsorbed on BCN, and M_f is the mass of BCN formula unit.

Chapter 3

Results and discussion

3.1. Structural stability of BCN

Three plausible configurations of BCN can be thought of which contain B, C and N atoms in the same stoichiometric ratio of 1:1:1, but the arrangement of atoms and the connectivity between them is different as represented in Figure 1(a), 1(b) and 1(c). They are made up of different hexagonal units as configuration (a) consists of $B_2C_2N_2$ unit while (b) is composed of $B_2C_2N_2$, B_2C_3N , BC_3N_2 , B_3N_3 units and (c) is made up of $B_2C_2N_2$, B_3N_3 , B_3C_3 , C_3N_3 units. Among all the three configurations, (a) is found to be relatively most stable energetically followed by (b) and (c). Monolayer configuration (a) and (b) have B-C, C-N, B-N, and C-C connecting bonds while (c) does not have any C-C bonds. Upon comparing the bond lengths, we found that C-C bonds is shortest with bond length of 1.38 Å followed by C-N, B-N and B-C with the bond length of 1.40 Å, 1.45 Å, 1.54 Å, respectively. This explains the less stability of monolayer (c) with respect to (a) and (b) as it does not have any strong C-C bonds, while monolayer (a) have the maximum number of C-C bonds and hence is found to be the most stable. This is in agreement with previous theoretical study stating that the most stable BCN structures tend to have the maximum number of B–N and C–C bonds [35]. The higher stability of configuration (a) is also previously reported on the basis of computed electronic energy and cohesive energy [34,35]. Henceforth, we have adopted configuration (a) of BCN monolayer to construct a $2 \times 4 \times 1$ supercell as presented in Figure 2 for investigating the suitability of BCN as a cathode material.



Figure 1. Three plausible configuration (a), (b) and (c) of BCN monolayer with their relative energies. Here, green, brown and grey colour represents B, C and N atoms, respectively.

3.2. Adsorption properties of AlCl₄

During charging of Al based dual ion battery, the AlCl₄ intercalates/adsorbs into the cathode material. Hence, the adsorption properties of AlCl₄ on BCN monolayer has been studied. For this, both planar and tetrahedral configuration of AlCl₄ have been considered for adsorption on BCN monolayer. However, AlCl₄ prefers tetrahedral geometry after the adsorption on monolayer BCN as reported earlier for other carbonaceous cathodes *[17,23-25]*. To identify the most stable site, all the available possibilities are considered for a $2 \times 4 \times 1$ supercell as shown in Figure 2. Nine stable adsorption sites could be identified which comprise of 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-C-B-N-B-N and C-B-N-C-B-N rings).



Figure 2. The top view of the possible adsorption sites on $2 \times 4 \times 1$ supercell of BCN.

The relative adsorption energies of all the available sites are given in Table 1. The adsorption energies ($E_{adsorption}$) corresponding to these sites have been calculated by using equation 3.1.

$$E_{adsorption} = (E_{BCN+AlCl_4} - E_{BCN} - E_{AlCl_4})$$
(3.1)

where, $E_{BCN+AlCl_4}$ represents the total energy of AlCl_4 adsorbed BCN monolayer and E_{BCN} represents the total energy of the BCN monolayer without AlCl_4, while, E_{AlCl_4} represents the total energy of one AlCl_4 molecule. Here, more negative value of adsorption energy signifies the more stable adsorption of AlCl_4 on that site. As a result, the AlCl_4 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 Figure 2. The average distance of Al of AlCl_4 from BCN monolayer on its adsorption at the hollow site surrounded by C-C-B-N-B-N ring is also least (3.85Å) among all the sites as represented in Table 1. The adsorption of AlCl_4 occurs in such a way that the three Cl atoms facing towards the

monolayer tend to stabilize themselves nearer to the B atoms of the monolayer. This may be due to the possibility of interaction between lone pairs of Cl and vacant p orbital of B atoms. As a result, AlCl₄ molecule undergoes a slight deformation as the three Al-Cl bonds facing towards the BCN monolayer get elongated to 2.17 Å (from 2.15 Å) while the one facing upward gets shortened to 2.13 Å.

Table 1. The relative adsorption energy of AlCl₄ for all possible binding sites available and the average distance of Al of the adsorbed AlCl₄ from BCN monolayer at each site.

	Sites	Relative adsorption	Average
		energy (eV)	distance (Å)
1	В Тор	0.03	3.91
2	С Тор	0.02	3.88
3	N Top	0.04	3.97
4	B-C Bridge	0.06	3.88
5	B-N Bridge	0.02	3.93
6	C-N Bridge	0.03	3.89
7	C-C Bridge	0.01	3.87
8	C-C-B-N-B-N Hollow	0.00	3.85
9	C-B-N-C-B-N Hollow	0.03	3.90

Now, in order to identify the type of interaction among the adsorbed AlCl₄ and BCN monolayer, charge density difference (CDD) has been evaluated by using equation 3.2.

$$\rho_{CDD} = \rho^{total} - (\rho^{BCN} + \rho^{AlCl_4}) \tag{3.2}$$

In the above equation, ρ^{total} represents the total charge density of the AlCl₄ absorbed BCN monolayer, ρ^{BCN} and ρ^{AlCl_4} gives the individual charge density of BCN monolayer and AlCl₄ consisting the system. The charge density of BCN monolayer (ρ^{BCN}) and AlCl₄ (ρ^{AlCl_4}) are obtained by using

the pseudo structure in which BCN monolayer and AlCl₄ molecule retains the same structure as that in the AlCl₄ adsorbed BCN monolayer while the remaining parts are deleted. The CDD plot of the AlCl₄ absorbed BCN system is depicted in Figure 3. The interaction between AlCl₄ and BCN monolayer is found to be ionic in nature as on adsorption the deposition of electronic charge takes place on each of the chlorine atom of AlCl₄, while depletion of electronic charge can be detected on the BCN monolayer. As a result, the oxidation of BCN monolayer cathode along with simultaneous reduction of AlCl₄ during the charging mechanism can be concluded. Moreover, the charge depletion can be seen to occur from C and N atoms and not from B atoms due to the difference in electron density among them. Bader charge analysis of the system also shows that AlCl₄ accepts a net electronic charge of 0.9 |e| from BCN monolayer upon adsorption signifying the cathode oxidation during charging.



Figure 3. The (a) side and (b) the top view of charge density difference plot for the AlCl₄ adsorbed BCN monolayer. Here, isosurface = 0.0011 (yellow represents the accumulation of electronic charge and blue represents the depletion in electronic charge).

3.3. Electrochemical and Electronic properties

To calculate the electrochemical properties like voltage and specific storage capacity for BCN cathode material, BCN monolayer is systematically subjected to adsorb different concentrations of AlCl₄. For different concentrations of adsorbed AlCl₄, all possible configurations have been considered to find out the most stable configurations as represented in Figure 4.



Figure 4. Side and top views of the most stable configuration of AlCl₄ absorbed BCN monolayer at different AlCl₄ concentrations (a) (AlCl₄)₂BCN (b) (AlCl₄)₄BCN (c) (AlCl₄)₆BCN (d) (AlCl₄)₈BCN (e) (AlCl₄)₁₀BCN (f) (AlCl₄)₁₂BCN (g) (AlCl₄)₁₄BCN

The maximum number of AlCl₄ adsorbed on a $2 \times 4 \times 1$ BCN monolayer is found to be 14. To investigate the variation in adsorption behavior of BCN monolayer with increasing concentration of AlCl₄ adsorption, we have calculated the adsorption energy for all the cases as presented in Table 2.

Table 2. The calculated adsorption energies and charge transfer per AlCl₄ to BCN for different concentration of AlCl₄ adsorbed on BCN monolayer.

Number of AlCl ₄	Adsorption	Charge transfer to per
adsorbed	energy/AlCl4 (eV)	AlCl ₄ molecule (e)
1	-2.36	-0.90
2	-2.21	-0.88
3	-2.05	-0.82
4	-1.95	-0.75
5	-1.85	-0.70
6	-1.79	-0.67
7	-1.74	-0.64
8	-1.70	-0.61
9	-1.63	-0.58
10	-1.59	-0.56
11	-1.55	-0.54
12	-1.52	-0.52
13	-1.46	-0.51
14	-1.38	-0.47

As the concentration of AlCl₄ adsorbed on BCN increases, the adsorption energy per AlCl₄ molecule as well as the charge transferred to per AlCl₄ molecule is found to decrease. This decrease in adsorption energy might be due to the increase in repulsive forces as the number of adsorbed AlCl₄ molecule increases on the monolayer. The AlCl₄ molecules occupy the most stable hollow site surrounded by C-C-B-N-B-N ring in the monolayer up to 12 AlCl₄ molecules. On further increasing the concentration, AlCl₄ molecules do not necessarily occupy the most stable site and instead try to maintain distance among themselves as shown in Figure 4(g). Maximum of 14 AlCl₄ molecules are adsorbed reversibly on a $2\times4\times1$ supercell of BCN monolayer. Further adsorption of AlCl₄ results in interaction among AlCl₄ molecules to dissociate into AlCl₃ and Cl which is not recommended for the reversible charging/discharging mechanism of a cathode material. However, the BCN monolayer is not found to show any kind of structural distortion on adsorption of 14 AlCl₄ molecules and remains stable to be used as cathode material.

The theoretical charging voltage calculated using equation 2.23 for the maximum AlCl₄ adsorbed system is 1.8 V, which is comparatively lower in comparison to that of experimentally calculated for the graphene cathode (2 V) *[16]*. However, the theoretical specific capacity calculated by equation 2.24 for BCN monolayer at maximum AlCl₄ adsorption is 316.9 mAhg⁻¹, which is much more than that experimentally reported for graphite cathode (70 mAhg⁻¹) *[16]*. Hence, BCN monolayer can be considered as a probable cathode material for high capacity Al based dual ion batteries.

Furthermore, the electronic conductivity of a material also has a major role in determining its suitability as a cathode material. We have plotted the total and partial density of states (DOS) of pristine BCN and AlCl₄ adsorbed BCN system near as represented in Figure 5. In a previous report, the configuration (b) of BCN has been found to be semiconducting in nature having a band gap of 1.5 eV using HSE06 density functional [34], however, in a recent study the band gap of configuration (a) has been found out to 1.18 eV by PBE method [49]. The DOS plots of pristine BCN of configuration (a) show the material to be semiconducting in nature with a smaller bandgap of 1.2 eV. However, the DOS picture completely changes on adsorption of AlCl₄ on the most stable site of BCN monolayer. As a result, the system undergoes transition from semi-conducting to metallic. 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, states are introduced at the Fermi level as there is interaction between the p states of AlCl4 and BCN. Hence, BCN monolayer satisfies the criteria for electronic conductivity of cathode material.



Figure 5. Total and partial density of states of (a) pristine BCN monolayer and (b) AlCl₄ adsorbed BCN monolayer.

3.4. Diffusion properties

Another crucial factor which 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 BCN monolayer using CI-NEB method. For studying the diffusion properties, a $2 \times 4 \times 1$ supercell of 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) available for AlCl₄ diffusion on BCN monolayer as illustrated in Figure 6.



Figure 6. Possible pathways for AlCl₄ diffusion on BCN monolayer and their corresponding diffusion energies.

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 energy barrier of 0.10 eV in comparison to that of path A and path B as represented in Table 3. Hence, we try to examine the stability of 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 Figure 7.



Figure 7. The optimized highest energy transition states for different possible pathways available for AlCl₄ diffusion.

As while trying to find the most stable orientations of AlCl₄ adsorption, we saw the tendency of three Cl atoms of AlCl₄ molecule remaining closer to B atoms of the BCN monolayer. On the same line of thought, we find that the Cl atoms of AlCl₄ for most stable highest energy transition state (corresponding to path C) maintain shorter average distance to their nearest B atoms of the monolayer compared to the corresponding transition states of path A and B as given in Table 3. Overall, we find the diffusion barrier for minimum energy pathway (0.10 eV) is lower than diffusion barrier for

graphite cathode (0.33 eV) [50]. This demonstrates the ability of BCN monolayer to allow trouble-free AlCl₄ diffusion.

Table 3. Diffusion energy barrier and average distance of Cl atoms of AlCl4from nearest B atoms in BCN monolayer.

Diffusion path	Diffusion energy barrier (eV)	Average distance of Cl atoms of AlCl ₄ from nearest B atoms in BCN (Å)
Path A	0.13, 0.13	3.50, 3.50
Path B	0.17	3.68
Path C	0.10	3.35

Chapter 4

Conclusion

By the means of DFT, the suitability of BCN monolayer as a potential AlCl₄ intercalating cathode material for Al based dual ion batteries has been identified. The results show that AlCl₄ adsorbs tetrahedrally with BCN monolayer with reasonable adsorption energy. Further, the Bader charge analysis and the CDD show significant charge transfer of 0.9 |e| from BCN monolayer to AlCl₄, demonstrating the oxidation of BCN and reduction of AlCl₄ during charging mechanism. Systematic step by step adsorption of AlCl₄ yields a maximum adsorption of 14 AlCl₄ molecules on our considered BCN monolayer. As the number of adsorbed molecules increase, the adsorption energy per molecule decreases due to repulsion among the anions. Also, the BCN monolayer retains its structure during the adsorption process implying reversibility of the AlCl₄ adsorption process. The voltage and capacity calculations reveal a significant output voltage of 1.8 V with an ultrahigh specific capacity of 316.9 mAhg⁻¹. The DOS calculations predict the transition from semiconducting to conducting behavior of the BCN cathode on AlCl₄ adsorption. Anisotropic properties are detected during the diffusion energy barrier calculations along different paths. The diffusion barrier of 0.1 eV obtained for AlCl₄ diffusion across the monolayer also predicts an unrestricted diffusion of AlCl₄ molecule. Overall, our study shows that the favorable AlCl₄ adsorption, sustainable voltage, ultra-high capacity, fast charge/discharge rate and the conducting nature AlCl₄ adsorbed BCN monolayer presents it as an outstanding cathode for Al based dual ion batteries.

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