Optimization of Ionic Liquid Electrolytes for Dual-Ion Batteries: DFT and ML Investigations

Ph.D. Thesis

by SURYA SEKHAR MANNA



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Optimization of Ionic Liquid Electrolytes for Dual-Ion Batteries: DFT and ML Investigations

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CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled **Optimization of Ionic Liquid Electrolytes for Dual-Ion Batteries: DFT and ML Investigations** in the partial fulfilment of the requirements for the award of the degree of **DOCTOR OF PHILOSOPHY** and submitted in the **DEPARTMENT OF CHEMISTRY**, **Indian Institute of Technology Indore**, is an authentic record of my own work carried out during the time period from December 2018 to December 2023 under the supervision of **Prof. BISWARUP PATHAK**, Professor, Department 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.

Surya Sekhar Manna 22.12.2023 Signature of the student with date (SURYA SEKHAR MANNA)

This is to certify that the above statement made by the candidate is correct to the best of my/our knowledge.

BANAK

22-12-2023 Signature of Thesis Supervisor with date (Prof. BISWARUP PATHAK)

SURYA SEKHAR MANNA has successfully given his Ph.D. Oral Examination held on 05-04-2024

05-04-2024 Signature of Thesis Supervisor with date

(Prof. BISWARUP PATHAK)

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Dedicated to My Parents §

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SYNOPSIS

1. Introduction

Energy demand is constantly increasing all over the world. Thus, it becomes imperative to look for renewable energy sources to address the issues related to climate change. However, the geographical variability of these renewable sources poses a challenge in providing a continuous power supply. Therefore, efficient energy storage devices are crucial to sustaining technological advancements by ensuring a steady electricity supply. Among all storage devices, batteries become the frontliner in facilitating uninterrupted electricity [1, 2]. Recently, lithium-ion batteries (LIBs) have dominated the commercial market, serving a wide range of applications from small-scale portable devices to large-scale electric vehicles. However, LIBs face challenges that make them less suitable for long-term energy solutions, including issues with the abundance of Li-metal, use of expensive transition metals (Ni and Co) as cathodes, and safety concerns [3, 4]. These challenges have led researchers to explore alternative storage devices that combine low cost with superior electrochemical properties. One such alternative is dual-ion batteries (DIBs), offering a promising alternative to LIBs [5]. The working principle of DIBs involves the interaction of both cations and anions with both the cathode and anode electrodes simultaneously. In contrast, LIBs involve Li ions interacting with one electrode (cathode/anode) at a time and called the rocking chair batteries. Aluminium anodes can be used in DIBs as they feature high volumetric capacity (~8040 mAh/cm³; four times that of lithium anode), high abundance and environmental inertness [6, 7]. Generally, in dual-ion batteries (DIBs), graphite serves as both the cathode and anode electrodes, and during the charging process, cations and anions intercalated into the graphite electrode [8, 9]. DIBs commonly employ lithium salts such as LiPF₆ and LiTFSI dissolved in carbonate solvents that serve as active electrolytes. However, these electrolytes encounter critical issues, including the decomposition of the carbonate solvent at high charging voltages (>4.5

V) and the co-intercalation of the solvent molecules [10]. To address these challenges, researchers have introduced ionic liquid (IL) electrolytes which can tolerate the high charging voltage without further decomposition.

Ionic liquids are low melting point salts and remain in liquid state under 100 °C. ILs show several interesting properties for electrochemical application such as low vapor pressure, broad electrochemical window (ECW) and higher ionic conductivity. The electrochemical reaction of the battery is mainly driven by the cathodic limiting (V_{CL}) and anodic limiting (V_{AL}) potentials of the electrolyte [11] and the gap between V_{CL} and V_{AL} is the ECW. In battery, the V_{CL}/V_{AL} must be placed above/below the Fermi energy level of anode/cathode to prevent the unwanted decomposition of the electrolytes. On the other hand, the ECW gap depends on the HOMO-LUMO gap [12]. Also, the open circuit voltage of the battery depends on the ECW values of the electrolytes. Therefore, the positions of V_{CL} , and V_{AL} are very important for the stability of a battery. Thus, we can calculate the electrolyte stability through the calculations of ECW values to understand the suitability of the IL based electrolytes for the high voltage DIBs.

On the other hand, ILs can play as active intercalant species along with the role of a solvent. Organic cation intercalated graphite-based DIBs are achieved high voltage (>4.5 V) comparable to LIBs. Different organic cations have their unique influences to make high voltage DIBs [13]. It is necessary to understand the exact mechanism of the organic cations intercalation into the graphite anode. However, one major problem is the exfoliation of the graphite electrode. Therefore, finding a suitable cation anion pair IL is essential for low-cost high voltage DIBs.

Thus, in this thesis using various computational approaches such as DFT, atomistic simulations (classical and *ab initio* molecular dynamics), and machine learning techniques, we report the role of electrochemical window towards the designing of ionic liquids based electrolytes for high voltage dual ion batteries.

2. Objectives

Our main objective of this thesis is to calculate the ECW of the ILs to find suitable IL electrolytes for high voltage DIBs.

- i. To calculate the ECW for the different organic cations coupled with AlCl₄ and OTf anions based ILs using various computational approaches.
- ii. To predict the ECW for the series of ILs electrolytes consisted of various cations and anions using machine learning techniques.
- iii. To investigate the intercalation mechanism of the imidazoliumbased aromatic cation (DMPI) inside the graphite anode as well as find the voltage of the this upon coupled with the AlCl₄ intercalated graphite cathode.
- iv. To calculate the voltage for the intercalation of the pyrrolidinium based non-aromatic organic cation inside the organic anode (coronene) over the graphite anode.
- v. To find the suitable pair of cation and anion based ILs for the high voltage DIBs using machine learning techniques.

3. Summary of the research work

The contents of each chapter included in the thesis are discussed as follows:

3.1. Introduction to DIBs and Computational Methods (Chapter 1)

In this chapter, we have briefly discussed about the different types of DIBs and their working mechanisms. A thorough discussion has been presented about the ILs and their properties. The concept of the ECW and its role in battery has been explained in detail. Also, the role organic cation intercalation into electrode has been explained properly.

All the properties of ILs have been calculated using the density functional theory (DFT), molecular dynamics (classical and ab initio method), and machine learning (ML) tools. Hence, we have discussed the basic principle behind all these computational methods as well as techniques at the end of this chapter.

3.2. Optimization of Computational Methods for DIBs (Chapter 2)

In this chapter, a series of IL and molten salt electrolytes has been considered for the calculation of electrochemical window using various computational methods. The ILs and molten salts consist of imidazolium, pyrrolidinium, urea and acetamide-based cations coupled with AlCl₄ and OTf (trifluoromethanesulfonate) anions (Figure 1). The thermodynamic cycle and classical molecular dynamics followed by DFT (MD+DFT) approaches have been implemented to calculate the ECW of all these electrolytes for Al DIBs. The oxidation and reduction potentials of the individual ions have been calculated with respect to the Al³⁺/Al electrode using the thermodynamic cycle method. Using the combined MD-DFT method have been deployed to calculate the cathodic (V_{CL}) and anodic (V_{AL}) potentials. We have classified MD+DFT method in two parts such as AIMD-min (minimization) and AIMD-sp (single point) methods. In the AIMD-min method, the classically simulated structure has further relaxed in *ab initio* method for few steps, then performed density of states (DOS) calculation to estimate the V_{CL} and V_{AL}. Whereas, in the AIMD-sp method, the classically simulated structures have considered for direct single point DOS calculation without further optimization. The calculated ECWs from the AIMD-min method are close to the experimental results compared to the other two methods. Classically equilibrated structures are not necessarily stable in DFT calculation, hence in AIMD-min method the structures are formed a stable potential energy surface (PES) which replicate the exact liquid structure present in experimental study. Overall, this study establishes a unique computational method to calculate the ECW accurately with respect to the experimental results.



Figure 1. Ionic liquids and molten salts (MSs) are investigated. Structures of cations: (a) Imidazolium moieties with a different alkyl group (where, n = 2, 3, 4, 6 and 8), (b) N, N-butylmethylpyrrolidinium (BMP) cations, (c) $[AlCl_2(U)_2]^+$, and (d) $[AlCl_2(AcAm)_2]^+$ (where U is urea and AcAm is acetamide) and structure of anions: (e) $AlCl_4$, and (f) trifluoromethanesulfonate (OTf).

3.3.Optimization of ML Techniques for DIBs (Chapter 3)

In this chapter, a data driven ML technique has been constructed to predict the ECW for IL electrolytes in DIBs. From our previous study (Chapter 2) it's confirmed that the AIMD-min method is the best among other methods to calculate the ECW accurately. However, calculating the ECW using AIMD-min method for large set of ILs is very difficult and computationally expensive. Hence, ML approach is a way forward to solve this challenge. To train the ML model we have considered ECW form the MD+DFT data along with few experimental values. A total of seven ML algorithms has been considered to train the machine. Among these algorithms extra trees regression (ETR) emerges as the optimal model with the lowest mean absolute error (MAE) of 0.37 V for the prediction of ECW (Figure 2). Our ML predicted MAE of 0.37 V is much lower compared to previous DFT computed MAE of 0.68 V for two different methods of ECW calculation. The model successfully predicted the ECW of 660 IL electrolytes. Furthermore, our predicted ECWs are in good agreement with the previously measured experimental results. Additionally, an interpretable

ML approach has been employed to understand the local and global features importance towards the prediction of ECW. Overall, this study promises to the alternative of the expensive computational study as well as helps to design suitable IL electrolytes for high voltage DIBs.



Figure 2. (a) The MAEs of seven considered ML models for the train (blue) and test (magenta) data set. (b) The scatter plot of ML predicted vs. DFT calculated ECW is shown for the ETR model.

3.4. Role of Aromatic Ionic Liquid for DIB (Chapter 4)

In this chapter, imidazolium based ionic liquid, 2,3-dimethyl-1-propyl imidazolium chloride (DMPI-Cl) with AlCl₃ salt has been implemented as an electrolyte, where DMPI-AlCl₄ IL has treated as an active intercalant species. During the charging process, the aromatic DMPI cations are intercalated inside the graphite anode (Figure 3) and counter AlCl₄ anions get intercalated into graphite cathode. DMPI intercalation followed the staging mechanisms by forming stage-1, stage-2, stage-3, and stage-4 upon intercalation into the graphite. Higher cell voltage of 3.7-4.6 V, comparable to LIBs 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. Overall, this study provides clear understanding of the organic cation (DMPI) intercalation into graphite anode and helps to fabricate low-cost dual graphite-based DIBs with better electrochemical properties.



Figure 3. 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.

3.5. Importance of Non-aromatic Ionic Liquid for DIB (Chapter 5)

Further to this study, a non-aromatic pyrrolidinium based IL, N-butyl-Nmethyl pyrrolidinium chloride (BMP-Cl) with the AlCl₃ salt has been employed as an electrolyte and polycyclic aromatic hydrocarbon based coronene as an anode. We have systematically studied the BMP cation intercalation inside the coronene anode (Figure 4). The BMP intercalated coronene has shown lower binding energy (-1.71 eV) compared to the graphite intercalated (-2.36 eV). Indicating an optimal interaction with the coronene electrode which facilitates the overall charge/discharge reversibility of the DIBs. Graphite intercalated non-aromatic (BMP) cation binding energy is less compared to aromatic DMPI cation (Chapter 4), due to presence of strong π - π interaction between aromatic DMPI and graphite layers. Our calculated discharge voltage of 3.1 V and 3.05 V, and maximum capacity of 116 mAh/g and 130 mAh/g have been observed for the graphite coronene dual ion battery (GCDIB) and dual graphite battery (DGB), respectively. Density of states (DOS) and Bader charge analysis reveals that BMP cation is intercalated successfully indicating reduction of electrode materials during charging process. These results support a clear understanding of BMP cation intercalation into both coronene, and graphite anodes and motivates towards fabrication of new class of low-cost organic anode DIBs with optimum electrochemical performance.



Figure 4. Optimized structures of different orientation of BMP cation intercalated coronene anode (a) S1, (b) S2, and (c) S3. The blue, cyan colours stand for N, C of BMP cation and brown colours represent the coronene carbons and magenta for hydrogen of the system.

3.6. Optimization of Voltage for DIBs (Chapter 6)

In this chapter, large-scale cations and anions are screened to find suitable IL electrolytes for the high voltage DGBs using an interpretable ML approach. We have predicted the cations binding energy (BE) using ML techniques. Few organic cation's BEs have calculated in DFT level to train the ML model. Among the eight considered ML algorithms, the XGBR is found to be the best fitted algorithm for the prediction of BE for the unknown dataset (Figure 5). Using the XGBR model, a total of 880 BEs have been predicted successfully.



Figure 5. The RMSEs and MAEs of eight considered ML models for the (a) train and (b) test data set. The scatter plots of ML predicted vs. DFT calculated binding energies for (c) XGBR and (d) GBR models.

Moreover, our predicted BEs are in good agreement with DFT level of accuracy. Furthermore, using these BEs of cations and anions, we have calculated a comprehensive set of 20,790 voltages, including various combination of stages with equal number of ions. Finally, we have designed different classes of ~500 DGBs having low to high voltage. Overall, this ML predicted voltage database can serve as a guidepost for experimental researchers to find the optimum ILs based electrolytes to enhance the fabrication of cost-effective dual-ion based electrochemical devices.

4. Conclusion

The conclusion of the thesis can be outlined as follows:

1. AIMD-min method plays as the best fitted approach for calculation of ECW among considered the three methods. In the thermodynamic cycle

approach, the ECWs of the considered ILs are dependent on the reduction potentials of the organic cation and oxidation potentials of anions. The accuracy of this method is not good which could be due to the non-availability of neighboring intermolecular interaction. The AIMD-sp method is unable to provide good accuracy of ECWs for IL electrolytes due to the formation of unstable potential energy surface (PES).

- 2. Our ML approach provides faster and accurate ECW predictions compared to the MD-DFT method. Out of the seven ML algorithms employed, the ETR model stands out as proficient in accurately predicting the ECW. Using the optimized parameters of our best fitted ETR model, we successfully predicted the ECW values for 660 ILs. Hence, our findings provide a foundation for accurately predicting ECW values of ILs, enabling advancements in the design of IL electrolytes for improved DIBs performance.
- 3. DMPI cation prefers to intercalate parallel over the perpendicular orientation into AB stacked graphite plane due to π - π interaction of aromatic imidazolium cation with graphite hexagonal rings. 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. 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). Thus, this study helps to design other organic cations intercalated graphite for high voltage DIBs.
- 4. The BMP cations are strongly interacting with the graphite layer due to having higher binding energy of 2.36 eV compared to the coronene binding energy of 1.71 eV. The theoretical voltage of GCDIB is

calculated to be 3.1 V which again very much in agreement with the experimental voltage range of 3.1-3.9 V. The cycle number of the GCDIB may increase due to the less exfoliation of the coronene compared to DGB.

5. For the prediction of cation BEs, the XGBR algorithm emerged as the most suitable, as lowest RMSE of 0.15 eV for predicting BEs from an unfamiliar dataset. From our ML+DFT approach yielded 495 graphite-based DIBs, where 69, 230, and 196 fell within the high voltage (HV) range of 4.0 < HV < 7.0, moderate voltage (MV) range of $2.5 < \text{MV} \le 4.0$, and low voltage (LV) range of $0.001 < \text{LV} \le 2.5$, respectively. On the other hand, ILs based on BF₄ and PF₆ anions exhibited high voltage behavior when coupled with most considered cations (except pyridinium and thiazolium).

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Acronyms

IL	Ionic Liquid
ECW	Electrochemical Window
DIB	Dual Ion Battery
DGB	Dual Graphite Battery
LIB	Lithium Ion Battery
PAH	Polycyclic Aromatic Hydrocarbon
HOMO	Highest Occupied Molecular Orbital
LUMO	Lowest Unoccupied Molecular Orbital
DFT	Density functional theory
BO	Born-Oppenheimer
LDA	Local density approximation
GGA	Generalized Gradient Approximation
PBE	Perdew-Burke-Ernzerhof
PAW	Projector augmented wave
VASP	Vienna Ab initio Simulation Package
AIMD	Ab initio Molecular Dynamics
AIMD-sp	AIMD-single point
AIMD-min	AIMD-minimization
PBC	Periodic Boundary Conditions
MEP	Minimum Energy Path
NEB	Nudged Elastic Band
PDOS	Projected Density of States
CDD	Charge Density Difference
EMIM	1-ethyl-3-methyl imidazolium
DMPI	1,2-dimethyl-3-propylimidazolium
BMP	N, N-butyl-methyl pyrrolidinium
TFSI	Trifluoromethanesulfonylimide
OTf	Trifluoromethanesulfonate
ML	Machine Learning

KRR	Kernel Ridge Regression
XGBR	eXtreme Gradient Boosting Regression
GBR	Gradient Boosting Regression
LGBM	Light Gradient Boosting Machine
ETR	Extra Trees Regression
RFR	Random Forest Regression
ABR	Adaptive Boosting Regression
DTR	Decision Tree Regression
PCC	Pearson correlation coefficients
BE	Binding Energy
LOOCV	Leave One Out Cross-Validation
RMSE	Root Mean Square Error
MAE	Mean Absolute Error
SHAP	SHapley Additive exPlanations



Introduction

1.1. Energy Storage Devices

Due to the unprecedented growth in science and technology, as well as the increase in the world population, energy consumption is increasing day by day. Despite the advancements in science and technology, fossil fuels are still the primary source of energy in the world. [1] As a result, the increased carbon footprint in the earth's atmosphere leads to climate catastrophe and global warming. Additionally, the unsustainability of non-renewable sources is raising concerns about future energy demand. As a result, it is imperative to take a bold and swift step towards the new energy sources. On the other hand, the sources of renewable energies like wind, solar and hydro powers are inexhaustible resources that serve a clean and sustainable way to address the growing energy problems. [2,3] Due to their intermittent nature, these resources are almost not usable in practical terms. Besides, these renewable sources are costly and limited by the geographical positions. Hence, this problem has carved the momentum to a new energy era. In this context, the energy storage devices (ESDs) are getting attention worldwide as key players to maintain the uninterrupted electricity to solve the constant energy demand. Besides, the ESDs can solve the old, centralized power network to grid scale energy storage system by making them decentralized and can be used in on-demand situations. The batteries are the frontrunner among ESDs because of their high voltage and capacity compared to other products like low-efficient solar power gadgets and capacitors. [4,5]

Batteries are electrochemical energy storage systems, which convert electrical energy and store it in the form of chemical energy during charging. The chemical energy is converted to electrical energy during the discharge process. Nowadays, batteries are used in all the devices from small portable electronic devices to large-scale grid storage devices like electrical vehicles. Till now, researchers have developed different types of battery technologies such as lead acid, nickel-based batteries and other metal ion based (Li, Na, K and Mg ions) batteries. Among these, the Li-ion batteries (LIBs) have largely captured the commercial energy market due to their high voltage and capacity. [6,7] The high energy demand, higher energy density and significant technology development has led to rapid scale up in the production of LIBs. [8] On the other hand, the Li metal resources are limited in the earth's crust and expensive transition metal derived materials are used as cathode in LIBs, which are making them more costly in nature. Moreover, the thermal runway effect of LIBs is not resolved properly and the various shortcomings of LIBs make them less suitable for long-run energy storage devices. [9,10] Regardless, other metal ion batteries, particularly Na-ion batteries, have become alternative storage devices, but they are facing various problems like low volumetric and gravimetric capacity and hard to achieve the boarder voltage window, albeit of high abundance of Na metal. [11] Therefore, the researchers are trying to develop a low-cost high voltage ESD using the most abundant materials.

1.2. Dual-Ion Batteries

Dual-ion batteries (DIBs) have emerged as a bright prospect in energy storage devices with low cost and high-performance electrochemical properties. The mechanism of DIBs and LIBS are different. The LIBs follow shuttle mechanism i.e., Li ions are interacting with one electrode at a time, whereas, in the DIBs, both ions are interacting with separate electrodes simultaneously (Figure 1.1).*[12,13]* Unlike LIBs, the anion has an immense role in DIBs mechanism. Hence, electrolytes play an important role in DIBs as the anions and cations originate from the electrolyte. With the advent of anion acceptor-type graphite intercalation compounds (GICs), the concept of DIBs was formed.*[14,15]* In 1989, McCollough and coworkers developed carbonaceous materials-based electrodes with non-aqueous electrolytes. Later, the dual-carbon batteries have been conceptualized as dual-graphite batteries (DGBs), as graphite is used as

both the electrodes as they are cheaper compared to LIBs. In 2012, Placke and coworkers first pioneered the definition of "dual-ion batteries" and this name is used till today.[17,18] Depending on electrolytes used, various types of DIBs have been introduced.



Figure 1.1: Working mechanism of (a) Rocking chair batteries like LIBs, where the Li ion shuttling between cathode and anode and (b) DIBs, where both the cations and anions are interacting cathode and anode simultaneously. Figure reprinted with permission from Ref. 13. Copyrights 2020, ELSEVIER.

1.2.1. Metal Salt-Solvent Based DIBs

Metal salt-solvent based DIBs involve metal salts combined with carbonate based organic solvents such as ethylene carbonate (EC), ethyl methyl carbonate (EMC), etc., to form the active electrolyte. Recently, LiPF₆ DIBs have emerged due to their high energy density and voltage (4.5 V).*[19,20]* Here LiPF₆ salt dissolved in organic solvent is used as electrolyte while Li metal and graphite are considered as anode and cathode, respectively.*[21]*

The PF₆ anions are intercalated/deintercalated into the graphite and Li cations are deposited/stripped during the charging/discharging process (Figure 1.2a).[22] Anion intercalation into the graphite cathode follow the systematic staging mechanism, as verified both computationally and experimentally.[23,24] Pathak and co-workers have studied the PF₆ anion intercalation into graphite computationally.[22] They have shown different types of staging mechanisms such as stage-1, stage-2, stage-3 and stage-4. Stage-4 is found to be the most stable at the initial state of charging. In the final state of charging, it follows the maximum intercalation by achieving the stage-1 mechanism. In experiments, it is observed that carbonate solvents can decompose at high voltage (> 4.5 V).[25] Furthermore, the solvent co-intercalation has also been observed into the graphite cathode which can reduce the overall performance of the DIBs.[25] Hence, DIBs based on ionic liquid electrolytes which are composed of bulkier ions is also being investigated.



Figure 1.2: Different types of DIBs: (a) metal-salt DIB (like LiPF₆), (b) Al anode-based DIB and (c) dual graphite-based DIB. Figure reprinted with permission from Ref. 15. Copyrights 2022, WILEY-VCH.

1.2.2. Ionic Liquids Based DIBs

To overcome the issues of organic solvents, researchers have introduced room temperature ionic liquids (RTILs) electrolytes in DIBs. Carlin and coworkers have introduced IL electrolytes which are combination of cations such as 1-ethyl-3-methyl imidazolium (EMIM), 1,2-dimethyl-3-propylimidazolium (DMPI), N, N-butyl-methyl pyrrolidinium (BMP) and anions such as CF_3SO_3 (OTf), AlCl₄, PF₆ and BF₄.[26-28] In 2015, Lin *et al.* have introduced ultrafast charging Al-DIBs using the EMIM-Cl/AlCl₃ IL electrolyte in graphite cathode (C_n) and Al anode system.[29] The cathodic and anodic reactions are as follows,

Cathode:
$$C_n + AlCl_4^- \leftrightarrow C_n[AlCl_4] + e^-$$
 (1.1)

Anode:
$$4Al_2Cl_7^- + 3e^- \leftrightarrow 7AlCl_4^- + Al$$
 (1.2)

The cathodic reaction is about the intercalation of AlCl₄ anions into the graphite cathode where AlCl₄ anion follows the proper staging mechanism inside the graphite layers. On the other hand, the Al₂Cl₇ anion also forms in the electrolyte medium, which gets reduced to Al to deposit on the Al surface of the anode (Figure 1.2b). However, in the Al-DIBs, limited voltage of up to 2.5 V can be achieved. Nevertheless, Lv *et al.* have introduced the organic cation (DMPI) intercalation into graphite anode as well as anion (AlCl₄) intercalation in DGBs (Figure 1.2c).[30] They have achieved a high voltage of ~4.6 V. Simultaneously, they have proved that the ILs can be used as an active intercalant material as well as solvents. Moreover, Li and coworkers have studied the pyrrolidinium based ILs electrolytes in DGBs.[31] Therefore, it's well understood that the electrolytes play a critical role in determining the electrochemical properties of DIBs.

1.3. Non-aqueous Electrolytes

Several types of non-aqueous electrolytes are developed over time such as organic solvents, additives, and ionic liquids, among others to increase the overall performance of the DIBs.

1.3.1. Organic Solvents

The organic solvents are mainly of carbonate based like ethyl methyl carbonate (EMC), ethylene carbonate (EC) and propylene carbonate (PC), and commonly used electrolytes due to having high ionic conductivity, excellent solubility for active salts, low viscosity, and low cost. [32, 15] On the other hands additives are used to improve the ionic conductivity of the organic solvents and save the active electrolytes from decomposition. The fluorine containing derivatives such as fluoroethylene carbonate (FEC), 2,2,2-trifluoroethyl carbonate (F-EMC) and tris(hexafluoro-isopropyl) phosphate (HFIP) are considered the suitable additives for the DIBs. [33,34] However, these organic-additive based electrolytes do not perform well in high voltage DIBs case as it undergoes decomposition due to having smaller electrochemical window. On the other hand, electrode exfoliation occurs due to co-intercalation of the solvent molecules. To overcome these issues, researchers are focusing on ionic liquids (ILs) as electrolytes which has the potential to address all those issues. In the following sections, we have discussed in detail about the importance of ILs in batteries.

1.3.2. Ionic Liquids

ILs are low melting point salts which are the combination of Bronsted acid and base. These salts maintain a liquid state below 100 °C, with many remaining liquids at room temperature due to the weak electrostatic interaction between cations and anions. Room temperature ionic liquids (RTILs) exhibit fascinating properties, including a wide electrochemical window (ECW), robust thermal and chemical stability, minimal volatility, and high ionic conductivity.[35,36] These distinctive features position them as ideal electrolytes for DIBs. Here, we have explained different types of ILs in the following section.

1.3.2.1. Different Types of Ionic Liquids Electrolytes

ILs present a versatile electrolyte platform with adjustable physicochemical and electrochemical properties, making them highly attractive for a broad spectrum of applications, especially in energy storage devices. These compounds comprise both organic and metal cations combined with various anions. The pioneering work of Carlin and colleagues in 1994 marked the use of ILs as electrolytes in DIBs. [37] They explored different imidazolium cations with varying alkyl groups, paired with anions like AlCl₄, BF₄, PF₆, CF₃SO₃ (OTf), trifluoromethanesulfonylimide (TFSI), and fluoromethanesulfonylimide (FSI).[30,31] Beyond imidazolium moieties, other organic moieties, such as pyrrolidinium and morpholium cations, have been investigated for DIB studies. In the realm of metal-based cations, Libased TFSI stands out as a commonly used electrolyte in DIB technology. Parallelly, the abundant metal-based K-FSI has found application as an IL electrolyte in DGB, where K⁺ and FSI anions intercalate into graphite electrodes.[24]

1.3.2.2. Broad Electrochemical Window (ECW) of Ionic Liquids

The ECW of the battery is thought to be characterized by the energy levels of the highest occupied molecular orbital (HOMO) and lowest occupied molecular orbital (LUMO) of the electrolyte. However, the stability of the electrolytes is determined by the oxidation and reduction potentials. While HOMO/LUMO are electronic structure properties of the electrolyte, oxidation/reduction potentials depend on the change of Gibbs free energy upon oxidation and reduction of the electrolyte. Peljo and co-workers have clarified the misconception between the HOMO/LUMO gap and ECW.[38] ECW is measured as the difference between cathodic limiting (V_{CL}) and anodic limiting (V_{AL}) potentials of the electrolyte (Figure 1.3) which lies within the HOMO/LUMO gap. For a stable electrolyte, the V_{CL} should remain above the Fermi energy of the anode (μ_A) and V_{AL} should remain below the Fermi energy of the cathode (μ_C).[39-41] Otherwise, electrolytes will undergo oxidation upon the electron transfer from HOMO of the electrolyte to the Fermi level of the cathode. Similarly, electrolyte reduction can occur upon the electron transfer from Fermi level of anode to LUMO of the electrolyte. Therefore, the exact position of the V_{CL} and V_{AL} are important to maintain the stability of the IL electrolytes. Several computational techniques have been established to calculate the ECW.



Figure 1.3: Systematic energy profile diagram of the HOMO/LUMO of electrolyte and Femi energy levels of electrodes, (a) schematic diagram of both electrodes Fermi energy levels and these are situated inside the HOMO-LUMO gap of electrolyte, (b) introduction of V_{AL} and V_{CL} instead of HOMO and LUMO to prevent unwanted decomposition of electrolyte, and (c) stable energy profile for electrochemical system. Figure reprinted with permission from Ref. 40. Copyrights 2020, Royal Society of Chemistry.

Banerjee and co-workers have developed the thermodynamic cycle approach to calculate the ECW using the oxidation and reduction potentials of the individual ions.[42] On the other hand, Ceder *et al.* have utilized combined molecular dynamics and density functional (MD+DFT) approach to calculate the ECW using the HOMO/LUMO values of the IL electrolytes.[39] Moreover, Maginn and co-workers have extended the MD+DFT method by introducing the AIMD-min and AIMD-sp methods.[41] Thus, measurement of the ECW is important to understand the stability of IL electrolytes as well as to determine the accessible voltage range of the battery.

1.3.2.3. Ionic Conductivity of Ionic Liquids

In general, ionic conductivity of the IL is calculated from the Stokes-Einstein equation (1.3).[40]

$$\kappa = \frac{Z^2 F e \rho}{6 \pi \eta M_w} \left(R_+^{-1} + R_-^{-1} \right) \tag{1.3}$$

Where, κ is the conductivity, Z is the charge on the ion, e is the electronic charge, ρ , η are the density and viscosity of the medium, Mw is the molecular weight of IL and R_+ , R_- are the ionic radii of the cation and anion. From equation 1.3, it has been observed that conductivity depends on ion's mobility, viscosity of the medium, number of charge carriers, ionic radius, density, and molecular weight. Viscosity is the most important parameter to determine the overall conductivity of the ILs. It has been observed that the conductivity is inversely proportional to the viscosity of the ILs. However, the contribution of anion is found to be more in the determination of viscosity compared to the cation. [43] For the imidazolium based ILs, the viscosity is affected more by the nature of anion than the cations (alkyl groups of the imidazolium ring). Among the cation part, the long chain alkyl group cations possess higher viscosity due to the strong van der Waals interaction of long hydrocarbon chain. However, the methyl substituted imidazolium ring led to high viscosity compared to the ethyl group.[43] Hence, ethyl and methyl substituted imidazolium ring is the most used cation in IL-based electrolyte in DIBs due to having optimum ionic conductivity.[24,29,40] Heterocyclic rings containing ILs also have higher conductivities due to lower molecular mass or the cation becoming more symmetrical.[44]

1.3.2.4. Ionic Liquids as Intercalant Species

In the previous section, we explored the utilization of ILs as a superior substitute for organic solvents/electrolytes, leveraging their exceptional attributes for enhancing the electrochemical performance of DIBs. Beyond serving as solvents, ILs act as active intercalant species, where both the cations and anions of the ILs intercalate into the layered host materials like graphite. This concept has seen limited exploration, both experimentally and computationally.[30,31,45] Carbonaceous host materials such as graphite and polycyclic aromatic hydrocarbons (PAHs) can act as electrodes, offering enough space to accommodate the bulky cations and anions of ionic liquids (ILs).[46,47] The development of dual graphite batteries (DGB) exemplifies this, wherein imidazolium-based DMPI cations and AlCl₄ anions intercalate into the graphite anode and cathode during the charging process. [30,45] Fan et al., introduced a novel IL of 1butyl-1-methylpiperidinium bis(trifluoromethylsulfonyl) imide (PP₁₄-TFSI) based DIBs, where the PP₁₄ cations and TFSI anions are intercalated inside the graphite electrode. [48] Later, a novel DGB was developed using the pyrrolidinium based BMP-TFSI IL with voltage of more than 3.6 V.[49] To reduce the exfoliation of the graphite the PAH based electrode (coronene) has been used for active organic cation intercalation. [46,50] Overall, the IL intercalation research can lead to design of cheap carbonaceous material based batteries with better electrochemical properties compared to traditional metal anode based batteries. Therefore, it's necessary to study DIBs with IL electrolytes to serve the future energy demand.

1.3.3. Molten Salts Electrolytes

Molten Salt (MS) electrolytes are the alternative low-cost electrolytes used in Al-DIBs which can replace the costly imidazolium based ILs. MS electrolytes operate at high temperature (~180 °C) and are the combination of binary and trinary salts of KCl, AlCl₃ and NaCl.*[51-53]* Due to high polarization power of small size cations (Na⁺ and K⁺), their strong adsorption upon intercalation inside the electrode reduces the overall reversibility of the battery. Therefore, smaller cations are substituted with long alkyl chain organic cations derived from amide and urea, possessing optimal size and moderate ionic conductivity. Various amide-based MS electrolytes, including urea, acetamide, propionamide, and butyramide, are explored in Al-DIBs, taking into account their physical characteristics like density, viscosity, and conductivity. The density and viscosity order of AlCl₃-amide derivatives are urea > acetamide > propionamide > butyramide.[54] These amides can form stable complex isomers with the AlCl₃ salt upon binding through their N and O atoms such as [AlCl₂(urea)₂]⁺[AlCl₄]⁻ and [AlCl₂(acetamide)₂]⁺[AlCl₄]⁻.[55] Urea based MS electrolyte have good prospects due to possessing higher ionic conductivity and broad ECW compared to others MS electrolytes. Furthermore, N-ethyl urea and N-methyl urea are also known to increase the overall performance of the Al-DIBs.[56,57]

1.4. Other Electrolytes

Non-aqueous electrolytes of AlCl₃ derivatives are highly hygroscopic in nature which requires to be operated in an inert gas atmosphere. Other than non-aqueous electrolytes, aqueous electrolytes are also a cost-effective and readily available option for use in DIBs. However, these electrolytes tend to decompose in Al-DIBs due to the high reduction potential of Al^{3+}/Al , leading to the generation of H₂ gas from aqueous electrolytes. To address this challenge, a novel class of electrolytes known as 'water-in-salt' electrolytes (WiSEs) has been developed. WiSEs primarily consist of superconcentrated active salts in water, enhancing the electrochemical window of aqueous electrolytes. [58-61] Researchers have also introduced polymer gel electrolytes for Al-DIBs. Sun et al. first derived the gel electrolytes with the combination of AlCl₃-acralamide along with the acidic IL of 1-ethtyl-3methylimidazolium chloride (EMIM-Cl)./62] A quasi-solid-state Al-DIBs battery has been reported by using the polymer gel electrolytes of Et₃NHCl/AlCl₃ which provides high voltage around ~2.9 V./63 / Moreover, hybrid electrolyte of LiAlCl₄ + [EMIM]Cl based DIBs have also been reported, where Li interacts with the LiFePO₄ cathode and Al deposition/stripping occurs at anode.[64]

1.5. Theory

In this part, we have presented a brief outline of the theory and computational methods used for our thesis work. In case of solid-state materials, due to their periodic nature, properties are highly correlated with their atomic arrangements. Now, we have discussed the interaction nature between electrons and nucleus that determines the atomic properties of the materials.

1.5.1. Schrödinger Equation

Electronic structural properties of the materials and molecules can be found by resolving the time independent Schrödinger equation expressed as follows,

$$\widehat{H}\Psi(r,R) = E\Psi(r,R) \tag{1.4}$$

Here, the properties of the system are descried by the Hamiltonian operator \hat{H} . Whereas, the wave function Ψ obtains the system information including nuclei and electrons, and operating \hat{H} on Ψ we obtain the total energy of the system E. The Hamiltonian operator \hat{H} for a many particles system can be given as,

$$\hat{H} = -\frac{h^2}{2m_e} \sum_{i} 2\nabla_i^2 - \sum_{I} \frac{h^2}{2M_I} 2\nabla_I^2 + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|r_i - r_j|} + \frac{1}{2} \sum_{I \neq J} \frac{Z_I Z_J e^2}{|R_I - R_J|} - \sum_{i,I} \frac{Z_I e^2}{|r_i - R_I|}$$
(1.5)

Here, m_e and r_i are the mass and position of the electron respectively. Whereas M_I , R_I and Z_I represents the mass, position, and charge of the nuclei respectively. In the equation 1.5, the first and second terms are denoted for the kinetic energy of the electron and nuclei, respectively. While the third and fourth terms represent the electron-electron and nuclei-nuclei repulsions respectively. And the last term arises from attractive interaction between electrons-nuclei.

But for solid state materials, the Hamiltonian operator becomes extremely complicated due to large number of electrons and nuclei present in the system. As a results, obtaining exact solution of the Schrödinger equation becomes practically impossible. To find a way out of this problem there is necessity of utilizing some approximation. Born-Oppenheimer (BO) approximation is quite useful in this context.*[65]*

1.5.1.1. Born-Oppenheimer (BO) Approximation

In generally, the nucleus is much heavier (~1836 times) than the electron mass, Born-Oppenheimer approximation considers the speed of the nuclei to be stationary compared to the electron.[65] Therefore, the kinetic energy of the nuclei can be neglected in comparison to the kinetic energy of electron from the Schrödinger Equation.

Hence, the Hamiltonian operator is as follows,

$$\widehat{H} = -\frac{h^2}{2m_e} \sum_i 2\nabla_i^2 + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|r_i - r_j|} + \frac{1}{2} \sum_{I \neq J} \frac{Z_I Z_J e^2}{|R_I - R_J|} - \sum_{i,I} \frac{Z_I e^2}{|r_i - R_I|}$$
(1.6)

Now, considering a system with single nucleus the above equation becomes,

$$\widehat{H} = -\frac{h^2}{2m_e} \sum_i 2\nabla_i^2 + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|r_i - r_j|} - \sum_{i,l} \frac{Z_l e^2}{|r_i - R_l|}$$
(1.7)

Even after employing the BO approximation to solve the Schrödinger Equation of a many electrons system exactly, in order to make it solvable some other approximations like Hartree-Fock theory (HF theory), density functional theory (DFT) etc. came to the picture. Therefore, in the next section we have discussed about density functional theory (DFT).

1.5.2. Density Functional Theory (DFT)

Density functional theory (DFT) considers the electron density of a manybody system to determine its electronic structure and properties. The approach is mainly depending upon the three positional coordinates, thereby bypasses the complexities associated with the wavefunction approach. The conceptual foundation for DFT was laid by Thomas-Fermi, who introduced the concept of using an ideal gas of non-interacting electrons. Additionally, Hohenberg-Kohn formulated two theorems, indispensable for DFT calculations. Subsequent sections will delve into an overview of DFT.[66,67]

1.5.2.1. The Hohenberg-Kohn Theorems

DFT is mainly built on the two theorems proposed by P. Hohenberg and W. Kohn as follows,

Theorem 1: The first theorem postulates that the ground state properties of the many electron systems can be described by the electron density $n(\mathbf{r})$ of the interacting electrons moving under the external potential of $V_{ext}(\mathbf{r})$. Principally, the ground-state energy of Schrödinger's equation is a unique functional of the electron density $n_0(\mathbf{r})$.

Theorem 2: The second theorem describes the universal total energy functional $E[\rho(r)]$ in terms of particle density $\rho(r)$ under the external potential of $V_{ext}(r)$. The functional can be written as,

$$E[\rho(\mathbf{r})] = E_{HK}[\rho(\mathbf{r})] + \int V_{ext}(\mathbf{r})\rho(\mathbf{r})d\mathbf{r}$$
(1.8)

where, $E_{HK}[\rho(\mathbf{r})]$ represents the internal and kinetic energies of all interacting particles within the system. It can be inferred that the groundstate energy of a many-body system can be determined only when the functional of the electron density, minimizing the system's energy, corresponds to the true ground state density $n_0(\mathbf{r})$. However, the actual form of the functional for a given electron density is still not clear from the theorems. Hence, further development is essential.

1.5.2.2. Kohn-Sham Equations

In continuation, Kohn and Sham formulated a new set of equations to establish the Hohenberg-Kohn theorems. Here, they have replaced many body problems with a simple one electron, non-interacting particle problem. The approach is to describe the single particles with an effective potential $V(\mathbf{r}_i)$, termed as Kohn-Sham potential. The total ground state energy can be given as,

$$E[\rho(r)] = T_0[\rho(r)] + \frac{1}{2} \iint \frac{\rho(r)\rho(r)'drdr'}{|r-r'|} + \int V_{ext}(r)\rho(r)dr + E_{xc}[\rho(r)dr] + E_{II}$$
(1.9)

where, the first term represents the kinetic energy of the non-interacting one electron system, second term describes the electron-electron Coulombic interaction, the third term represents the potential energy of the valence and the core electrons and the fourth term accounts for the exchange-correlation interaction, considering all non-classical many-body effects between electrons. The last term denotes the nuclei-nuclei interactions. Furthermore, the above Kohn-Sham equation can be reduced to,

$$\left[-\frac{1}{2}\nabla^2 + V_{eff}(r)\right]\Psi_i(r) = E_i\Psi_i(r)$$
(1.10)

Where instead of wave function, $\Psi_i(r)$ represents the Kohn-Sham orbitals, and V_{eff} can be represented as,

$$V_{eff} = V_{Hartree} + V_{ext} + V_{xc} \tag{1.11}$$

Therefore, the effective potential of the simple non-interaction single particle can be shown in the form of the Coulomb interaction, external potential and exchange correlation. The above equation is an exactly solvable one, only if the exchange correlation potential is known. However, finding out the exact exchange correlation potential is not an easy task, and here also several approximations developed. Most of the approximations proposed for the solvation of the equation 1.10 and 1.11 are widely used during the simulation of molecular and solid-state problems.*[68]*

1.5.2.3. Exchange-Correlation Functional

The above mentioned exchange correlation potential functional in the Kohn-Sham equation can again be divided into two parts termed as, exchange part and another is correlation part.

$$E_{xc}(n(\mathbf{r})) = E_x(n(\mathbf{r})) + E_c(n(\mathbf{r}))$$
(1.12)

In this equation $E_{xc}(n(\mathbf{r}))$ is the exchange-correlation functional. Whereas $E_x(n(\mathbf{r}))$ and $E_c(n(\mathbf{r}))$ describe the exchange and correlation part of the system, respectively. $E_{xc}(n(\mathbf{r}))$ can be approximated using some local functional, which we have discussed in next sections.

1.5.2.4. Local Density Approximation (LDA)

LDA serves as an approximation method for deriving the exchangecorrelation functional. This approach involves considering a homogeneous electron gas to define the exchange-correlation functional,

$$E_{xc}^{LDA} = \int d^3 r \, n(\boldsymbol{r}) \, \mathcal{E}_{xc}^{hom}(n(\boldsymbol{r})) \tag{1.13}$$

In the above equation, $\mathcal{E}_{xc}^{hom}(n(\mathbf{r}))$ is the exchange-correlation energy per particle with the electron density $n(\mathbf{r})$ in the homogeneous gas.[69,70] LDA approximation is generally useful for finding the ground state properties of solid state materials, where density varies very slowly. However, this approximation limits in accurately finding some crucial

properties like cohesive energy, formation energy, bond dissociation energy and adsorption energies when compared to the experimentally observed values. Furthermore, this method is incapable to calculate the band gap of semiconductor and insulator materials exactly.[71]

1.5.2.5. Generalized Gradient Approximation (GGA)

To address the constraints inherent in the LDA approximation, the GGA has been introduced. GGA incorporates the electron density gradient to characterize the exchange-correlation functional. In this scenario, the exchange-correlation functional can be expressed as follows.

$$E_{xc}^{GGA} = \int d^3 r \, n(\mathbf{r}) \, \mathcal{E}_{xc}^{GGA} \big(n(\mathbf{r}), \nabla n(\mathbf{r}) \big) \tag{1.14}$$

where, $\mathcal{E}_{xc}^{GGA}(n(\mathbf{r}), \nabla n(\mathbf{r}))$ is the exchange-correlation energy per electron gradient. For the systems with rapidly varying density GGA approximation is extremely useful. Also, it can calculate the total, cohesive, formation, and adsorption energies of a system accurately with correct determination of lattice parameters etc. In this regard, the most widely used GGA approximation was developed by Perdew, Burke and Ernzerhof recognized as GGA-PBE functional. According to GGA-PBE functional, the exchange energy of the system can be estimated as,

$$E_x^{PBE} = \int d^3 r \, n(\boldsymbol{r}) \, \mathcal{E}_x^{PBE} \big(n(\boldsymbol{r}), s(\boldsymbol{r}) \big) \tag{1.15}$$

In the above equation, the PBE exchange energy is the product form of the enhancement factor F_x^{PBE} and the LDA exchange as given below.

$$\mathcal{E}_{x}^{PBE}(n(\boldsymbol{r}), s(\boldsymbol{r})) = \mathcal{E}_{x}^{LDA}(n(\boldsymbol{r})) * F_{x}^{PBE}(s(\boldsymbol{r}))$$
(1.16)

Moreover, some other GGA approximations are also developed and can calculate of the exchange correlation energy of the system such as Perdew and Wang (PW91), revised PBE, PBEsol etc.[72-74]

1.5.2.6. Projector Augmented Wave (PAW) Method

The electronic wave function exhibits distinct behaviour for core and valence electrons. The wave function for core electrons exhibits rapid oscillations, while that for valence electrons is considerably smoother. Typically, conventional basis set, such as the plane wave basis set are employed to represent valence electrons. However, plane wave basis sets are not suitable for describing core region electrons due to their complex wave functions. Consequently, the partial wave expansion is employed to depict electrons in the augmented region, and this approach is referred to as the projector augmented-wave method (PAW).[75-78]

This method is based on the linear transformation operator (T). According to this approach, all the electron wave functions (Ψ_n) are replaced by a pseudo wave function $(\widetilde{\Psi}_n)$ which is a function of the original electron wave functions (Ψ_n) as follows,

$$|\Psi_{\rm n}\rangle = T|\widetilde{\Psi}_{\rm n}\rangle \tag{1.17}$$

Both $|\Psi_n\rangle$ and $|\widetilde{\Psi}_n\rangle$ can be represented as linear combination of partial waves for each augmentation regions,

$$|\Psi_{\rm n}\rangle = \sum_i c_i |\phi_i\rangle \tag{1.18}$$

$$|\tilde{\Psi}_{n}\rangle = \sum_{i} c_{i} |\tilde{\phi}_{i}\rangle \tag{1.19}$$

The transformation operator, *T* is defined as

$$T = 1 + \sum_{i} (|\phi_n\rangle - |\phi_n\rangle) \langle \tilde{p}_i| \tag{1.20}$$

where, $\langle \tilde{p}_i |$ is the projection function. The pseudopotential employed effectively addresses challenges associated with core electrons, adeptly converting the rapidly oscillating wave function into a smoother form. This method is highly beneficial for exploring the properties of solid-state materials. Additionally, the PAW method has been integrated with ultrasoft pseudopotentials and linear augmented-plane-wave features. In this thesis, we have employed the PAW method as implemented in the Vienna *ab-initio* simulation package (VASP).[79-81]

1.5.3. Dispersion in Density Functional Theory

Above discussed methodologies are insufficient to account the dispersion interactions at any distance R. Particularly, the Coulomb interaction and exchange interaction depend on the electron transition density of the interacting units. To determine the dispersion forces between interacting fragments, long-range interactions have a major role. In order to account these effects accurately, particular methodologies like dispersion-corrected density functional theory (DFT-D), van der Waals (vdW) functionals, or empirical force fields, are generally utilised. These methods describe the long-range interactions and develop a complete understanding of dispersion interactions in molecular or solid-state systems.

$$E_{Disp}^{(2)} = \sum_{ia} \sum_{jb} \frac{(ia|jb)[(ia|jb)-(ja|ib)]}{\varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j}$$
(1.21)

Here, addition of all the particles hole excitation between orbitals $i \rightarrow a$ and $i \rightarrow b$ is localized on A and B fragments, respectively. Here, E is the corresponding energy of the orbital. These excitations are not considered for standard DFT.[82] Empirical corrections are often used to describe the dispersion interactions. However, the most widely used method to account dispersion correction is the Grimme's DFT-D_n method. The general formula utilised by this approach can be expressed as follows.[83]

$$E_{Disp}^{DFT-D} = \sum_{AB} \sum_{n=6,8,10,\dots} S_n \frac{C_n^{AB}}{R_{AB}^n} f_{damp(R_{AB})}$$
(1.22)

Here, C_n^{AB} define the dispersion coefficient for AB, the distance between A and B is denoted by R_{AB}^n , S_n represent the adjusted correction for the repulsion and $f_{damp(R_{AB})}$ is the double counting effect of correlation used at intermediate distances.[84,85]

In this thesis, for most of the DFT calculations we have accounted the nonbonded interactions using Grimme's DFT-D3 method, which considers

the triplet atoms for three body effects. Consideration of dispersion correction does not influence any molecular property like wave function, but mainly contributes based on the atomic forces. As a result, a different relaxed geometry is obtained after optimization in comparison to the nodispersion calculation.

1.5.4. Other Computational Tools

Along with the VASP package we have utilised some other computational tool in our thesis work to understand the properties of the solid state materials, such as nudged elastic band (NEB) method, Bader charge analysis, etc.

1.5.4.1. Nudged Elastic Band (NEB) Method

There are two most important factors in chemical reactions such as kinetic nature and the diffusion pathways of the reaction. These properties can be obtained by using the NEB method which is implemented in VASP package. Where, the concept is to find out the saddle point of the minimum energy pathway (MEP) between the reactant and product of a reaction. The method is based on the harmonic approximation of transition state theory (hTST)[81] where the rate constant of the reaction for the transition around the saddle points can be given as,

$$k^{hTST} = \frac{\prod_{i}^{3N} v_{i}^{init}}{\prod_{i}^{3N-1} v_{i}^{\#}} e^{-\binom{E^{\#} - E^{init}}{k_{B}T}}$$
(1.23)

In this equation, $E^{\#}$ and E^{init} are the energies of the saddle point and initial state i.e., reactant, whereas $v^{\#}$ and v^{init} are the normal mode of frequencies for the saddle point and the initial state, respectively. Generally, NEB finds the optimized geometries of a few intermediate structures between reactant and product. To optimize the intermediates a spring force along the band between images is added. In our thesis work we have used a code developed Henkelmann to generate the intermediate images.[86]
1.5.4.2. Bader Charge

In Bader charge analysis, is used to calculate the charges associated with each atom within the molecules separating the molecules into atoms. This method is based on the Bader partitioning scheme [87] and electronic charge density is utilized for the analysis. Furthermore, a 2-D surface, where the charge density is minimum perpendicular to the surface determines the density partitioning. This surface is known as zero-flux surface. Conducting Bader charge analysis facilitates the straightforward determination of multipole moments for interacting atoms or molecules.

In this thesis, we took help of an algorithm developed by Henkelman and coworkers to calculate Bader charges.[88] This algorithm operates swiftly based on the charge density grid and is designed for decomposing the electronic charge density of the molecule into its atomic contributions.

1.5.5. Molecular Dynamics Simulations

Here, we have discussed the time evolution of a system by solving Newton's equations of motion for a particular system. Solution of the equation will yield a trajectory composed of the Cartesian coordinates of each atom for each timescale. The trajectories from the molecular dynamics (MD) simulation can be analyzed using various tools, providing insights at both structural and thermodynamic levels.

1.5.5.1. Evaluating the Equation of Motion

Here, we are describing the concise overview of Newton's equations of the motion and explain their application in molecular mechanics. [89,90] For an N particle system, the force (F_i) working on the ith particle can be given as,

$$F_i = m_i a_i \tag{1.24}$$

where m_i and a_i are the mass and acceleration of the ith particle, respectively.

Also from the potential gradient, the force can be obtained as,

$$F_i = -\frac{\delta U(r^N)}{\delta r_i} \tag{1.25}$$

Generally, the Hamiltonian operator \mathcal{H} relate the total energy of a system with the position and momenta of its particles. Where, the instantaneous position (r_i) and momentum (p_i) of the ith particle can be defined as

$$p_i = -\frac{\delta \mathcal{H}}{\delta r_i} \tag{1.26}$$

$$r_i = -\frac{\delta \mathcal{H}}{\delta p_i} \tag{1.27}$$

$$\mathcal{H}(p_i, r_i) = \sum_{i=1}^{N} \frac{P_i^2}{2m_i} + U(r_i)$$
(1.28)

The Hamiltonian for a closed system can be expressed as a sum of kinetic energy (E_k) and potential energy (U). Where, the kinetic energy and potential energy are the function of coordinates and momenta of the particles.

$$r = r_1, r_2, r_3, \dots, r_N \tag{1.29}$$

$$p = p_1, p_2, p_3, \dots, p_N \tag{1.30}$$

$$\mathcal{H}(r,p) = E_k(p) + U(r) \tag{1.31}$$

The kinetic energy can be given as,

$$E_k = \sum_{i=1}^N \frac{1}{2m_i} \left(p_{ix}^2 + p_{iy}^2 + p_{iz}^2 \right)$$
(1.32)

where m_i , P_{ix} , P_{iy} , and P_{iz} are the mass and momenta along x, y, and z directions of the ith particle, respectively. If we know the potential function, the entire trajectory over time can be obtained. Though, for an N-particle system, finding exact solutions is often impractical. Instead, there are various approximate methods based on several finite-difference integration. All these uses Taylor series expressed as,

$$r(t + \Delta t) = r(t) + \Delta t V(t) + \frac{1}{2} \Delta t^2 a(t) + \frac{1}{6} \Delta t^3 b(t) + \dots$$
(1.33)

$$v(t + \Delta t) = v(t) + \Delta t a(t) + \frac{1}{2} \Delta t^2 b(t)$$
 (1.34)

$$a(t + \Delta t) = a(t) + \Delta t b(t)$$
(1.35)

Here, r, v, a, b represent position, velocity, acceleration, and the third derivative, respectively. Numerous algorithms are available for these calculations, known for their computational efficiency and ability to

conserve energy and momentum. Among these, the Verlet algorithm stands out as a well-established method for integrations.[91] It combines Taylor expansions for positions at both time t and $t - \Delta t$.

$$r(t + \Delta t) = r(t) + \Delta t V(t) + \frac{1}{2} \Delta t^2 a(t) + \dots$$
(1.36)

$$r(t - \Delta t) = r(t) - \Delta t V(t) + \frac{1}{2} \Delta t^2 a(t) - \dots$$
(1.37)

Adding equations 1.36 and 1.37,

$$r(t + \Delta t) = 2r(t) - r(t - \Delta t) + \Delta t^2 a(t)$$
(1.38)

Therefore, through the estimation of positions at the current and previous timesteps and accelerations at the current timestep, the Verlet algorithm can project the new positions of the system. The velocity of the system can be calculated using the following equation,

$$v(t) = \frac{r(t+\Delta t) - r(t-\Delta t)}{2\Delta t}$$
(1.39)

In principle, the Verlet algorithm operates in two steps by computing the position at two distinct times. To execute this algorithm, additional computer memory is necessary as it stores positions from three consecutive timesteps. Hence, an improved version of this algorithm, known as the velocity Verlet algorithm, has been introduced. In the velocity Verlet algorithm, velocity is first calculated at step n + 1, followed by the computation of coordinates at step n + 1. This approach allows the calculation of positions and velocities using the formula expressed as,

$$r(t + \Delta t) = r(t) + \Delta t V(t) + \frac{1}{2} \Delta t^2 a(t)$$
(1.40)

$$v(t + \Delta t) = v(t) + \frac{1}{2}\Delta t[a(t) + a(t + \Delta t)]$$
(1.41)

In this context, equation 1.40 is utilized to predict the position of the subsequent timestep, which is then employed to estimate the acceleration at the new time. Additionally, equation 1.41 allows for the calculation of velocity based on the position and acceleration.

Another updated form of the Verlet algorithm is the leapfrog algorithm. In this approach, velocities v are computed at time $t + \frac{1}{2}\Delta t$, and these velocities are then employed to calculate the positions at time $t + \Delta t$.

Accordingly, the velocities "leap over" the positions, and vice versa, providing the benefit of explicitly calculating velocity independently of the positions.

$$r(t + \Delta t) = r(t) + \nu \left(t + \frac{1}{2} \Delta t \right) \Delta t$$
(1.42)

$$v\left(t + \frac{1}{2}\Delta t\right) = v\left(t - \frac{1}{2}\Delta t\right) + a(t)\Delta t$$
(1.43)

The leapfrog algorithm offers an advantage over the Verlet algorithm in that it only necessitates the storage of one set of positions and velocities, whereas the Verlet algorithm requires three consecutive positions for a single set of velocities.

1.5.5.2. Timestep

One important element consistently addressed in prior algorithms is the timestep, denoted as Δt . The frequency of integration is evaluated by this parameter Δt . From a mathematical standpoint, employing a larger timestep facilitates the simulation of extended-time dynamics with reduced computational cost. Nonetheless, an enlarged timestep introduces a notable truncation error during integration, leading to a rapid increase in the system's energy over time.

Therefore, for standard MD simulations, it is necessary to maintain a timestep within the range of 1 femtosecond (fs) or lower to accurately capture the rapidest motions within the system.

1.5.5.3. Statistical Ensembles

Statistical mechanics is the bridge between the microscopic particles of a system and its macroscopic observables. Performing MD simulations with a macroscopic number of particles is currently computationally impractical. Therefore, the incorporation of statistical mechanical methods becomes essential for extracting meaningful information. A macroscopic observable is composed of numerous distinct microscopic states, and an ensemble encompasses all possible microstates under specific constant parameters.

For instance, isolated systems fall under the microcanonical ensemble (NVE), where the total number of particles (N), volume (V), and total energy (E) remain constant. Within this ensemble, the energy of each microstate must remain constant. Consequently, exploration of the potential energy surface is constrained in the microcanonical ensemble due to higher free energy barriers relative to the total energy of the system.

An alternative to the microcanonical ensemble is the canonical ensemble (NVT) and the isobaric-isothermal ensemble (NPT), where volume and temperature or pressure and temperature are kept constant. The NVT ensemble is commonly employed during the heating phase, resembling a closed system capable of transferring heat from an external source. In contrast, the production run of MD simulations often utilizes the NPT ensemble to represent real conditions more accurately. However, in these ensembles, the system's energy is not fixed, allowing systems to spontaneously surmount large potential energy barriers through fluctuations in total energy.*[91-93]*

1.5.5.4. Long Range Interactions

In general, and from a computational standpoint, the calculation of bonded interactions is less demanding, focusing solely on atom pairs connected by 1-3 covalent bonds. While nonbonded interactions involve all possible pairs of atoms in the system, making it practically infeasible to compute all these interactions. The primary objective is to strategically neglect specific interaction pairs, improving simulation efficiency though maintaining the authenticity of the obtained results. After a certain distance, both Lennard-Jones (LJ) and Coulombic potentials can be ignored as their influence becomes negligible compared to simulation errors. To achieve this, a cut-off scheme is employed to exclude long-range interactions beyond a defined distance. While the intermolecular electrostatic interaction extends over a greater range than the LJ interaction, hindering the use of the former method, the Particle Mesh Ewald (PME) scheme is widely adopted for

electrostatic interaction calculations in MD simulations.[94] In this scheme, electrostatic potentials are categorized into short- and long-range interactions. Short-range interactions, like LJ potentials, decay rapidly. Electrostatic charges are distributed on a grid, and potentials are computed from this grid. Ultimately, the force acting on each particle is determined based on its position in the grid space.

1.5.5.5. Temperature and Pressure Coupling

Chemical reactions are typically performed under constant temperature conditions. To align with these experimental parameters, it is recommended to execute MD simulations in a canonical (NVT) ensemble. Additionally, to ensure a consistent pressure, simulations should be conducted in the isobaric-isothermal (NPT) ensemble. In the NPT ensemble, the number of particles remains fixed, while the volume and total energy can fluctuate. Various methods are available to control the pressure and temperature of a system. For instance, the Langevin and Andersen thermostats operate by constraining a system variable to a predetermined distribution function.[95,96] The Andersen thermostat, one of the earliest thermostats developed for MD simulations, assigns a new velocity to a random particle from a Boltzmann distribution during a collision event, thereby maintaining the preselected temperature. Another commonly used thermostat is the Berendsen thermostat, which employs weak coupling methods to bring a variable (temperature or pressure) closer to the desired value.[97] In contrast, strong coupling methods enforce strict adherence to the exact, predetermined value. The subsequent section delves into the specifics of the Berendsen thermostat.

The time average of the kinetic energy is related to the simulation temperature as follows,

$$\langle E_k \rangle = \frac{1}{2} \sum_{i=1}^N m_i v_i^2 = \frac{3}{2} N k_B T$$
(1.44)

Since the velocity is directly proportional to the temperature, velocity can be controlled by regulating the temperature. This thermostat employs weak coupling by an external heat bath at temperature T_{bath} , with a softening effect determined by the time constant r. All velocities are adjusted by a factor λ at each timestep. Therefore, for a specific time t, if the temperature is T(t), the change in temperature can be approximated using the following equation,

$$\Delta T = \frac{1}{2} \sum_{i=1}^{N} \frac{2}{3} \frac{2m_i (\lambda v_i)^2}{Nk_B} - \frac{1}{2} \sum_{i=1}^{N} \frac{2}{3} \frac{2m_i v_i^2}{Nk_B}$$
(1.45)

$$\Delta T = (\lambda^2 - 1)T(t) \tag{1.46}$$

After rescaling the velocities, the temperature change rate becomes directly proportional to the temperature difference between the system and the heat bath,

$$\frac{dT(t)}{dt} = \frac{1}{\tau} \left(T_{bath} - T(t) \right) \tag{1.47}$$

Now, the temperature change between timestep is,

$$\Delta T = \frac{\delta \tau}{\tau} \left(T_{bath} - T(t) \right) \tag{1.48}$$

where τ controls the coupling strength between the system and the heat bath. The scaling factor can be given as,

$$\lambda^2 = 1 + \frac{\delta t}{\tau} \left(\frac{T_{bath}}{T(t)} - 1 \right) \tag{1.49}$$

For high τ values the coupling becomes weak. Theoretically for $\tau > 100 \Delta T$, system possesses natural temperature fluctuation around the average value. Throughout the equilibration phase of Molecular Dynamics (MD) simulations Berendsen thermostat is commonly employed due to its effectiveness in achieving the target temperature. Whereas, more precise thermostats are often utilized for production run due to their tendency of energy drift and the inability to form a canonical ensemble. One widely used alternative is the Nosé-Hoover thermostat.[98] In this thermostat, a novel fictitious variable, denoted as ζ , is introduced. This variable functions as

friction, either accelerating or decelerating the particles until the desired temperature is attained. This can be formulated as,

$$m_i \frac{d^2 r_i}{dt^2} = F_i - \zeta m_i v_i \tag{1.50}$$

$$\frac{d\zeta(t)}{dt} = \frac{1}{Q} \left[\sum_{i}^{N} m_{i} \frac{v_{i}^{2}}{2} - \frac{3N+1}{2} k_{B} T \right]$$
(1.51)

Where, Q is the coupling strength of the friction $\zeta(t)$. Here, larger Q brings weak coupling. The temperature is not completely fixed here, instead tends to the target value.

Applying similar methods discussed for thermostat, pressure can also be reached to the target value. Here, to scale the dimensionality of the system, positions and simulation box sizes are altered. Such as, the Berendsen barostat, couples the pressure to a pressure bath given as,

$$\lambda = 1 - \kappa \frac{\delta T}{\tau_P} (P - P_{bath}) \tag{1.52}$$

$$r_i = \lambda^{\frac{1}{3}} r_i \tag{1.53}$$

Here, r_i is the rescaled coordinates, τ_P is the time constant, and κ is the isothermal compressibility which mainly controls the coupling strength to the pressure bath. The isothermal compressibility can be correlated to the volume fluctuations as,

$$\kappa = \frac{1}{V} \left(\frac{\delta V}{\delta P} \right) T = \frac{1}{k_B T} \frac{\langle V^2 \rangle - \langle V \rangle^2}{\langle V^2 \rangle}$$
(1.54)

There are numerous ways of scaling the pressure, such as isotropic pressure scaling (simultaneously scaled all dimensions), semi-isotropic pressure scaling (any given dimensions are scaled).

1.6. Machine Learning Techniques

Machine learning (ML) constitutes a branch of artificial intelligence (AI) dedicated to constructing algorithms and statistical models that empower computers to collect insights and make informed predictions or decisions based on data.[99,100] Within the realm of materials science, particularly in the domain of batteries, ML acts a pivotal role in accelerating research, development, and optimization endeavors. Various high-accuracy ML

models have been documented to exhibit success across diverse facets of battery research. Over the past decade, the primary focus within the research community has been directed towards identifying suitable non-aqueous electrolytes for high voltage DIBs. The application of these ML models is imperative for finding potentially active electrolytes from the extensive collection of non-aqueous electrolytes. ML methods are broadly classified into three categories: supervised learning, unsupervised learning, and reinforcement learning. Each category serves distinct objectives and finds application in diverse contexts. Here is a concise explanation of each learning type,

1.6.1. Supervised Learning

Supervised learning is the most common type of ML, where a model is trained on labeled data, pairing input examples with corresponding outputs. *[101]* The model is expert at learning to make predictions or classifications by leveraging this labeled data. This type of learning is particularly suitable for datasets with known properties, allowing the model to extend its predictions to unknown datasets. In our research, we mainly used supervised learning, which further categorized into two principal subtypes: regression and classification.

1.6.1.1. Regression

The regression ML model involves the prediction of a continuous numeric value or quantity. In this context, the target variable is a real number, and the model is trained to establish a mapping from input features to this numeric output.[102] Regression models aim to capture and predict patterns in the data that relate to the magnitude of the output variable. Regression model is applicable for the task involves predicting quantities or values, such as predicting house prices, stock prices, temperature, or a person's age based on various input features.

1.6.1.2. Classification

Classification, a key facet of supervised learning, turns around the categorization of input data into predefined classes or categories. In this case, the target variable is discrete, representing distinct classes or labels. The model undergoes training to accurately assign input data points to specific classes by recognizing patterns and relationships inherent in the dataset. This type of model finds applications in diverse domains such as spam email detection, sentiment analysis, and medical diagnosis (e.g., classifying tumors as malignant or benign) etc.[103]

1.6.2. Unsupervised Learning

Unsupervised learning is designed for unlabeled data, where algorithms are designed to unveil patterns, relationships, or structures within the dataset without predefined target variables. The primary objective is to group or cluster similar data points together. This approach proves instrumental in tasks such as clustering, dimensionality reduction, and anomaly detection. Unsupervised learning serves as a valuable tool for exploring and comprehending the intrinsic characteristics of a dataset.[104]

1.6.3. Reinforcement Learning

Reinforcement learning (RL) is centered around training agents to make sequences of decisions through interaction with an environment.[105] Diverging from supervised learning, where models rely on labeled data, RL algorithms learn through feedback in the form of rewards or penalties. Agents navigate the environment, refining their strategy to maximize cumulative rewards over time. It's a process alike to human learning through trial and error. Key components include the agent, which takes actions; the environment, where actions are taken; and the reward signal, which guides the learning process. RL has found applications in various fields, including game playing, robotics, and autonomous vehicles.

1.6.4. Data

Data is the central part of any ML problem, and its significance is paramount. In the context of ML, data serves as the foundation upon which models are built, trained, and evaluated. Here we have explained the purpose of training and test datasets.

1.6.4.1. Training Data

Training data constitutes the portion of the dataset employed to instruct a ML model in making predictions or decisions. By recognizing patterns and relationships within the training data, the model reaches the ability to generalize and extend predictions to an unknown dataset. The quality and quantity of training data directly impacts a model's ability to learn. More diverse and representative data can lead to better model performance. Training data is used to identify relevant features and relationships within the data, helping the model understand the underlying structure. During training, the model adjusts its parameters to minimize errors and fit the training data, which is essential for accurate predictions. It's important to have a sufficiently large and diverse training dataset that accurately represents the domain of the problem to avoid overfitting (fitting the training data too closely).

1.6.4.2. Test Data (Validation Data)

Test data represents a distinct portion of the dataset that remains unseen by the model during its training phase. Its purpose is to evaluate the model's performance and estimate its efficacy in making precise predictions for an unfamiliar dataset. The utilization of test data ensures an impartial evaluation of the model's generalization capabilities. This evaluation observes whether the model has truly captured meaningful patterns or just memorized the training data. If a model exhibits strong performance on the training data but fails on the test data, it may be indicative of overfitting. Thus, test data also helps to detect overfitting issues. It can be used to finetune model hyperparameters to achieve better generalization. The train and test data are mainly composed of input and output value where the input known as the feature and the output considered as the target variable. In the next section, we have discussed the various types of features and their importance for ML study.

1.6.5. Features

Features serve an important role in ML, and these are the characteristics or properties of the data that are used as input for building predictive models. The choice and quality of features play a crucial role in the success of ML project. The choice of features in ML project can significantly impact the model's performance. Properly handling and preprocessing various types of features is essential to ensure that the model can effectively learn from the data and make accurate predictions or classifications. Feature engineering and selection are crucial steps in the ML process to optimize model performance. Here are various types of features and their importance in ML as follows,

1.6.5.1. Numerical Features

Numerical features are continuous or discrete numeric values. They are the most common type of features in many ML applications. Numerical features are essential for various algorithms, including regression and clustering. They can represent quantities, measurements, and real-valued properties of data, making them versatile for many tasks.

1.6.5.2. Categorical Features

Categorical features represent discrete categories or labels, such as colors, types of products, or countries etc. Categorical features require special encoding techniques to convert them into a numerical format that ML algorithms can understand. Proper encoding is crucial to ensure these features contribute effectively to the model's prediction.

1.6.5.3. Elemental Features

Elemental features refer to the fundamental characteristics or properties associated with individual elements in the periodic table. These features include atomic number, atomic mass, electron configuration, and chemical reactivity. Electron configuration describes how electrons are distributed in atomic orbitals. Chemical reactivity is determined by the arrangement of electrons, influencing an element's ability to form compounds. Elemental features are crucial for understanding the behavior of elements in chemical reactions.[106]

1.6.5.4. Molecular Features

Molecular features comprise characteristics related to the structure and composition of molecules. These include properties such as molecular weight, bond lengths, bond angles, and torsional angles. Other features include electronegativity, which influences polarity, and molecular symmetry, crucial for understanding a molecule's stability and reactivity. Molecular features are central to elucidating the behavior and interactions of compounds in various scientific explorations from chemistry to bioinformatics.

1.6.6. Various ML Algorithms

Different ML algorithms are developed to study the statistics of any dataset, however, here we have briefly explained a few of them which are used in our work.

1.6.6.1. Kernel Ridge Regression (KRR)

The KRR algorithm is a part of supervised learning, primarily employed for regression tasks. It shares similarities with standard Ridge Regression but incorporates a non-linear mapping of input data into a higher-dimensional space, referred to as the feature space, facilitated by a kernel function.*[107]*

This mapping allows the algorithm to recognize more intricate relationships between input variables and the target variable. In KRR, the objective is to identify a function f(x) that effectively maps input variables x to the target variable y, utilizing a set of training data (x_i, y_i), where i = 1, 2, ..., n. The function f(x) is expressed as a linear combination of kernel functions K(x, x') evaluated at the training data points x_i,

$$f(x) = \sum_{i=1}^{n} \alpha_i * K(x, x_i)$$
(1.55)

Where, α_i are the coefficients of the linear combination.

1.6.6.2. eXtreme Gradient Boosting Regression (XGBR)

XGBR algorithm used for predicting continuous numerical values. We have a training set of N examples, where each example has M input features (x_1 , x_2 ,..., x_M) and a corresponding continuous numerical output value y. The XGBR algorithm aims to learn a prediction function F(x) that can exactly predict the value of y for any new input x.[108] In XGBR, the prediction function F(x) is modeled as the sum of T individual decision trees, each of which outputs a prediction value $f_i(x)$ for the input x. The final prediction value is considered by obtaining the weighted sum of the T individual predictions as follows,

$$F(x) = \sum_{t=1}^{T} ft(x) \tag{1.56}$$

1.6.6.3. Gradient Boosting Regression (GBR)

The GBR model is a comprehensive ML algorithm created through the mixture of weak regression trees.[109] Given the training set $D = \{(x_1, y_1), (x_2, y_2)..., (x_n, y_n)\}$, the number of leaf nodes in every regression tree is J. We divided the input data into J disjoint areas and defined each regression tree as $t_m(x)$. The training goal of GBR is to minimize the loss function L, and the parameters of decision tree θ_m are determined through empirical risk minimization,

$$\theta_m = \sum_{i=1}^n L(y_i, f_{(m-1)}(x_i) + t_m(x_i))$$
(1.57)

1.6.6.4. Light Gradient Boosting Machine (LGBM) Regression

LGBM belongs to the family of gradient boosting techniques and is known for its high efficiency and speed. LGBM creates an ensemble of decision trees in an order where each tree corrects the errors of the previous one.[110] LGBM handles large datasets and performs well in terms of training speed and memory usage. It employs a leaf-wise strategy for tree growth, prioritizing nodes with the maximum loss reduction. This makes LGBM particularly effective for tasks requiring accurate predictions with large and complex datasets. The prediction $F_t(x)$ of the ensemble at the iteration of t for input x is as follows,

$$F_t(x) = F_{t-1}(x) + \gamma \cdot h_t(x)$$
(1.58)

Where, the $F_{t-1}(x)$ is the prediction of the ensemble up to iteration of (t-1), γ is the learning rate and $h_t(x)$ is the weak learner tree added at t iteration.

1.6.6.5. Extra Trees Regression (ETR) and Random Forest Regression (RFR)

The ETR approach is an evolved strategy originally derived from the RF model. In the conventional top-down methodology, the ETR algorithm builds an assembly of decision or regression trees. In the RFR, two key steps, bootstrapping and bagging, are involved. During bootstrapping, each tree in the ensemble is grown using a randomly sampled training dataset. The bagging step is employed to partition the decision tree nodes after forming the ensemble. This requires selecting multiple random subsets of the training data in the initial bagging process. The decision-making process involves choosing the optimal subset and its associated value. The RFR incorporates a series of decision trees, where each tree represents a predictor [$G(x, \theta_r)$]. The uniform independent distribution vector (θ_r) is assigned before the tree's growth. The ensemble is formed by combining and averaging all the trees, resulting in a forest of constructed trees, as expressed by the following equation, [111]

$$G(x,\theta_1,\dots,\theta_r) = \frac{1}{R} \sum_{r=1}^R G(x,\theta_r)$$
(1.59)

There is distinction between ETR and RFR such as,

- 1. In the ETR, all cutting points are utilized, and nodes are divided through random selection from these points.
- 2. The ETR employs the entire set of learning samples to grow trees, aiming to minimize bias.

1.6.6.6. Adaptive Boosting Regression (ABR)

In ABR, the algorithm combines several weak learners to form a strong predictor.[112] The mathematical form can be explained by following points,

- 1. Initialize the weight of each training sample as $w_i = 1/N$, where N is the total number of training samples.
- 2. For each iteration $t=1,2,3,\ldots,T$:
 - a. Train a weak learner on the training data with the current weights.
 - b. Calculate the error of the weak learner (ϵ_t),

$$\epsilon_t = \frac{\sum (w_i * |(y_i - f_t(x_i))|)}{\sum w_i}$$
(1.60)

Where, y_i is the target value for the ith training sample, $f_t(x_i)$ is the prediction of the weak learner for the ith sample, and $\sum w_i$ is the sum of weights over all training samples.

c. Next calculate the weight of the weak learner (α_t),

$$\alpha_t = \ln(\frac{(1-\epsilon_t)}{\epsilon_t}) \tag{1.61}$$

d. Now, update the previously training sample (w_i),

$$w_i = w_i * e^{\alpha_t |(y_i - f_t(x_i))|}$$
(1.62)

3. The final predictor is the weighted combination of the weak learners, where the weight of each learner is proportional to its alpha value.

1.6.6.7. Decision Tree Regression (DTR)

The DTR involves recursively partitioning the feature space into regions and fitting a simple model (typically a constant value) in each region. [113] The output of a decision tree regression can be represented by the following equation,

$$y = \sum C_i * I(x \in R_i) \tag{1.63}$$

where, the predicted output y is determined by the constant value C_i associated with the region R_i to which the input x belongs. The regions R_i are defined by the splits in the decision tree, dependent on the input feature values. The objective is to find optimal splits that minimize the mean squared error between predicted and actual values in the training data. The indicator function $I(x \in R_i)$ returns 1 if x is in region R_i and 0 otherwise.

1.6.7. Hyperparameter Tunning

Hyperparameters are predefined configurations or settings that are not learned from the training data but are established prior to the model training process. Tuning these hyperparameters is essential to optimize model's performance.[114] There are several methods for hyperparameter tuning, each with its own advantages and use cases. Here, we have briefly explained different techniques of hyperparameter tuning being used in our study.

1.6.7.1. Grid Search

Grid search is a systematic approach where a range of values is given for each hyperparameter, and the search algorithm evaluates all possible combinations of hyperparameters to find the best set. Grid search is a straightforward method for small hyperparameter spaces but becomes inefficient when dealing with many hyperparameters and large search spaces.

1.6.7.2. Random Search

Unlike grid search, hyperparameters are sampled randomly from specified distributions. It explores a wider range of hyperparameter combinations

with fewer evaluations. Random search is particularly useful for a large hyperparameter space to find optimum hyperparameter quickly.

1.6.8. Cross-Validation techniques

Cross-validation (CV) is a critical technique in ML for assessing and validating the performance of a predictive model. It helps to determine the model's stability and generalizability for the prediction of unknown data. Various CV methods have been discussed in this section as follows,

1.6.8.1. K-Fold Cross-Validation

In this CV method, the dataset is partitioned into 'k' equally sized folds. The model undergoes training on 'k-1' folds and is evaluated on the remaining one. This process iterates 'k' times, each time using a different fold as the test set. The final performance metric is usually an average of the 'k' results. K-fold CV is a versatile and widely adopted technique for evaluating model performance. It strikes a balance between the amount of data used for training and testing, offering a robust assessment and mitigating the risk of overfitting.[115]

1.6.8.2. Leave One Out Cross-Validation (LOOCV)

In the LOOCV technique, one data point is always out from the total dataset and treated as the test data point and model is trained by the remaining data point. The process will be repeated for the total number of data points and each iteration score will be printed. For example, we have 'n' number of points in one dataset, one point is out for test and remaining 'n-1' data is used for training. The process will be repeated up to 'n' steps.[116]

1.6.9. Interpretable Machine Learning

All the ML algorithms we have considered fall into the category of black box models, operating in a manner that poses challenges for understanding and interpreting the specific features influencing their predictions. To overcome this limitation and to gain insights into both local and global trends for particular features, we incorporated interpretable models. Various interpretable models are elucidated as follows,

1.6.9.1. Local Interpretable Model-agnostic Explanations (LIME)

LIME is a model-agnostic method that approximates the behavior of a complex model in the vicinity of a specific data point by training an interpretable for a specific instance or prediction.[117] The process involves selecting an instance from the dataset and perturbing it to create a synthetic dataset. The complex model is then queried on these perturbed instances, and the responses are used to train a simpler, interpretable model, such as a linear model or decision tree. This interpretable model is expected to approximate the complex model's behavior locally, providing insights into how the model arrives at its predictions for that specific instance.

1.6.9.2. SHapley Additive exPlanations (SHAP)

SHAP values are based on cooperative game theory and provide a way to attribute a model's output to individual features.[118] They offer a unified approach to feature importance and explainability. However, SHAP is a model dependent technique which only works on the tree and boosting based ML models. SHAP values consider all possible combinations of features and their interactions, calculating the average contribution of each feature across all possible combinations. From there, SHAP values offer a comprehensive and globally consistent explanation for individual predictions using the waterfall and force plots.

1.7. References

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Optimization of Computational Methods for Dual-Ion

Batteries

2.1. Introduction

Melting of glaciers, forest fires and flash floods are various catastrophes occurring nowadays due to climate change and global warming induced by utilization of non-renewable fuels. Shifting from non-renewable and polluting sources to green energy is very urgent to maintain both the high-tech growth and eco-friendly environment.[1] Tapping renewable energy sources require the development of efficient energy storage devices such as batteries and capacitors.[2] In recent years, dual ion batteries (DIBs) based on aluminium and graphite electrodes are emerging as attractive alternatives to high-cost lithium-ion batteries (LIBs).[3-5] Such DIBs exhibit attractive features such as high voltage, low cost and high volumetric capacity.[6-8] However, the limited electrochemical window (ECW) potential of commonly used organic electrolytes causes intense side reactions and reduced working voltage for all batteries.[4,9]

Ionic liquids (ILs) are used as electrolytes as they are salts which remain in liquid state below the temperature of 373K. Their physicochemical properties depend on cationic size (due to the presence of different alkyl groups) as well as the ionic interaction of the system. In general, ILs deliver interesting properties such as low vapor pressure, high thermal stability, low toxicity, low flammability, large electrochemical window, and relatively high conductivity.*[10-12]* Thus, ILs are considered as a potential alternative electrolyte over flammable organic electrolytes. Carlin and co-workers have introduced metal free ILs based organic moieties such as AlCl₄, OTf, PF₆, and BF₄ as electrolytes in DIBs.*[13]* Due to the higher electrochemical window potential of the IL electrolyte, it has been primarily studied as they possess high oxidative and reductive stability, which are important for high charging/discharging voltage (4.0-5.0 V) of the DIBs.

The electrochemical window (ECW) of electrolytes is an important criterion for its usage in electrochemical applications. The ECW can be defined as the difference between the cathodic limiting (V_{CL}) potential and

anodic limiting (V_{AL}) potential, at which reduction and oxidation takes place, respectively.[14-16] Usually, ILs show a large electrochemical window range of 4 to 7 V, which are promising for high voltage batteries.[17-19] Experimentally, a cyclic voltammetry study can be conducted using different working electrodes such as Pt or glassy carbon (GC) to determine ECW using the current-voltage polarization curve.[20] However, measurement of ECWs depend on many factors such as electrodes, cutoff currents, and impurities of medium. [21] Therefore, the ECW can vary significantly in different experimental setup for a given IL. It is difficult to study the oxidation and reduction potentials of IL constituent ions experimentally. Koch and coworkers have found that anodic limiting potential is correlated well to the highest occupied molecular orbital (HOMO) energy of 1,2-dimethyl-3-propylimidazolium based ILs. [22] In the same way, Buijs and coworkers found that experimental ECW was correlated with the lowest unoccupied molecular orbital energy of ILs. [23] In the same context, Ceder and coworkers have considered an explicit solvent-based molecular dynamics-density functional theory (MD-DFT) method where, cathodic and anodic limits are represented by the energies of HOMO and LUMO of constituent ions for IL. [14] In most of the ILs, it is commonly assumed that the anode and cathode limiting potentials are dependent on the oxidation of anion and reduction of cations, respectively.[24] However, this is not true for all ILs. For instance, the bis(trifluoromethylsulfonyl)imide (TFSI) anion undergoes easier reduction compared to its corresponding N, N-propylmethylpyrrolidinium (Pyr1,3) cation.[14] Therefore, it is necessary to find individual oxidation and reduction potentials of constituent ions for a given IL, to determine the electrolyte with high electrochemical window potential.

In this study, we have investigated the ECW for commonly used imidazolium and pyrrolidinium based ILs for Al DIBs using effective computational screening methods. Here, we have considered sixteen ionic liquid and molten salt electrolytes as shown in Figure 2.1. Different
computational techniques such as thermodynamic cycle method and MD-DFT method have been utilized to find the most suitable way of calculating ECW. The considered ILs (imidazolium and pyrrolidinium based cations coupled with AlCl₄ and OTf anions) are mostly used electrolytes in Al DIBs. Besides, we have also investigated the role of cations towards the ECW values as we move from aromatic (imidazolium) to non-aromatic (pyrrolidinium) based cations. On the other hand, AlCl₄ and OTf are only two anions used in Al DIBs till now. Also, the contribution from cationic and anionic part towards ECW is noted.



Figure 2.1: Ionic liquids and molten salts (MSs) are investigated. Structures of cations: (a) Imidazolium moieties with a different alkyl group (where, n = 2, 3, 4, 6 and 8), (b) N, N-butylmethylpyrrolidinium (BMP) cations, (c) $[AlCl_2(U)_2]^+$, and (d) $[AlCl_2(AcAm)_2]^+$ (where U is urea and AcAm is acetamide) and structure of anions: (e) $AlCl_4$, and (f) trifluoromethanesulfonate (OTf).

2.2. Methodology

2.2.1. Thermodynamic Cycle Method

Our main goal is to estimate the oxidation and reduction limiting potential for the considered ILs and MSs. We have investigated the structural (alkyl group variation on imidazolium and pyrrolidinium) effect of cations and anions on ECW with respect to Al^{3+}/Al reference electrode. For this, we have considered thermodynamic cycle technique[24-26] to calculate the

oxidation and reduction potentials of individual ions for the Al^{3+}/Al electrode as shown in Figure 2.2.

(a)
$$Al(g) \xrightarrow{\Delta G_e(Al)} Al^{3+}(g) + 3e^{-}$$

 $\Delta G_{vap}(Al) \xrightarrow{\Delta G_{ref}} Al^{3+}(sol) + 3e^{-}$
(b) $R(g) \xrightarrow{\Delta G_{red}(R_g^+)} R^+(g) \xrightarrow{\Delta G_{ox}(R_g^+)} R^{2+}(g) + e^{-}$
 $\Delta G_{sol}(R) \xrightarrow{\Delta G_{red}(R_{sol})} R^+(g) \xrightarrow{\Delta G_{ox}(R_{sol})} R^{2+}(g) + e^{-}$
 $R(sol) \xrightarrow{\Delta G_{red}(R_{sol})} R^+(sol) \xrightarrow{\Delta G_{ox}(R_{sol})} R^{2+}(sol) + e^{-}$
(c) $A^{2-}(g) \xrightarrow{\Delta G_{red}(R_{sol})} R^+(sol) \xrightarrow{\Delta G_{ox}(R_{sol})} A(g) + e^{-}$
 $\Delta G_{sol}(A^{2-}) \xrightarrow{\Delta G_{red}(A_{sol})} A^-(g) \xrightarrow{\Delta G_{ox}(A_{sol})} A(g) + e^{-}$
 $A^{2-}(sol) \xrightarrow{\Delta G_{red}(A_{sol})} A^-(sol) \xrightarrow{\Delta G_{ox}(A_{sol})} A(sol) + e^{-}$

Figure 2.2: Thermodynamic cycle for calculating the oxidation potential of (a) Al metal and oxidation/reduction potentials of (b) cation, and (c) anion of the ionic liquid.

Three electron reaction process is observed for Al^{3+}/Al electrode instead of one electron process as is the case for the Li⁺/Li electrode. Whereas the oxidation and reduction of cations (R⁺) and anions (A⁻) are observed to be one electron transfer process as shown in Figure 2.2. To calculate the free energy change (ΔG_{ref}) of Al^{3+}/Al reference electrode (Figure 2.2a), equation 2.1 is used:

$$\Delta G_{ref} = \Delta G_{vap}(Al) + \Delta G_e(Al) + \Delta G_{sol}(Al^{3+})$$
(2.1)

Where, ΔG_{vap} is the free energy of vaporization of Al, which is calculated to be 246.1 kJ/mol. ΔG_e and ΔG_{sol} are the free energies of ionization and solvation of Al metal, respectively.

From Figure 2.2b and c, the oxidation free energies of cation $(\Delta G_{ox}(R_{sol}^+))$ and anion $(\Delta G_{ox}(A_{sol}^-))$ of the ILs in solution phase can be calculated using equation 2.2 and 2.3, respectively.

$$\Delta G_{ox}(R_{sol}^+) = \Delta G_{ox}(R_g^+) + \Delta G_{sol}(R^{2+}) - \Delta G_{sol}(R^+)$$
(2.2)

$$\Delta G_{ox}(A_{sol}^{-}) = \Delta G_{ox}(A_{g}^{-}) + \Delta G_{sol}(A) - \Delta G_{sol}(A^{-})$$
(2.3)

Similarly, the reduction free energies of cation $(\Delta G_{red}(R_{sol}^+))$ and anion $(\Delta G_{red}(A_{sol}^-))$ of ILs can be calculated using equations 2.4 and 2.5, respectively.

$$\Delta G_{red}(R_{sol}^+) = \Delta G_{red}(R_g^+) + \Delta G_{sol}(R) - \Delta G_{sol}(R^+)$$
(2.4)

$$\Delta G_{red}(A_{sol}^{-}) = \Delta G_{red}(A_{g}^{-}) + \Delta G_{sol}(A^{2-}) - \Delta G_{sol}(A^{-})$$
(2.5)

The Gibbs free energy change of ionization $(\Delta G_{ox}(R_g^+))$ of the cations in gas phase (Figure 2.2b) is obtained using the equation 2.6.

$$\Delta G_{ox}(R_{sol}^+) = \{G(R^{2+}(g)) + G(e^-)\} - G(R^+(g))$$
(2.6)

Where, $G(e^{-})$ is the free energy of the electron, which will be cancelled out while calculating the oxidation/reduction potentials of the systems.[24] Overall, the standard redox potentials can be calculated using the equations 2.7 and 2.8 with respect to the Al³⁺/Al reference electrode.

$$E_{ox}^{0}[V](vs.Al^{3+}/Al) = -\left(\frac{(-\Delta G_{ox}(R^{+}/A^{-})_{sol}[J] + \Delta G_{ref}[J])}{nF}\right)$$
(2.7)

$$E_{red}^{0}[V](vs.Al^{3+}/Al) = -\left(\frac{(-\Delta G_{red}(R^{+}/A^{-})_{sol}[J] + \Delta G_{ref}[J])}{nF}\right)$$
(2.8)

Where, F is the Faraday constant and n is the number of electron transfers in reference electrode process. Therefore, the ECW of the ionic liquids can be calculated by the difference between two redox potentials,

$$ECW = E_{ox}^0 - E_{red}^0 \tag{2.9}$$

2.2.2. Molecular Dynamics and Density Functional Theory (MD+DFT) Method

The cathodic limiting (V_{CL}) and anodic limiting (V_{AL}) potentials are correlated with the LUMO and HOMO of IL electrolytes, respectively and ECW can be measured from their difference. [16] Here, we have considered a combination of classical molecular dynamics (MD) simulation and ab *initio* MD (AIMD) using the periodic boundary condition (PBC) in density functional theory (DFT) approach to calculate the HOMO and LUMO for a unit cell containing cations and anions of ILs in their liquid form. Initially, we equilibrated each IL through classical MD simulation. From the last 2 ns equilibrated simulation, we have considered five equilibrated snapshots of each 0.5 ns interval. Now we have considered two pathways, AIMD-sp and AIMD-min methods. In AIMD-sp method, HOMO/LUMO energies of each snapshot are calculated from the single point (sp) density of states (DOS) calculation without further geometry optimization. If we perform optimization, the optimized structure does not actually represent the exact structural orientation of the cations and anions of IL at room temperature. This is because the geometry optimization done at 0 K and hence after optimization, all optimized configurations may lead to the same geometry. Therefore, the DOS calculations on the optimized geometries will provide almost the same cathodic and anodic limiting potentials. So, we will not be able to sample our calculated limiting potentials from different snapshots. Hence, we have not considered the optimization process for all ILs snapshots. In AIMD-min, further we have relaxed each snapshot in AIMD

method and performed DOS calculation to measure the HOMO/LUMO energies of each snapshot.

2.2.3. Computational Details

2.2.3.1. Thermodynamic Cycle Method

All the calculations have been performed in Gaussian 09 package.[27] The molecular geometries have been fully optimized in gas phase using Pople diffuse basis set of 6-31+G(d,p) at MP2 level of theory.[28] The 6-31+G(d,p) diffuse basis set has been used for all ILs.[29-31] For the solvent phase calculation, we have considered self-consistent reaction field (SCRF) methodology. The conductor-like polarizable continuum model (CPCM) has been implemented which is an implicit dielectric screening solvent model.[32,33] We have considered the static dielectric constant and refractive index from the previous report.[34] Moreover, we have included the zero-point vibrational energy (ZPVE) and thermal correction terms for the calculation of reaction free energy at room temperature (298.15 K) and 1 atm pressure. The reaction free energy (ΔG) change has been calculated as the difference between initial and final chemical species of IL.

2.2.3.2. Molecular Dynamics Simulation

To generate the equilibrium structure of ILs, we have performed classical molecular dynamics simulation with interacting potentials of PCFF forcefield[35] using velocity-varlet algorithm in the LAMMPS package.[36,37] Atomic charges of ILs have been explicitly calculated using the CHelpG procedure in the MP2/6-311++G(d,p) level of theory.[38] Initially, we considered a large system containing 128 ion pairs of EMIM-AlCl₄ (1-ethyl-3-methyl imidazolium-AlCl₄) IL to perform classical simulation. However, carrying out AIMD for this large system would be time consuming. Thus, we have reduced our system to 9 ion pairs maintaining volume to density ratio with a fixed box dimension of 15 Å. We have compared our results with the large system (128 ion pairs) where

the liquid density and pair distribution function are not much changing from small size system (Figure 2.3). In this study, we have fixed the volume of the box and changed the numbers of ion-pairs. Following this, we have kept the box dimension fixed (15 Å) for all the ILs and number of ion pairs has been chosen concerning their volume to density ratio. Equilibration runs were performed in a melt-quench procedure as follows: (i) NVT ensemble was considered at 600 K temperature for 1 ns with a timestep of 0.1 fs, (ii) then cooling from 600 to 300 K using NVT ensemble for 1 ns with a timestep of 0.25 fs, (iii) further equilibration in NVT at 300 K for 1 ns with



Figure 2.3: The calculated equilibrated density plots of (a) 128 ion pairs, (b) 9 ion pairs for EMIM-AlCl₄ ionic liquid, and (c) the pair distribution function (g(r)) of two systems.

a timestep of 0.5 fs, and (iv) final production run has been performed in NPT ensemble for 47 ns at 300 K temperature and 1 atm pressure with the timestep of 1 fs. A cut-off distance of 14 Å has been implemented for van-

der Waals as well as electrostatic interactions and three-dimensional periodicity has been considered for all simulations. Nosé-Hoover thermostat and barostat have been used for all NVT and NPT simulations.[39-41] To confirm the system equilibration, we have checked pair distribution function plots for each ionic liquid (Figure 2.4). From Figure 2.4, it has been observed that all the IL structures are well relaxed. From the last 2 ns MD trajectories, we have considered 5 snapshots of each



Figure 2.4: Calculated pair distribution function plot of (a) AlCl₄ and (b) OTf anions containing ILs.

0.5 ns interval to perform the AIMD simulation. The obtained potential energy surfaces (PESs) from classically applied forcefield are not stable in high level DFT theory. The classical simulation snapshot models may not necessarily provide a stable configuration at DFT level. Therefore, we have performed an AIMD relaxation for each classical MD snapshot for AIMD-min method. AIMD and DOS are performed using the projected augmented

wave (PAW) method[42] in the Vienna *ab initio* simulation package (VASP.5.4.4).[43,44] The generalized gradient approximation of Perdew-Burke-Ernzerhof (GGA-PBE) functional account exchange-correlation has been implemented.[45] For comparisons of ECW values, we have considered the modified version of PBE functional such as revPBE (revised PBE) and RPBE functionals.[46,47] An energy cutoff of 470 eV is implemented for the plane wave basis set. The AIMD simulation has been performed in NVT ensemble at 300 K temperature for 3 ps with the timestep of 1 fs. Nosé-Hoover thermostat [39] was implemented with a Nosé mass of 0.01 to control the temperature throughout the simulation. Single point density of states was performed on the AIMD relaxed geometry to obtain the HOMO and LUMO energies of the ILs. Owing to large system, we have considered the Γ-centered k-points of $1 \times 1 \times 1$ for DOS calculation.

2.3. Results and Discussion

2.3.1. Consideration of Different Ionic Liquid Electrolytes

Two types of IL are considered for calculation of ECW: (i) room temperature ionic liquid electrolytes (RTILs) and (ii) molten salt IL electrolytes. Here, we have mainly considered two different types of organic cations (imidazolium and pyrrolidinium moieties) with two different types of anions (AlCl4 and OTf) as shown in the Figure 2.1. The imidazolium and pyrrolidinium based RTILs are also modelled with varying alkyl group substitution as shown in the Figure 2.1. The cations and anions of ILs could form different intermolecular forces because of this steric hindrance. This can also lead to the changes in physical and chemical properties of IL such as density, conductivity, and electrochemical window.*[48,49]* By varying the alkyl group of imidazolium ring, we have modelled six organic cation systems: 1-ethyl-3-methyl imidazolium (EMIM), 1-propyl-3-methyl imidazolium (PMIM), 1,2-dimethyl-3-propyl imidazolium (DMPI), 1-butyl-3-methyl imidazolium (BMIM), 1-hexyl-3-methyl imidazolium (MMIM) and 1-octyl-3-methyl imidazolium (OMIM). These cations

combined with two different types of anions (AlCl₄ and OTf) can form a total number of 12 IL electrolytes. Similarly, for pyrrolidinium based IL we have considered mostly used electrolyte of N, N-butyl-methyl pyrrolidinium (BMP) cation with AlCl₄ and OTf anions. For the molten salt electrolytes, we have considered two systems, urea (U) and acetamide (AcAm) which can form complex isomers in the presence of AlCl₃ but not in the presence of OTf anion. The most stable isomer complexes, $([AlCl_2(U)_2]-AlCl_4)$ and $([AlCl_2(AcAm)_2]-AlCl_4)$, are considered. [50] Thus, a total of nine AlCl₄ and seven OTf anions containing ILs are considered for ECW study. Among these, the AlCl₄ based IL optimized structures are taken from our previous study [15] and OTf based IL structures have been optimized as shown in the Figure 2.5. The AlCl₄ based ILs are stabilized through H-bonding where the Cl atom forms the maximum number of H-bonds with organic cation within the distances of 2.5-2.9 Å. [51] Similarly, in OTf anion-based ILs, the H-bonds are formed between the most electronegative F and O atoms of OTf anion and the H atoms of the organic cation.



Figure 2.5: The optimized structures and relative energies (R.E. in eV) of OTf anion containing ionic liquids. Color codes: pink, grey, blue, red, green, and yellow are for hydrogen, carbon, nitrogen, oxygen, fluorene and sulfur atoms of ILs, respectively.

2.3.2. Electrochemical Window from Thermodynamical Cycle Method

2.3.2.1. Oxidation Potentials of Cation and Anion of Ionic Liquids

The oxidation potentials of cations and anions are derived from the Gibbs free energy change with respect to the reference Al^{3+}/Al electrode. From

equation 2.1, we have calculated the reference Gibbs free energy change (ΔG_{ref}) of 661.61 kJ/mol for the Al³⁺/Al reference electrode. The oxidation Gibbs free energy of cation and anion reactions have been shown in Figure 2.2. As described by equation 2.2, the required free energy parameters of IL cation are the oxidation Gibbs free energy of the gaseous state $(\Delta G_{ox}(R_g^+))$, the solvation free energy of its oxidized state $(\Delta G_{sol}(R^{2+}))$, and the solvation free energy ($\Delta G_{sol}(R^+)$). Similarly in equation 2.3, the required parameters of IL anion are oxidation Gibbs free energy of gaseous state $(\Delta G_{ox}(A_g^-))$, solvation free energy of its oxidized form $(\Delta G_{sol}(A))$, and solvation free energy ($\Delta G_{sol}(A^{-})$). The Gibbs free energy of the gas-phase oxidation of cation and anion is computed using equation 2.6, which calculates the difference between the Gibbs free energy of the ion and its oxidized version in the gas phase. Gibbs free energies are calculated for oxidized ions and their cations. The standard oxidation potentials with respect to the Al³⁺/Al reference electrode can be calculated using equation 2.7. The calculated oxidation potentials of IL cations and anions have been shown in Table 2.1 using the thermodynamic cycle method.

Table 2.1: Calculated values of E_{ox}^0 and E_{red}^0 potentials (vs. Al³⁺/Al reference electrode) of the cations and anions of IL using the thermodynamical cycle method. Where '---' indicates that the experimental data are not available.

Ionic Liquids		tion E ⁰ _{red} (V)	$\frac{E_{ox}^{0}}{(V)}$	hion E ⁰ _{red} (V)	ECW (V)	ECW (V) (expt.)
EMIM- AlCl4	0.4704	-1.7965	0.2886	-1.8649	2.0851	3.7[52]

PMIM-	0.4874	-1.7926	0.2886	-1.8649	2.0812	4.7[53]
BMIM- AlCl4	0.5054	-1.7948	0.2886	-1.8649	2.0834	4.7[54]
DMPI-						
AlCl ₄	0.3607	-1.8354	0.2886	-1.8649	2.1240	3.6[17]
HMIM-	0.4065	1 7007	0.2896	1.9640	2 0772	
AlCl4	0.4965	-1./88/	0.2886	-1.8049	2.0773	
OMIM- AlCl4	0.5772	-1.7649	0.2886	-1.8649	2.0535	
BMP- AlCl4	0.7710	-2.1209	0.2886	-1.8649	2.1535	
Urea- AlCl4	0.6705	-1.6363	0.2886	-1.8649	1.9249	3.6[55]
AcAm- AlCl4	0.6665	-1.4865	0.2886	-1.8649	1.7751	
EMIM- OTf	0.4704	-1.7965	0.2730	-2.1982	2.0695	
PMIM- OTf	0.4874	-1.7926	0.2730	-2.1982	2.0656	
BMIM- OTf	0.5054	-1.7948	0.2730	-2.1982	2.0678	
DMPI- OTf	0.3607	-1.8354	0.2730	-2.1982	2.1084	

HMIM- OTf	0.4965	-1.7887	0.2730	-2.1982	2.0617	
OMIM- OTf	0.5772	-1.7649	0.2730	-2.1982	2.0379	
BMP- OTf	0.7710	-2.1209	0.2730	-2.1982	2.3939	

From Table 2.1, the absolute redox oxidation potentials are not found to change significantly, upon changing the alkyl group of the imidazolium cation. This suggests that the oxidation mainly occurs on the aromatic imidazolium ring and not on the long alkyl carbon chain, which matches with the previous report.[24] However, the pyrrolidinium based BMP cation shows higher redox oxidation potentials of 0.77 V (vs. Al³⁺/Al), which is much higher than the imidazolium-based IL cations. Interestingly, the HOMO of the BMP cation is dominated by the long alkyl carbon chain (Figure 2.6) *i.e.*, the tightly bonded σ electrons of carbon chain are not easily oxidizable compared to the loosely bonded π electron of the aromatic imidazolium ring. This indicates that the pyrrolidinium cation might tolerate high oxidation potentials during the charging process.



Figure 2.6: HOMO and LUMO orbitals of the (a) imidazolium and (b) pyrrolidinium cations and (c) their corresponding energy diagram. Color codes: blue, grey, and pink are for nitrogen, carbon, and hydrogen atoms, respectively.

Similarly, we have calculated the absolute redox oxidation potentials of AlCl₄ and OTf anions and summarized them in Table 2.1. We obtained almost comparable oxidation potentials of 0.288 and 0.273 V for AlCl₄ and OTf anions, respectively. The oxidation potential of OTf anion is slightly lower compared to that of AlCl₄ anion, *i.e.*, OTf anion can oxidize easily compared to AlCl₄ anion. The imidazolium cations show higher oxidation potentials compared to any of the studied anions. Therefore, it is expected that the oxidation limit of ECW is very much dependent for such anions.

2.3.2.2. Reduction Potentials of Cation and Anion of Ionic Liquids

Likewise, for the oxidation potentials, we have calculated the reduction potentials of IL cation using the equation 2.4. The required constraints are the reduction Gibbs free energy of its gaseous state $(\Delta G_{red}(R_g^+))$, the solvation energy of its reduced form $(\Delta G_{sol}(R))$, and solvation Gibbs free energy $(\Delta G_{sol}(R^+))$. Similarly, the anion reduction Gibbs free energy can be calculated from equation 2.5, and the required constraints are the reduction Gibbs free energy of its gaseous state $(\Delta G_{red}(A_g^-))$, the solvation energy of its reduced form $(\Delta G_{sol}(A^{2-}))$, and solvation Gibbs free energy $(\Delta G_{sol}(A^-))$. The standard reduction potential with respect to Al³⁺/Al can be obtained from equation 2.8.

The information in Table 2.1, demonstrates that the absolute redox potentials of cations remain relatively unchanged when the alkyl group of the imidazolium ring is altered. The LUMOs of the cations are mainly dominated by the imidazolium ring orbitals and not the alkyl chain (Figure 2.6). As the chain is changing but the ring remains fixed, very less change has been observed in the reduction potential values of cations. However, the

reduction potential of pyrrolidinium-based BMP cation shows a higher value of -2.12 V compared to the imidazolium-based cations (-1.76 to -1.83 V) shown in Table 2.1. The LUMO of the pyrrolidinium cation is positioned at the higher energy of 1.70 eV compared to imidazolium rings (1.56-1.62 eV), and LUMO is mainly contributed by the non-aromatic pyrrolidinium ring. The electrons are more delocalized in aromatic ring (imidazolium) through π - π conjugation which in turn stabilizes the π^* orbital (LUMO). On the other hand, σ^* (LUMO) of the five membered cyclic ring (pyrrolidinium) will be in higher energy compared to the π^* (LUMO) of imidazolium cation. Hence, the electron acceptance in σ^* LUMO of pyrrolidinium cation is less favourable compared to π^* LUMO of imidazolium ring. Hence, the reduction of pyrrolidinium ring cation is very less probable compared to imidazolium ring. Therefore, the pyrrolidinium system could resist the solid electrolyte interface (SEI) layers formation to some extent due to the LUMO position of the pyrrolidinium ring compared to the imidazolium-based cation.

The reduction potentials of the anions are -1.86 and -2.19 V for AlCl₄ and OTf anions, respectively. Lower reduction potential of the AlCl₄ anion indicates that it can be easily reduced compared to the OTf anion. Hence, it is expected that OTf anion is more stable against the reduction. In contrast to the anions, imidazolium cations have lower reduction potentials, so they are less stable towards reduction. Therefore, we believe that the reduction potential of the ECW is set by the imidazolium cations for all the imidazolium based ILs.

2.3.2.3. Evaluation of ECW

The results in Table 2.1., show that the reduction potentials of the imidazolium and molten salt cations have lower negative values compared to their anion counterparts and therefore, imidazolium and molten salt cations are less stable towards the reduction reaction. However, the reduction potential of AlCl₄ anion is lower in presence of BMP cation

compared to any other cations. Further, the redox oxidation potentials of the studied anions (AlCl₄ and OTf) are lower compared to the counter cations. Therefore, anions are less stable towards the oxidation reaction. Hence, the ECWs of the ILs are calculated by the difference between limiting reduction potentials of cations and limiting oxidation potentials of anions, as given in equation 2.10, and reported elsewhere. [24] Whereas in the case of BMP-AlCl₄ IL, we find that the ECW would be calculated as the difference between limiting oxidation and reduction potentials of anions only. Our calculated ECW of EMIM-AlCl₄ is 2.08 V, which is far from the experimentally measured ECW of 2.8-3.7 V.[52] In this thermodynamic cycle method, molecules are treated as an individual system. This could be a reason that the thermodynamic cycle method calculated ECWs are not in comparable to the experimental measured values. In spite of this, the quantum mechanical calculation is a quicker processing method for estimating the ECW values of non-aqueous electrolytes from a large number of ILs.

$$ECW = E_{ox}^{0}(anion) - E_{red}^{0}(cation)$$
(2.10)

2.3.3. Electrochemical Windows from MD+DFT Method

The cathodic limiting (V_{CL}) and anodic limiting (V_{AL}) potentials can be calculated using LUMO and HOMO energies of the system, respectively.[16] In Al DIBs, the anodic oxidation and cathodic reduction potentials are set by 3e and 1e transfer reactions, respectively.[5,56] Hence, V_{CL} and V_{AL} are calculated using the following equation and ECW can be measured from their difference.

$$ECW = V_{AL} - V_{CL} = \frac{-E_{HOMO}}{3e} - \frac{-E_{LUMO}}{e}$$
 (2.11)

2.3.3.1. AIMD-sp and AIMD-min Methods

We have used AIMD-sp and AIMD-min methods to calculate the ECWs of the modelled electrolytes. In the AIMD-min procedure, we have relaxed each of the classically equilibrated snapshots through the quantum mechanically to get the stable potential energy surface and perform DOS. Whereas, we have performed only DOS for AIMD-sp without further AIMD relaxation of the snapshots. Using equation 2.11, we have calculated ECW of the considered ILs as represented in Figure 2.7. The rectangular bars imply the potential stability region of each IL. The minimum stable potential is called the anodic limit (beyond that the IL is to be oxidized), while the maximum stable potential is called the cathodic limit (beyond that the IL is to be reduced). The limiting potentials are calculated by taking the average of five snapshots of each ILs.

Table 2.2: Summary of ECWs from E_{ox}^0 and E_{red}^0 , V_{CL} and V_{AL} from thermodynamical cycle, and MD+DFT methods, respectively. Where, C/A, and '--' are represents the cation/anion and non-availability of experimental ECWs, respectively.

Ionio		Cycle		А	IMD-mir	1	1	AIMD-sp	þ	Expt
	F 0	F 0	ECW		X 7	ECW	X 7	X 7	ECW	ECW
Liquias	E_{ox}°	E [°] _{red}	(V)	VCL	VAL	(V)	VCL	VAL	(V)	(V)
EMIM-	0.28	-1.79	2.08	-3.07	0.24	3 3 1	1.00	0.17	1.26	3.7
AlCl ₄	(A)	(C)	2.00	(C)	(A)	5.51	-1.09	0.17	1.20	[52]
PMIM-	0.28	-1.79	2.08	-2.76	0.34	3 20	1.02	0.12	1 14	4.7
AlCl ₄	(A)	(C)	2.00	(C)	(A)	5.20	-1.02	0.12	1.14	[53]
BMIM-	0.28	-1.79	2.08	-2.76	0.34	3 10	0.70	0.25	0.96	4.7
AlCl ₄	(A)	(C)	2.00	(C)	(A/C)	5.10	-0.70	0.25	0.90	[54]
DMPI-	0.28	-1.83	2.12	-3.19	0.29	3.48	-1.20	0.22	1.37	3.6
AlCl ₄	(A)	(C)	2.12	(C)	(A/C)					[17]
HMIM-	0.28	-1.78	2.07	-2.55	0.30	2.86	-0.64	-0.03	0.60	
AlCl ₄	(A)	(C)	2.07	(C)	(A)	2.00	-0.04	-0.05	0.00	
OMIM-	0.28	-1.76	2.05	-2.36	0.42	2 70	-0.72	0.00	0.72	
AlCl4	(A)	(C)	2.05	(C)	(A)	2.19				
BMP-	0.28	-1.86	2.15	-3.93	0.13	4.06	-3.62	-0.20	3 /1	
AlCl4	(A)	(A)	2.15	(C/A)	(A)	4.00	-5.02	-0.20	5.41	
Urea-	0.28	-1.63	1 92	-3.85	-0.14	3 71	-1.80	-0.37	1 43	3.6
AlCl ₄	(A)	(C)	1.72	(C)	(A)	5.71	-1.80	-0.37	1.75	[55]

AcAm-	0.28	-1.48	1 77	-3.67	-0.08	3 58	1 55	0.21	1 33	
AlCl ₄	(A)	(C)	1.//	(C)	(A)	5.50	-1.55	-0.21	1.55	
EMIM-	0.27	-1.79	2.06	-2.94	0.12	3.06	1.24	0.32	0.01	
OTf	(A)	(C)	2.00	(C)	(A)	5.00	-1.24	-0.32	0.91	
PMIM-	0.27	-1.79	2.06	-1.30	0.12	1.42	0.70	0.21	0.40	
OTf	(A)	(C)	2.00	(C)	(A)	1.42	-0.70	-0.21	0.49	
BMIM-	0.27	-1.79	2.06	-2.36	0.25	2.61	0.35	0.04	0.31	
OTf	(A)	(C)	2.00	(C)	(A)	2.01	-0.55	-0.04	0.51	
DMPI-	0.27	-1.83	2.10	-2.42	0.25	2.19	0.62	0.16	0.46	
OTf	(A)	(C)	2.10	(C)	(A)	5.10	-0.02	-0.10	0.40	
HMIM-	0.27	-1.78	2.06	-1.60	0.30	1 00	0.10	0.00	0.19	
OTf	(A)	(C)	2.00	(C)	(A)	1.00	-0.19	-0.00	0.18	
OMIM-	0.27	-1.76	2.03	-1.60	0.27	1.84	0.25	0.04	0.20	
OTf	(A)	(C)	2.03	(C)	(A)	1.04	-0.25	-0.04	0.20	
BMP-	0.27	-2.12	2 20	-3.46	0.73	2.00	2.45	0.27	2.92	
OTf	(A)	(C)	2.39	(A/C)	(A)	5.90	-5.45	43 0.37	3.83	
	1		1	1	1	1	1	1	1	

The calculated values using both levels are in given in Table 2.2. Table 2.2 illustrates that the ECW values calculated by the AIMD-min method are highly consistent with the available experimental data. Therefore, in the following sections we have discussed the ECW values calculated by the AIMD-min method.

The calculated ECWs from the AIMD-min procedure for both anions (AlCl₄ and OTf) are shown in Figure 2.7a and discussed in this section. The calculated ECWs are not much changing along with the alkyl chain length of the organic ring moieties. We didn't observe a clear trend in ECW values upon changing the alkyl chain length of organic moieties. Therefore, we can say that the ECW values do not depend on the alkyl chain lengths.*[57]* The calculated ECW of the commonly used imidazolium-based IL electrolyte of EMIM-AlCl₄ is 3.31 V, which is higher than that in the EMIM-OTf of 3.06 V. The experimentally reported ECW of EMIM-AlCl₄ is in the range of 2.8-3.7 V, which is in good agreement with our calculated value using the AIMD-min method.*[52]* The EMIM-OTf has higher ECW compared to the

other imidazolium-based cations with OTf anion. The calculated ECW of BMP-AlCl₄ (4.06 V) is little higher compared to the BMP-OTf of (3.90 V). Our calculated ECW using AIMD-min of BMP-AlCl₄ is 4.06 V, which is comparable to the experimentally reported pyrrolidinium based IL of Pyr1,3-AlCl₄ (3.7 V).[58] The AIMD-min calculated ECW value of DMPI-AlCl₄ is 3.48 V, which is higher compared to the calculated values of other imidazolium-based ILs, which is also in agreement with the previous report.[17] In Figure 2.7a, we have observed that our calculated ECWs of the AlCl₄ containing IL electrolytes are higher compared to the OTf based ILs. Therefore, the AlCl₄ anion can play as a superior counter ion compared to the OTf anion.



Figure 2.7: The calculated ECWs of ILs from (a) AIMD-min and (b) AIMD-sp methods, where the magenta and green coloured rectangular bars are for AlCl₄ and OTf anions respectively.

2.3.3.1.1. Electronic Structures of AlCl₄ Anion Containing ILs

We have performed the density of states calculation to understand the cationic and anionic contribution to the measurement of the V_{CL} and V_{AL} . Figure 2.8 represents the projected DOS of the considered nine AlCl₄ containing ILs, and the plot shows that there is a significant contribution of cation and anion towards the measurement of the V_{CL} and V_{AL} . The projected DOS of cation and anion allow us to reveal the IL species that contribute towards the HOMO (anodic limit) or LUMO (cathodic limit)

levels. Except in the case of DMPI-AlCl₄ and BMIM-AlCl₄ ILs, the projected DOS plot shows that HOMO is mainly constituted of the AlCl₄ anion, which implies that anodic stability is set by the AlCl₄ anion. Similarly, the LUMO is mainly constituted by the imidazolium cation and therefore, the cathodic limits depend on the reduction limit of the imidazolium cation. All these findings are very much in agreement with our findings using the thermodynamical cycle approach. On the contrary, the projected DOS plot of DMPI-AlCl₄ shows that there is a significant mixing of DMPI cation and AlCl₄ anion in the HOMO, which implies that DMPI cation could contribute to the oxidative stability when coupled with AlCl₄ anion *i.e.*, oxidation stability is no more limited by the anion only. On the other hand, the projected DOS of BMIM-AlCl₄ shows that there is a very little contribution of BMIM cation in the HOMO, which indicates that the oxidative stability depends on the BMIM cation. All these of our findings are also very much agreement with the previous report.[14] Furthermore, the projected DOS of BMP-AlCl₄ shows that LUMO is composed of the BMP cationic and AlCl₄ anionic states which implies that there is a possibility that AlCl₄ anion could contribute to reductive stability along with the BMP cation. This type of observation has been previously noticed both experimentally and theoretically by Howlett et al. for the TFSI anion pair with pyrrolidinium system of Pyr1,3 cation. [59] Hence, the AlCl₄ anion can determine the cathodic limit in BMP-AlCl₄ IL. Overall, these observations challenge the prevailing hypothesis that it is still anion and cation that determine the oxidative and reductive stability of the IL system, respectively.



Figure 2.8: Total density of states of AlCl₄ anion containing ionic liquids: (a) EMIM-AlCl₄, (b) PMIM-AlCl₄, (c) DMPI-AlCl₄, (d) BMIM-AlCl₄, (e) HMIM-AlCl₄, (f) OMIM-AlCl₄, (g) BMP-AlCl₄, h) AlCl₂(U)₂-AlCl₄, (i) AlCl₂(AcAm)₂-AlCl₄.

2.3.3.1.2. Electronic Structures of OTf Anion Containing ILs

Figure 2.9 shows the projected DOS of the OTf anion containing ILs. The projected DOS plots of all imidazolium based ILs represent that HOMOs are contributed from OTf anion, which implies that anodic stability is maintained by the OTf anion itself. Similarly, the LUMOs are contributed from the imidazolium-based cation, which indicates that the reductive stability is governed by the cation only. Imidazolium based OTf ILs follow the general trend, where the oxidative and reductive stabilities are maintained by the OTf anion and imidazolium cations, respectively.



Figure 2.9: Total density of states for OTf anion containing ionic liquids: (a) EMIM-OTf, (b) PMIM-OTf, (c) DMPI-OTf, (d) BMIM-OTf, (e) HMIM-OTf, (f) OMIM-OTf, and (g) BMP-OTf.

Whereas the projected DOS of the BMP-OTf shows that the LUMO is mainly contributed by the OTf anion, which implies that the reductive stability is set by the anion only. Thus, there is a possibility of cathodic instability of the OTf anion when paired with the pyrrolidinium based cation (BMP). This phenomenon is not only observed in BMP-OTf IL but also has been observed in the pyrrolidinium system of Pyr1,3 cation with TFSI anion.[59] Therefore, it is expected that the anion can determine the anodic stability of electrochemical window. Such observations have also been found while studying using the thermodynamic cycle method of the OTf anion based ILs. Overall, from the MD-DFT method we can calculate the individual cathodic and anodic limiting potentials as well as we can find out the contribution of anion/cation in their respective HOMO/LUMO state.

2.3.3.2. Applicability of AIMD-min Method

To generalize our proposed AIMD-min method for the calculation of ECW, we have performed several calculations such as robustness, sensitivity to the liquid density, and the equilibration time at AIMD level.

Firstly, we have assessed the responsiveness of the AIMD-min method based on liquid density of the ILs system received from the classical MD simulation. For EMIM-AlCl₄, the applied classical forcefield calculated liquid density is 1.44 g/cm³ at 300 K temperature, which is slightly higher than the experimental liquid density of 1.30 g/cm³ due to the applied classical forcefield parameters are not well optimized in the liquid phase. We have observed a maximum relative error of 10%, whereas the classically applied forcefield considers a maximum error of 5%. [16] To evaluate the robustness of the AIMD-min method, we have altered the size of the simulation box manually by $\pm 10\%$ to reflect the changes in density. Then, we performed the 50 ns simulation for further equilibration and allowing to achieve the artificial change of liquid density. Later, we calculated the ECWs using AIMD-min method and the results are summarized in Table 2.3. Our calculated ECWs with respect to change of density are within the experimental range. Hence, the ECW is found to be insensitive towards the change of liquid density, suggesting the method is robust with the change of density upto $\pm 10\%$.

EMIM-AlCl4	Density (g/cm ³)	ECW (V)
	1.44	3.31
Theoretical	1.58 (+10%)	3.43
	1.29 (-10%)	3.97
Experimental	1.30	2.8-3.7[49]

Table 2.3: Calculate ECW (V) of EMIM-AlCl₄ with respect to change in density.

Secondly, we have tested the equilibration time at the AIMD level. In general, the ILs are having high viscosity and lead to slow dynamics. So, an extremely long run simulation is required to obtain the sampled PES. Therefore, the sample PES is obtained by using classical molecular dynamics simulation in this work. AIMD level equilibration requires confirming that the structural configuration must be stable on the PES. Generally, AIMD simulations are computationally expensive and highly time-consuming processes for large systems. Here, we have carried out AIMD relaxation for 300 and 3000 steps for each snapshot of classically equilibrated structure. The HOMO/LUMO level is calculated for each structure after equilibration of 300 and 3000 steps. Our calculated average ECWs are tabulated in Table 2.4. Without AIMD equilibrated configurations (AIMD-sp) the calculated ECW is 1.26 V. Upon equilibration of 300 and 3000 steps, the calculated ECWs are 3.27 and 3.31 V, respectively, which are in agreement with the experimental values. Hence, the lower length of equilibration didn't change the ECW significantly, which is always preferred for the AIMD case. Moreover, we have performed only AIMD up to 3000 steps without classical equilibration for the EMIM-AlCl₄ IL. Then we have calculated the ECWs of the geometries obtained at 1000 and 3000 AIMD steps and the values are far

EMIM-AICl4	Steps	ECW (V)		
	0	1.26		
Theoretical	300	3.27		
	3000	3.31		
Experimental	2.8-3.7	[49]		

 Table 2.4: Calculated ECWs of the different lengths of the AIMD-min

 method for EMIM-AlCl₄ IL

from the experimental range (Table 2.5). This suggests that the classical equilibration followed by AIMD is necessary to achieve the experimental ECW value. However, the calculated ECW is little higher for 3000 compared to 300 equilibration steps in AIMD-min method. Hence, we have used 3000 equilibration steps for ECW calculation.

Table 2.5: Calculated ECWs of the different lengths of the AIMD simulation without classical simulation.

Methods	ECW (V)	Experimental ECW (V)
AIMD-1ps	2.04	
AIMD-3ps	2.25	2.8-3.7 [49]
AIMD-sp	1.26	
AIMD-min	3.32	

Thirdly, we have tested functional dependencies on the ECW calculation for the EMIM-AlCl₄ IL. We have considered three functional such as PBE,

revPBE and RPBE to calculate the ECW. Our calculated ECWs are tabulated in Table 2.6. As these are the revised version of PBE functional, a small improvement in ECW values can be observed. From PBE to revPBE/RPBE the changes of ECWs are very small (0.09/0.1 V). Hence, the changes of ECWs are very small upon changing the functional, so we continued PBE functional for all the considered ILs.

 Table 2.6: Comparison of ECWs from different functionals for EMIM AlCl4 IL.

Functional	ECW (V)	Change of ECW with respect to PBE
PBE	3.32	-
revPBE	3.41	0.09
RPBE	3.42	0.10

Overall, our proposed AIMD-min method is insensitive to the changes in the liquid density of ILs obtain from classical simulation, insensitive to the short length equilibration and also less dependency of the functional. Therefore, we propose that the AIMD-min method can be a promising model for IL based systems for ECW calculation.

2.3.4. Summary of Thermodynamic Cycle and MD+DFT Methods

Table 2.2 summarizes the oxidation, reduction potentials from the thermodynamic cycle and cathodic, anodic limiting potentials from the MD+DFT methods. In thermodynamic cycle method, intermolecular interactions from the neighbouring molecules are not considered to the ions stability. It would be computationally challenging to deploy explicit solvents in this DFT-based cycle method, so we have used an implicit solvent model in lieu of real solvent. This could be a reason that the method

could not provide adequate accuracy while calculating the ECWs of the modelled ILs. In the MD+DFT method, the liquid structure of IL is explicitly considered, along with all interior interaction has been taken into account in such a way that simulated IL can behave as a true solvent system. The calculated ECWs from this method are found to be more acceptable compared to thermodynamic cycle method. The calculated ECWs from the AIMD-sp method are not comparable with experimental measured ECWs which could be due to the classical model used in the calculations. The major drawback of this MD+DFT method is finding the suitable forcefield that can take account of all essential physics of liquid system to perform the MD simulation. This drawback is not problematic for well-known systems such as organic solvents, as the forcefields for these systems are well developed. However, our considered three methods, AIMD-min behaves as a best fitted method for the calculation of ECWs. The AIMD-sp method is not suitable since it can underestimate the accuracy of the ECWs calculation. Where the thermodynamic cycle method falls between these two AIMD methods. We believe that our calculated ECWs from the AIMDmin method is a good comparison for future experimental and theoretical studies and certain ILs such as EMIM, DMPI, BMIM and BMP cations coupled with anions and urea-AlCl₄ would be better electrolytes in DIBs technology.

2.4. Conclusion

In this study, we have systematically studied three different techniques to calculate the electrochemical window (ECW) potentials and find suitable IL electrolytes for future DIBs. Here, we have considered a series of imidazolium and pyrrolidinium based cations coupled with AlCl₄ and OTf anions. The thermodynamic cycle method calculates the oxidation/reduction potentials of cations/anions relative to the Al³⁺/Al reference electrode to determine the ECWs of ILs. The ECWs of the considered ILs are dependent on the reduction potentials of the organic

cation and oxidation potentials of anions. Whereas the oxidation and reduction potentials are set by the anion only for BMP-AlCl₄ case. The accuracy of this method is not good which could be due to the nonavailability of neighbouring intermolecular interaction. On the other hand, in the MD+DFT method, all interior interactions have been deployed to understand the essential physics of the liquid structure. In AIMD-min method, we have further equilibrated the classically simulated structure followed by calculation of cathodic (V_{CL}) and anodic (V_{CL}) limiting potentials from density of states (DOS) calculation. In AIMD-sp, we obtained the V_{CL} and V_{AL} from the single point calculation of DOS without further optimization. The AIMD-min method provides better ECWs for considered ILs compared to AIMD-sp method. Our calculated ECW of EMIM-AlCl₄ is 3.31 V from the AIMD-min method, which is in good agreement with the experimental range of 2.8-3.7 V. The AIMD-sp method is unable to provide good accuracy of ECWs for IL electrolytes due to the formation of unstable potential energy surface (PES). AIMD-min method plays as the best fitted model for calculation of ECW among considered the three methods. All the interior physics of the ILs are considered in the AIMD-min method, therefore the IL represent a stable potential energy surface which is not observed in the AIMD-sp method. Also, solvation effects of IL have not considered in the thermodynamic cycle approach. Thus, the calculated ECWs from thermodynamic cycle method are far from experimental measured ECWs. Moreover, our proposed AIMD-min method is insensitive towards the change of liquid density upto (\pm 10%) and short length equilibration does not impede the accuracy of ECW value. Thus, AIMD-min method is highly robust for the calculation of ECW in liquid systems. We believe that our calculated ECWs data of the IL electrolytes can guide experimental researchers in the selection of IL electrolytes for given electrode materials. Determining the ECWs of ILs is essential for designing high-voltage rechargeable dual-ion batteries (DIBs) as it plays an imperative role. It is expected that ILs having broad ECW can deliver better

voltage compared to the narrow ECW based systems. Therefore, this study could help a step forward to accelerate the development of nonaqueous electrolytes in the DIBs technology.

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Optimization of Machine Learning Techniques for Dual-Ion Batteries

3.1. Introduction

With the increasing energy demand, lithium-ion batteries (LIBs), having higher capacity, stable cycle, and low self-discharge properties dominate the electronics markets over other batteries. [1-3] The non-uniform distribution and intermittent occurrence of Li metal, coupled with the exorbitant cost of transition metal oxide cathodes, present formidable obstacles to the sustainable and enduring implementation of LIBs.[4-5] These challenges have prompted researchers to explore alternative devices that offer superior electrochemical performance, cost-effectiveness, and environmental sustainability. In this regard, dual-ion batteries (DIBs) have emerged as a promising alternative due to their unique and attractive properties. [6-8] In DIBs, cations/anions are intercalated into the cathode/anode based on the charging/discharging process, whereas in LIBs, Li cations shuttle between two electrodes. [9,10] The novelty of DIBs mechanism over metal ion batteries is the contribution of anions in electrochemical process.[11,12] The intercalant active anions are coming from the salt-solvent based electrolytes. Recently, ionic liquid-based salt solvents have emerged as promising alternatives in DIBs due to their unique properties. In our study we have considered ionic liquid (IL) as an electrolyte as well as a solvent, playing a dual role. Therefore, solvation is not important as in the other cases.[13]

Room temperature ionic liquids (RTILs) show interesting properties such as low vapor pressure, high ionic conductivity, and broad electrochemical window (ECW), which are essentials for the electrochemical application.*[14-16]* Recently, organic cations and anions of ILs are used as active intercalant species in dual graphite batteries (DGBs).*[7,8,17,18]* Carlin and co-workers have studied the DIBs with observed voltage of 2.30-3.20 V, using IL electrolytes composed of cations such as 1-ethyl-3methyl imidazolium (EMIM⁺), and 2,3-dimethyl-1-propyl imidazolium (DMPI⁺) coupled with anions like AlCl₄, CF₃SO₃, PF₆, and BF₄.*[18-20]* The broad range of the ECW of the ILs allows us to achieve the high cutoff charging voltage range of 4-5 V.

The ECW can be defined as the difference between the anodic (V_{AL}) and cathodic (V_{CL}) limit potentials at which the oxidation and reduction of IL take place, respectively.[14,21,22] Such limiting potentials can be measured with respect to their reference electrode, where the ECW depends on the working electrode. It is assumed that the cathodic and anodic limiting potentials are governed by the reduction of cation and oxidation of anion, respectively.[23] However, recent experimental and theoretical studies have demonstrated that this is not always true.[24] Usually, ECW is measured using a linear voltammetry by calculating the individual anodic/cathodic currents which are responsible for oxidation/reduction of electrolytes.[25] However, such measurements of limiting potential depend on various factors such as electrode, use of arbitrary current cutoff to determine the onset redox potentials among others.[15] Hence, the reported ECWs in literature are varied widely. Other difficulty is handling the ILs experimentally because of the sensitivity.[26,27] In this context, computational techniques such as the MD-DFT method has been developed, where the combined molecular dynamics and density functional approach (MD-DFT) and followed by electronic structure calculation has been considered to calculate the ECW value with good accuracy. [21,23,28] However, the main drawback of this approach is the finding suitable forcefield to perform the classical MD simulation of large systems.

To overcome the obstacles, a high throughput data driven machine learning approach has been adopted in this work to predict the ECW for a series of ILs.[29-33] We have considered ILs comprising of 10 distinct organic cation moieties paired with 12 different anions, as illustrated in Figure 3.1. To facilitate the accurate prediction of their ECWs, we have incorporated significant input features to train the machine and predicted ECW for 660 ILs. Our model's generalizability and reliability have been

rigorously assessed through comparisons with experimental ECW value from prior studies. Moreover, interpretable machine learning techniques have been considered to unravel the key features influencing ECWs. Our findings emphasize the tremendous promise of our ML model in precisely predicting ECW values for IL-based electrolytes.



Figure 3.1: Different organic cation and anion-based moieties used to model the ionic liquids.

3.2. Methods

3.2.1. Data Generation

The ECW values of very few ILs have been reported experimentally. As a result, several computational techniques, such as thermodynamic cycle

and MD-DFT methods have been developed to calculate the ECW. Ceder and coworkers have developed the MD-DFT technique for the ECWs and later on Maginn and coworkers have proposed the AIMD-min method which is an extended MD-DFT technique.[21,23] In our previous report we have used *ab initio* MD method (AIMD-min) to calculate the ECWs, where we have equilibrated each IL in classically to allow the formation of stable liquid structure (Scheme 3.1).[26] After the classical simulation we have further equilibrated each configuration for 3ps using the AIMD-min to obtain a stable potential energy surface (PES) and perform the density of states (DOS) calculations of each configuration to calculate the ECW (more details in section 2.2.2, chapter 2).[28] We extracted the HOMO/LUMO energies from the calculated density of states (DOS) and utilized them to compute both the anodic and cathodic limiting potentials, which were subsequently used for the ECW calculation. Peljo and coworkers demonstrated that there is a notable difference between the HOMO-LUMO gap (Eg) and ECW and the ECW window must be within the Eg range for the electrolyte stability.[34] Our training dataset was constructed using ECW values calculated through the AIMD-min method from our previous study as well as the reported experimental values.



Scheme 3.1: The steps used for the calculations of electrochemical windows of ionic liquids.

For the prediction of the ECW, different organic moieties-based cations have been considered as shown in Figure 3.1. We also varied the alkyl groups of the organic cationic moieties and coupled them with the listed anions to generate different types of ILs (Figure 3.2). Further, the structural optimization has been performed for all the considered cations to obtain the most stable geometry using the Gaussian 09 package.[35] The structural optimization has been done using the B3LYP functional and 6-31++G(d,p) Pople basis set and CPCM solvent model.[36-39]



Figure 3.2: The possible organic cations from the different organic moieties. The individual cation can be defined by the below number and methyl, ethyl, propyl, and butyl groups are defined by 1, 2, 3, and 4. Color code: pink (H), grey (C), blue (N), red (O), green (P), and yellow (S).

3.2.2. ML Models

For the ML study, a complete work flowchart from data set bifurcation to user understanding has been shown in scheme 3.2. In our supervised ML model, we have divided the ECW data in 80:20 ratio as the train and test data set.[40-41] This division was carefully designed to ensure a wellsampled representation of the overall dataset, rather than a random splitting approach. The train and test data sets are used for training and evaluating the performance of the ML model. We performed various ML algorithms consisting of supervised regression models such as, Kernel Ridge Regression (KRR), eXtreme Gradient Boosting Regression (XGBR), Extra Trees Regression (ETR), Random Forest Regression (RFR), Adaptive Boosting Regression (ABR), Decision Tree Regression (DTR), and Gradient Boosting Regression (GBR) using Scikit-learn package 0.23.1 running in Python version 3.8.2 (more details in section 1.6.6, chapter 1).[42-44] To find the best fitted ML model, we have implemented randomized search cross-validation technique with hyperparameter tunning of each regression algorithm. The accuracy of the prediction performance of each model can be evaluated by the mean absolute error (MAE) using the following equation.

$$MAE = \frac{1}{n} \sum_{i=1}^{n} (Y_i - y_i)$$
(3.1)

Where, n is the total number of data points, Yi, and y_i are the calculated and ML predicted ECWs, respectively. Using the hyperparameter tunning method to identify the best set of parameters to obtain the well optimized ML model. Finally, we considered the optimized ML model with lowest MAE to predict the ECW for unknown data set. Furthermore, an interpretable ML technique has been performed using cooperative game theory based SHAP (SHapley Additive exPlanations) library to understand the contribution of local and global feature importance towards the predicted output.[45] The Shapley value (ϕ_i) signifies the importance of each feature and it can be computed using equation 3.2.

$$\phi_i = \sum_{S \subseteq F, \{i\}} \frac{|S|!(|F| - |S| - 1)!}{|F|!} \left[f_{S \cup \{i\}} (x_{S \cup \{i\}}) - f_S(x_S) \right]$$
(3.2)

Where, F represents all set of features and S indicates the subset of all features obtained from F after removing of ith feature. $f_{S\cup\{i\}}$ and f_S are the prediction model of with and without ith feature, respectively. x_S represents the value of the input features in the S set.



Scheme 3.2: The machine learning workflow and interpretable analysis used for the study.

3.3. Results and Discussion

3.3.1. Structural Orientation of the Ionic Liquids

In the methods section we have explained the generation of the ILs by coupled with different cations and anions by varying the alkyl groups of the cationic moieties. Majorly, the alkyl chain length from methyl (1) to butyl (4) groups have been considered, and those are used as electrolytes in battery study (Figure 3.2). Besides, we have considered a few methoxy (OMe) and ethoxy (OEt) functional groups containing cations. Owing to the acyclic structure of the ammonium, phosphonium and sulfonium cations, which could accommodate long chain alkyl groups on the hetero atom without steric hindrance. Thus, we have considered the long chain alkyl groups containing cations for ammonium, phosphonium and sulfonium based system. The long chain alkyl group containing ILs are stable by the hydrophobic interaction of their long carbon chain.

3.3.2. Data Pre-processing and Features Engineering

The prediction of the ECW for completely unknown ILs from ML model trained with small dataset is quite a challenging task. However, to prevent the obstacles because of the small training dataset, we have incorporated different cations anions based ILs ECW in train set to make a well sampled data set and bring the homogeneity in the training set so that the ML predicted result must not be biased for some ILs.[46,47] In this context, we have considered the ECW of the ILs (imidazolium cations coupled with AlCl₄ and OTf anions) calculated by AIMD-min method from our previous studies.[28] Besides, experimental ECWs have been considered for the 2-(cyano) pyrrolide (CNPyr) and 1,2,4-trazolide (124triz) anions-based IL from the previous study.[21] Thus, we have incorporated the ECW data of 50 ILs in the training dataset extracting from various computational and experimental reports to train ML models. Incorporating a hybrid dataset consisting of both computational and experimental ECW values into the training data can enhance the

machine's ability to recognize the overall patterns within the dataset. This integration could mitigate the risk of outperformance and improve the predictions of ECWs for unknown dataset as such hybrid approach may be able to reduce the experimental and technological gaps[48] for the prediction of ECW. Considering the complexity of describing the change of ECW with changing the cations and anions of the ILs, it is difficult to extract exact correlated features. Whereas, the ECW is the purely experimental phenomena, to compute in data science exercise is challenging to find out its dependency on the physical observable parameters. However, we have considered both molecular and elemental features (Table 3.2) to tune the ECW with changing the ILs. We have extracted elemental features using the Corelated Based Features Vector (CBFV).[49] It has been reported that the measurement of oxidation and reduction potentials can be done based on the HOMO and LUMO energies of the anion and cation, respectively.[22,23] Hence, we have considered the HOMO and LUMO energies of the individual cation and anion instead of HOMO/LUMO energies of neutral IL molecule.

Molecular features	Elemental features
1. Molecular weight (g/mol)	8. Average (avg.) ionic radius (Å)
2. Cation HOMO (eV)	9. Avg. Pauling electronegativity(EN)
3. Cation LUMO (eV)	10. Avg. number of valence electron
4. Anion HOMO (eV)	11. Avg. 1st ionization energy (IE)(kJ/mol)
5. Anion LUMO (eV)	12. Avg. polarizability (Å ³)
6. Cation dipole moment (D)	13. Avg. boiling point (K)

Table 3.1: Molecular and elemental features of ionic liquids.

7 Anion dipole moment (D)	14. Avg. heat of vaporization
7. Amon dipole moment (D)	(kJ/mol)

A better understanding of the features nature of the data set is often effective to speed up the machine learning process. The features should be dependent directly or indirectly on the target property and must be independent to each other. If the features are highly corelated to each other, we need to perform the dimensionality reduction process to reduce the complexity of the ML model and remove the unnecessary noise from the dataset. The assessment of the features correlations often provides insight towards the prediction of the ECW. In order to understand the linear correlation among the considered features, including the target variable (ECW), the correlation matrix has been plotted with Pearson correlation coefficients (PCCs) in Figure 3.3. The PCC helps to understand the co-relation among the features-features and features-target



Figure 3.3: Reduced Pearson's correlation matrix for features (elemental and molecular feature details listed in Table 3.1) and target ECW (15).

variable. The strongly correlated features are average boiling point and average heat of vaporization (PCC=0.99), average number of valence electrons and average Pauling electronegativity (PCC=0.97) as shown in Figure 3.4. Hence, we have dropped two features (average boiling point and average number of valence electron) by keeping average heat of vaporization and average Pauling electronegativity in training dataset and final engineered features correlation plot has been shown in Figure 3.3. Including the average heat of vaporization in the dataset can potentially influence the ECW values of ILs, particularly because these are lowvapor-pressure liquids. Moreover, retaining the average Pauling electronegativity in the dataset shows a stronger direct correlation with ECW (PCC=0.32) compared to the average number of valence electrons (PCC=0.22) (Figure 3.4). The positive PCCs indicate the features are tandem, these are holding a liner relationship, while the negative correlation indicates the inverse relationship between them. In the correlation matrix, the deep brown and light-yellow colors indicate strong positive and negative correlation and light red colors indicate no correlation. Here, we have used a hybrid dataset for the training using experimental ECW values as well as the DFT calculated ECW values. The glassy carbon electrode is used in all those experiments. Hence, some information related to the glassy carbon electrode is already there in the experimental dataset. Therefore, all the ML predicted ECW values can be considered with respect to the glassy carbon electrode.



Figure 3.4: Pearson's correlation matrix between all features (features numbers are tabulated in Table 3.1) and target output ECW (15).

3.3.3. Machine Learning Algorithms

We have applied seven ML algorithms on the training dataset to train the model. To maximize the performance of the ML algorithms we have implemented hyperparameter tuning using RandamizedSearchCV method



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Figure 3.5: (a) The MAEs of seven considered ML models for the train (blue) and test (magenta) data set. (b) The scatter plot of ML predicted vs. DFT calculated ECW is shown for the ETR model.

as implemented in the scikit learn package.[44] Hyperparameters are model dependent parameters, which change upon changing the ML algorithms. After optimizing the hyperparameters for each algorithm, we fed the optimize algorithm on the test data to evaluate the model performance based on MAE. Figure 3.5a shows the test and train MAEs for all the considered ML algorithms, represented by magenta and blue columns, respectively. A smaller MAE is the criteria used to determine the best ML algorithm. From Figure 3.5a, it is evident that the test MAEs for all the considered ML algorithms range from 0.35 to 0.58 V. The lowest test MAE of 0.35 V has been observed for the KRR algorithm, whereas the corresponding train MAE is 0.61 V. This indicates that the machine was not adequately trained to predict the ECW for the unknown dataset. In the case of the XGBR model, the test MAE is 0.49 V, which is significantly higher compared to the train MAE of 0.001 V. This suggests that the XGBR model may be prone to overfitting when predicting ECW. Additionally, the GBR, ADR, and RFR algorithms exhibited higher test MAEs of 0.58, 0.52, and 0.42 V, respectively, in comparison to the ETR model (0.37 V). Therefore, these algorithms are not suitable for accurate ECW prediction. On the other hand, in the DTR model, the train and test MAEs are in the same range, albeit with a slightly higher train MAE of 0.46 V compared to the test MAE of 0.44 V. Based on our observations of the train and test MAEs, it can be concluded that the ETR model is wellsuited to predict ECW for the unknown dataset, as it exhibits the lowest test MAE of 0.37 V, coupled with a train MAE of 0.05 V. Interestingly, our ML predicted MAE (0.37 V) for the ETR model is less compared to the previously DFT calculated MAE (0.68 V) for two different methods of ECW calculation. [50] The scatter plot depicted in Figure 3.5b

demonstrates a close alignment between the test data and the training data, effectively reducing the potential issue of outperformance when predicting the ECWs for unknown data. This intriguing finding further supports the notion that incorporating a hybrid ECW data (comprising of both experimental and computational values) used in our training data set, enhances the model's ability to accurately predict the ECW compared to pure DFT based methods. Our machine learning approach intelligently amalgamates the experimentally and computationally derived data, resulting in improved ECW predictions. This successful combination of diverse datasets contributes to the overall effectiveness of our ML-based approach to predict the ECW accurately. Furthermore, to assess the model's generalizability and acceptability, we randomly predicted ECWs for a few ILs and compared them with their experimental values. The details of these predictions are provided in the following section.

3.3.4. Prediction of ECW

In this section, the ECW values have been predicted for the unknown dataset using the best parameters of the ETR model. We have successfully predicted the ECW values of 660 IL electrolytes for DIBs (Figure 3.6). Among them, the ECW values are validated with experimental findings, as given in Table 3.2. From Table 3.2, it has been observed that our ML predicted ECWs are in good agreement with the experimentally measured values. The absolute errors (difference between ML predicted and experimental ECW values) of ECWs are lesser than the test MAE (0.37 V) of best fitted ETR model for the considered ILs except P1113-FSI IL. The experimental ECW value reported for the P1113-FSI IL is with respect to the Pt electrode. However, our trained experimental dataset is with respect to the glassy carbon electrode. So, this could be the reason for the higher MAE compared to the test MAE.

Organic Moieties	Ionic Liquids	ML Predicted ECW (V)	Experimental ECW (V)	Abs. Error
Morpholium	N1(EtOMe)- TFSI	4.81	4.68[51]	0.13
Pyridinium	N(Pro-OH)- TFSI	3.78	3.81[51]	0.03
	N(Hex)- TFSI	3.76	3.90[51]	0.14
Ammonium	N1133-TFSI	5.11	5.12[52]	0.01
Phosphonium	P1113-FSI	4.63	5.05[53]	0.42

Table 3.2: ML predicted vs. experimentally reported ECW values of ILs.

In the field of battery technology, achieving improved electrochemical performance often relies on electrolytes with well-accepted electrochemical windows (ECWs) starting from values higher than 4.00 V. Higher ECWs in electrolytes generally correspond to higher discharge voltages in DIBs, as they can withstand higher charging voltages without decomposition. By analyzing Figure 3.6, we observed that pyridinium and thiazolium-based cations offer relatively smaller ECW ranges when combined with various anions compared to other cation moieties.

					Su		Ani	ions	FSI		TFSI(12	U		
		BF₄	PF	DCA	lfate	AICI	τo	FSI	(EH3)	TFSI	C2F5)	4triz	NPyr		
	- 54	5.12	4.88	3.72	4.22	2.88	5.31	4.43	4.36	4.51	4.33	3.85	3.42		L 1.5
	- 23	5.42	4.62	3.52	3.87	2.95	3.98	4.35	3.99	4.35	4.13	3.57	3.12		
	52	6.04	4.28	3.52	3.75	4.18	3.73	4.42	3.82	4.42	4.18	3.33	2.82		
	- 21	5.80	4.34	3.56	3.68	3.74	3.54	4.35	3.72	4.38	4.12	3.44	2.88		
	- 20	5.57	4.47	3.54	3.67	4.56	2.91	4.35	3.73	4.37	4.13	3.41	2.82		
	- 49		4.53	3.50	3.66	3.35	3.67	4.29	3.64	4.43	4.22	3.39	2.75		- 2.0
	48 -			4.26	4.22	4.06	4.23	4.90	4.35	4.72	4.40	4.13	3.54		- 2.0
	47 4	5.22	4.99	4.11	4.09	3.86	4.27	4.82	4.43	4.80	4.45	3.94	3.46		
	16 4			4.25	4.19	4.00	4.33	4.92	4.45	4.81	4.51	4.10	3.55		
	5 4	5.30	5.20	4.24	4.14	3.94	4.28	4.96	4.37	4.84	4.50	4.07	3.56		
	4 4	4.02 5.20	5.24	4.04	4,11	3.84	4.31	4.99	4.41	4.89	4.53	4.09	3.60		
	3 42	4.90	4.96	4.00	3.85	3.79	4.15	4.40	3.99	4.44	4.15	3.97	3.49		- 2.5
	2 41	4.90	4.98	3.98	3.85	3.77	4.15	4.41	4.00	4.44	4.15	3.96	3.49		
	1 40	5.01	5.03	3.91	3.87	3.90	4.04	4.45	3.93	4.21	4.09	3.96	3.40		
	- 39	5.05	4.99	3.86	3.91	3.94	4.02	4.40	3.91	4.06	4.12	3.94	3.37		
	- 38	5.04	4.86	3.74	3.88	3.87	3.95	4.24	3.82	3.95	4.08	3.91	3.32		
	37	5.02	5.11	4.13	3.98	3.89	4.36	4.64	4.20	5.14	4.48	4.10	3.53		
	- 36	5.04		4.08	3.96	3.91	4.27	4.65	4.14	5.14	4.41	4.07	3.52		- 3.0
	35	4.87	4.91	4.11	3.99	3.91	4.23	4.43	4.11	4.88	4.89	4.04	3.60		
	34	4.94		4.09	3.95	3.92	4.22	4.45	4.09	4.88	4.47	4.00	3.53		
	33	5.02		4.04	3.94	3.96	4.23	4.61	4.04	4.83	4.36	4.01	3.50		
	32	4.90	5.00	4.10	3.98	3.90	4.25	4.45	4.08	4.86	4.59	4.02	3.58		
	31	4.78	4.86	4.12	4.05	3.98	4.23	4.44	4.12	4.81	4.59	4.07	3.69		
Ü	30	5.23	5.24	4.35	4.14	4.02	4.29	4.95	4.31	5.00	4.62	4.16	3.68		- 3.5
at	- 29	4.99	4.69	3.85	4.08	3.91	3.92	4.15	3.82	4.14	4.11	3.89	3.17		
.0	- 58			4.26	4.21	4.09	4.27	4.81	4.19	4.59	4.44	4.21	3.57		
Su	27			4.20	4.00	3.98	4.21	4.83	4.22	4.87	4.47	3.99	3.63		
	- 26	5.03	5.17	4.33	4.11	3.98	4.41	4.77	4.33	4.96	4.70	4.12	3.71		
	25 2	4.85	4.98	4.30	4.16	3.98	4.38	4.64	4.26	4.90	4.73	4.15	4.04		
	4 2	4.94	5.08	4.31	4.12	3.96	4.43	4.73	4.27	4.92	4.70	4.11	3.71		- 4.0
	3	5.25	5.20	4 30	4 16	4.00	4 35	4.00	4.43	5.04	4.67	4.18	3.00		
1	5	4.64	4.20	3.31	3.47	3.85	3.51	3.98	3.61	3.69	3.70	3.38	3.07		
	1 20	4.54	4.22	3.34	3.53	3.79	3.51	4.08	3.67	3.81	3.80	3.39	3.07		
	19	4.66	4.32	3.28	3.51	3.71	3.65	3.98	3.66	3.64	3.75	3.36	3.12		
	- 18	5.29	5.29	4.23	4.14	3.91	4.21	4.85	4.17	4.63	4.39	4.11	3.49		- 4.5
	11	5.23	5.39	4.35	4.09	3.93	4.22	4.92	4.19	4.60	4.41	4.11	3.54		-
	- 16	5.19	5.24	4.53	4.03	4.01	4.25	5.06	4.21	5.24	4.51	4.10	3.61		
	5 - 13	4.73	4.68	3.12	3.64	3.60	3.83	4.03	3.68	3.63	3.85	3.47	3.13		
	14	4.72	4.67	3.11	3.64	3.60	3.83	4.03	3.67	3.65	3.84	3.46	3.12		
	13	4.73	4.66	3.12	3.64	3.60	3.83	4.03	3.68	3.65	3.84	3.46	3.13		
	1 1	4.55	4.43	3.20	3.57	3.63	3.63	3.97	3.55	3.82	3.82	3.29	3.03		- 5.0
	-	4.62	4.53	3.14	3.58	3.69	3.60	3.97	3.58	3.79	3.81	3.30	3.04		
	6 -	4 74	4 56	3.09	4.08	3.67	4.54	3.98	4.42	3.70	4.59	3 38	3.02		
	- 00 -			4.28	4.11	3.84	4.31	5.00	4.42	4.88	4.54	4.10	3.60		
	-	5.29	5.22	4.23	4.13	3.92	4.27	4.94	4.35	4.81	4.49	4.06	3.55		
	9 -		5.36	4.35	4.07	3.92	4.21	4.99	4.20	4.72	4.44	4.09	3.54		- 3.5
	<u>ا</u> م		5.28	4.51	4.03	4.00	4.26	5.04	4.21	5.13	4.49	4.11	3.61		
	4 -		5.18	4.40	3.97	3.90	4.34	4.91	4.22	4.75	4.48	4.10	3.60		
	m -	5.03	4.68	3.62	3.86	3.70	3.75	4.11	3.73	4.02	4.00	3.70	3.00		
	N -		4.65	3.64	3.86	4.15	3.45	4.13	3.75	3.95	4.00	3.73	3.05		
		5.39	4.49	3.69	3.87	3.93	3.84	4.15	3.86	4.01	3.98	3.73	3.08		
		5.09	4 78	3.81	3.89	3.46	4.04	4 34	3.97	4 77	3 99	3 93	3 30		6.0

Figure 3.6: The ML predicted ECWs for 660 considered ILs (Structures correspond to the cations given in Figure 3.2).

Similarly, ILs containing 2-(cyano)pyrrolide (CNPyr) anions were predicted to have narrow ECWs, making them unsuitable electrolytes for DIBs studies. On the other hand, PF₆ and BF₄ anions exhibited broader ECW ranges (4-6 V) when combined with almost all cations. Consequently, these two anions are commonly used in DIBs as electrolytes.[54,55] The OTf, sulfate, TFSI, and AlCl₄ anions provided moderate ECW ranges (3.50-5.00 V) when paired with different cations. Furthermore, our ML-predicted ECW values were validated with the previously reported experimental values. This validation demonstrates that our ML predictions are consistent with existing research findings, further affirming the stability and prediction ability of our best fitted ETR model when applied to unknown data sets. Nevertheless, this comprehensive data set of ML-predicted ECWs can serve as a valuable guide for researchers in selecting suitable electrolytes for high-voltage battery technology.

3.3.5. Interpretability of Algorithm

3.3.5.1. Global Features Importance

In our study, all the machine learning (ML) algorithms we considered are categorized as black box models. This means that they operate in a way that makes it challenging to understand and interpret the specific features driving their predictions. To address this limitation and gain insights into both local and global trends for particular features, we turned to an interpretable model. To facilitate this interpretability, we implemented the game theory based SHAP (SHapley Additive exPlanations) library. SHAP provides a methodology for understanding the contribution of different features to the overall prediction made by the ML algorithms. By employing SHAP, we can assess the global feature contributions and gain a clearer understanding of the factors influencing the predictions made by the ML models. By utilizing the SHAP library, we can reveal valuable insights into the relationship between the features and the predictions, shedding light on both the individual feature contributions and the overall

trends. This allows us to better comprehend the underlying mechanisms and patterns driving the ML model's predictions.



Figure 3.7: Visualization of global SHAP feature importance of each feature towards the prediction of ECW.

In Figure 3.7, the blue bars represent the global features contribution towards the prediction of ECW values. Among the various features considered, the energy of the cation LUMO, the dipole moment of the anion, and the energy of the anion HOMO are identified as the top three most influential features. Figure 3.7 demonstrates that the energies of the cation LUMO and the anion HOMO have a significant impact on the ECW values of the ILs. Previous studies on calculating ECWs of ILs have indicated that the limiting potentials of cathodic reduction and anodic oxidation are influenced by the LUMO energy of cations and HOMO energy of anions, respectively.*[22,23]* Consequently, there exists a direct correlation between the ECW value and the LUMO energy of cations, as

well as the HOMO energy of anions, and any alterations in their energy levels can impact the ECW. Furthermore, the plot indicates a relationship between the dipole moment of the anion and the ECW of the ILs. This correlation aligns with the findings from the correlation plot (Figure 3.3), suggesting that the electrostatic interactions play a role in determining their ECW. Additionally, the average first ionization potential energy is correlated with the oxidation potentials of the ILs. Therefore, the contribution of the ionization energy of the ions can also influence the ECW of the ILs. While other features may contribute to the prediction of ECW, their individual contributions are relatively small (less than 0.10). Overall, the global feature analysis reveals that the most significant factors influencing the ECWs are the energy of the cation LUMO, the dipole moment of the anion, and the energy of the anion HOMO.

3.3.5.2. Local Features Analysis

Similarly, the SHAP library was utilized to analyze the individual contributions of features for a specific IL. The SHAP visualization plots, displayed in Figure 3.8, highlight the results for the P2224-CNPyr IL, which exhibits minimal deviation and accurate ECW predictions by the ML model (predicted ECW: 3.74 V vs. DFT calculated ECW: 3.70 V). Figure 3.8a and 3.8b present the SHAP waterfall and force plots, respectively, for the instance of the P2224-CNPyr IL. The SHAP waterfall plot illustrates the contribution of each feature value to the default prediction. Red and blue bars represent positive and negative contributions, respectively. In this plot E[f(x)] = 4.27 is the baseline (average expected value) and the final predicted value is the f(x) = 3.74. Each row's SHAP value signifies the feature's contribution and interaction towards the final prediction for this instance. For example, the anion dipole moment (D) of 5.32 has a negative effect on the target ECW, which decreases 0.26 to the prediction from the baseline.



Figure 3.8: (a) SHAP waterfall plot and (b) force plot for the least deviated ECW prediction of phosphonium based P2224-CNPyr IL.

Similarly, anion HOMO (eV) of -5.05 and average 1st IE (kJ/mol) of 1246.71 have the negative effect for ECW prediction by the decreases of 0.16 and 0.08, respectively. On the other hand, the average ionic radius (Å) of 0.43 and the cation LUMO (eV) of -0.64 have positively influenced the ECW prediction, which increase by 0.07 and 0.05, respectively. For this instance, the negative contribution is more compared to the positive contribution for the ECW prediction. Moreover, the anion dipole moment and anion HOMO are turned out as the most important features for this instance, while the contribution of the cation LUMO is less. Overall, the negative contributions of individual features outweigh the positive contributions. Quantitively, the predicted value f(x) is the total of average prediction of

all observation (E[f(x)]) and sum of all SHAP values (ϕ_i) as shown in following equation,

$$f(x) = E[f(x)] + \sum_{i=1}^{N} (\phi_i)$$
(3.3)

Here, N is the subsets of the features and ϕ_i can be calculated from equation 3.2. Figure 3.8b shows the SHAP force plot which is the qualitative projection of the waterfall plot. From the force plot we have observed that red color features are pushed to model prediction score higher (towards the right) and the blue colored features are pushed the model prediction score lower (towards the left). Likewise, the SHAP waterfall and force plots are presented in Figure 3.9 for the Pyr14-DCA IL, which exhibited the most deviation in predictions (ML predicted ECW: 4.03 V vs. DFT calculated ECW: 4.62 V). Interestingly, the anion dipole moment (1.16 D) has a slightly positive effect on the ECW prediction for this instance, deviating from the overall trends observed in global features. Overall, the negative effects outweighed the positive effect on the ECW prediction, although the positive effect was higher for this instance compared to the more accurately predicted P2224-CNPyr IL. Therefore, the SHAP waterfall and force plots provided valuable insights into the individual feature contributions of the P2224-CNPyr and Pyr14-DCA ILs, highlighting their respective characteristics and their impact on ECW predictions.



Figure 3.9: (a) SHAP waterfall plot and (b) force plot for the most deviated ECW prediction of pyrrolidinium based Pyr14-DCA IL.

3.4. Conclusion

In this study, we employed supervised machine learning (ML) techniques to accurately predict the electrochemical window (ECW) potential of ionic liquid (IL) electrolytes for their application in dual-ion batteries (DIBs). Our ML approach provides faster and accurate ECW predictions compared to the MD-DFT method. Out of the seven ML algorithms employed, the ETR model stands out as proficient in accurately predicting the ECW with low MAE of 0.37 V. Notably, this ML predicted MAE of the ETR model outperforms the previously DFT computed MAE (0.68 V) from two different methods of ECW calculation. This substantial improvement in predictive accuracy highlights the effectiveness and superiority of our ML-based approach in estimating the ECW potential for the studied ionic liquid electrolytes. Using the optimized parameters of our best fitted ETR model, we successfully predicted the ECW values for 660 ILs. To ensure the stability and transferability of our model, we validated the ML-predicted ECW values of selected ILs against experimental values, finding excellent agreement between them. In addition, to uncover the intricate relationships between the considered features and the target ECW values, we employed the interpretability model of the game theory based SHapley Additive exPlanations (SHAP) library. Notably, we identified the energy of the cation LUMO, the anion dipole moment, and the energy of the anion HOMO as the top three most influential features in predicting ECW. Furthermore, we visualized the feature contributions using SHAP waterfall and force plots, providing local interpretations of individual features in relation to ECW predictions for specific instances. Interestingly, the positive and negative SHAP values of each feature played a role in fine-tuning the ECW of individual ILs. Importantly, our ML-predicted results exhibited strong agreement with previously reported experimental ECW values. Therefore, our findings provide a foundation for accurately predicting ECW values of ILs, enabling advancements in the design of IL electrolytes for improved DIBs performance.

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Role of Aromatic Ionic Liquid for Dual-Ion Battery
4.1. 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 Liion/2-4], Na-ion/5-7], Mg-ion/8,9], Zn-ion/10,11] and Al-ion/12,13] 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./17-20] In 1989, McCullough et al. first reported a DIB using graphite as both the cathode and anode along with the nonaqueous electrolyte of ClO₄./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. [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.[26,27] Commonly used DIBs have lithium salts (like LiPF6, 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).[28] (ii) graphite exfoliation due to solvent co-intercalation along with ion intercalation,[28] (iii) active battery material loss due to solid-electrolyte interphase (SEI) formation.[29] Hence, compatible electrolytes and electrodes are required to reduce the exfoliation of graphite and replace the lithium metal. Carlin *et al.* have presented the room temperature ionic liquids (RTILs) as a better alternative to replace the conventional volatile organic solvents.[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.[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.[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⁺), Nbutyl-N-methyl pyrrolidinium (BMP⁺) can be intercalated into the graphite anode.[37-39] The broad range of electrochemical window stability of ILs allow for high cut-off charging voltage (4.0-5.0 V)./37-39/ Carlin and coworkers, 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 CF₃SO₃⁻, AlCl₄⁻, C₆H₅CO₂⁻, PF₆⁻ and BF₄⁻ as electrolytes in dual ion battery.[30,25] Our previous reports have shown AlCl₄ anion

along with different ILs based organic cation (imidazolium, pyrrolidinium) can be used as electrolytes in Al DIBs.[33,40] 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 LiPF₆) 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 imidazolium-based IL, 2,3-dimethyl-1-propyl imidazolium chosen chloride (DMPI-Cl) with AlCl₃ 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. [41,42,12] 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.

4.2. Computational Details

The first principles calculations have been performed using the Vienna *ab initio* simulation package (VASP).[43,44] All geometry optimizations and

respective calculations have been performed using generalized gradient approximation of Perdew-Burke-Ernzerhof (GGA-PBE) functional.[45] The projected augmented wave (PAW) method is used for treating interaction between the ions core and valence electron. [46] An energy cut off of 470 eV has been implemented. During the structural optimization, the Brillouin zone has been sampled with Γ centered k-point grid of 11 \times 11×5 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 $\leq 0.01 \text{ eV/Å}$ 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. [47] We have modelled four different stages for both DMPI cation and AlCl₄ 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 Γ centered k-point mesh of 9 × 9 × 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. [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/511 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 (Cl-NEB).[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 AlCl₄ 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 AlCl₄-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.[27,53] The zero-point energy (ZPE) corrections have also been included for diffusion barrier calculation using the formula, $ZPE = \sum_i \frac{hv_i}{2}$, where h is the Planck's constant and v_i is the vibrational frequency. The ZPE is calculated by considering the degrees of freedom of intercalated DMPI into graphite system.

4.3. Results and Discussion



4.3.1. Structural Changes and Stable Binding Sites

Scheme 4.1: 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 4.1) 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 4.1a, b).



Figure 4.1: 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, compared to the EMI. In our earlier report we have studied the effect of alkyl group variation in N1 position of imidazolium ring.[33] 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

Table 4.1: Relative energy (eV) of the different binding sites of the DMPI cation intercalated graphite system.

Sites	Relative Energy (eV)	
Тор	0.009	
Hollow	0.000	
Bridge 1	0.045	
Bridge 2	0.038	

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 4.1c-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 4.1 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 sites are unaltered, the intercalated DMPI cation shifts from most stable site (Hollow) to second most stable (Top) site of binding as shown in Figure 4.2. 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.



Figure 4.2: Schematic representation of changing adsorption sites between Hollow and Top sites of the DMPI cation inside the graphite anode through the molecular dynamics simulation at 300 K temperature, (a) Hollow to Top and (b) Top to Hollow.

4.3.2. 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 parallelly 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 $6 \times 6 \times 2$ supercells 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 4.3. 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.



Figure 4.3: 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.

Hence, the DMPI 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 4.4) 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.

Furthermore, we have considered the maximum possible intercalation in our supercells for each stage. In the case of stage-1, stage-2 and stage-4 of 288 carbon containing graphite systems can intercalate a maximum of 16 DMPI cations (Figure 4.5a), 8 DMPI cations (Figure 4.5b) and 4 DMPI cations (Figure 4.5d), respectively. A $6 \times 6 \times 3$ supercell containing 432 carbon containing graphite system has been chosen for the stage-3 and it can intercalate a maximum of 8 DMPI cations (Figure 4.5c).



Figure 4.4: Comparative study of stage-1 and stage-2 DMPI intercalated graphite system for different concentration of the DMPI cation, (a) 4 DMPI and (b) 8 DMPI. Increase in DMPI concentration, stabilises the stage-1 DMPI intercalated graphite systems. R.E unit is eV.

Other lower stoichiometry of DMPI has been chosen for all the stages. 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. 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 4.5: 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.

4.3.3. 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.

$$E_{Binding} = \frac{E_{[(DMPI)_{\mathcal{X}}}c_m] - E_{C_m} - xE_{DMPI}}{x}$$
(4.1)

where, x is the number of DMPI cations, $E_{[(DMPI)_x C_m]}$, E_{C_m} and E_{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 4.2. At a low concentration of DMPI cations intercalation into graphite is less favourable for every stage with lower binding energy (~ -2.5 eV) compared to intercalation at higher concentrations.

Stagog	No. of DMPI	Binding Energy	Interlayer Distance	
Stages	cations	(eV)	(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	
	1	-2.64	4.37	
4	2	-4.17	4.39	
	3	-4.54	4.38	
	4	-3.90	4.47	

Table 4.2: Binding Energy per DMPI cation (eV) and Interlayer Distance (Å) for All the Stages with Different Concentration.

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.[25,27] Moreover, binding energy (~ -3.5 eV) of DMPI cation intercalation is found to be higher than the anion (AlCl₄:-1.5 eV; PF₆: -2.9 eV) binding in graphite, which can be possible due to the π - π interaction between aromatic DMPI cations and the graphite layers.[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 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.[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.[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[60], where the C2 carbon of DMPI has an almost double charge (0.493 |e|) than C2 carbon (0.288 |e|) of EMI (Figure 4.6). 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.[59] 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.



Figure 4.6: Schematic representation of NBO charge analysis on the C2 carbon atom of (a) DMPI and (b) EMI cations.

4.3.4. 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.[25] 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),[61] 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.[54,55] The average interlayer distance can be calculated by the following formula,

Average interlayer distance =

total height of the stage-n having n-1 galleries or n graphite layers n-1 galleries or n graphite layers

The average interlayer distance for all the stages has been included in Table 4.2. The distance between two layers of DMPI intercalated graphite *i.e.*, the intercalant gallery height (d_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. [59] Our simulated XRD pattern of DMPI intercalated system for all the stages (n=1-4) as shown in Figure 4.7, 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_{00n+1} represents the spacing between adjacent layers. The intercalant gallery height (d_i), gallery expansion (Δd) and periodic repeating distance (I_c) of a particular stage index 'n' are calculated using the d-spacing values as, $I_c = d_i + (n-1) \times 3.35 = \Delta d + n \times 3.35 =$ $(n + 1) \times d_{00n+1}$; similarly for d_{00n+2} , $I_c = (n + 2) \times d_{00n+2}$; where $\Delta d = d_i - 3.35$ and 3.35 Å is the interlayer distance between two consecutive graphite layers.[62] In the case of pristine graphite an intense peak is found at $2q = 26.5^{\circ}$ belonging to its (002) plane generally./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 4.7. 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./25/ Consequently, 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 4.4), which also agrees with an experimental study by Sutto et al.[59]



Figure 4.7: Schematic diagram of simulated XRD pattern of pristine graphite and different stages of DMPI intercalated systems where 2q ranges in $22^{\circ} - 34^{\circ}$.

4.3.5. 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 AlCl₄ anions. Upon charging, the DMPI cations and AlCl₄ 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 AlCl₄ anion intercalation into graphite cathode.

4.3.5.1. AlCl₄ Intercalation into Graphite Cathode

Anion intercalation phenomena for layered structure like graphite been electrode has well studied both theoretically and experimentally.[54,12] Our previous study has also established the exact staging mechanism pathway for AlCl₄ anion intercalation into the graphite cathode. [54] Motivated by those studies, we have modelled four stages (n =1-4) for AlCl₄ anion intercalation keeping the concentration of AlCl₄ anion fixed. From our relative energy calculations, we could confirm that in the initial period of charging process, stage-4 AlCl₄ intercalation is more favourable (Figure 4.8). From our simulated XRD data, we could identify (005) and (006) planes at $2\theta = 23.32^{\circ}$ and 28.07° with the dspacing of 3.81 and 3.17 Å, respectively. For experimental diffraction patterns, 2θ 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]



Figure 4.8: Systematic illustration of different staging mechanism of AlCl₄ anion intercalation, (a) graphite, (b) stage-4, (c) stage-2, and (d) stage-1, where R.E (eV) is the relative energies of same concentration of AlCl₄ ions. Here, brown, blue and green colour represents carbon, aluminium and chlorine, respectively.

4.3.5.2. 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-AlCl₄) 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,

Cathode reaction:
$$C_n(AlCl_4)_y + e^- \leftrightarrow C_n + yAlCl_4^-$$
 (4.2)

Anode reaction: $C_m(DMPI)_x \leftrightarrow C_m + xDMPI^+ + e^-$ (4.3)

Overall:
$$C_m(DMPI)_x + C_n(AlCl_4)_y \leftrightarrow xDMPI^+ + yAlCl_4^- + C_m + C_n$$

$$(4.4)$$

where, x and y are the number of DMPI cations and AlCl₄ 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 ΔG_{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 (ΔV_{cell}) and entropy (ΔS_{cell}) of the reactions are negligible. Thus, the Gibbs free energy change only depends upon the change of internal energy (ΔE_{cell}).

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

$$\Delta E_{cell} = \left\{ x E_{DMPI^+} + y E_{AlCl_4^-} + E_{C_m} + E_{C_n} \right\} - \left\{ E_{[C_n(AlCl_4^-)_y]} + E_{[C_m(DMPI^+)_x]} \right\}$$
(4.5)

where, $E_{[C_n(AlCl_4)_y]}$, $E_{[C_m(DMPI^+)_x]}$, E_{AlCl_4} and E_{DMPI^+} are the total energy of AlCl₄ intercalated graphite system and DMPI intercalated graphite system, AlCl₄ 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 AlCl₄ anions and DMPI cations as a molecular species due to the nonavailability of their crystal structure.

Then the average voltage would be,

$$V = \left(\frac{\left\{E_{[C_n(AlCl_4^-)y]} + E_{[C_m(DMPI^+)x]}\right\} - \left\{xE_{DMPI^+} + yE_{AlCl_4^-} + E_{C_m} + E_{C_n}\right\}}{z}\right) \qquad (4.6)$$

To understand the exact mechanism of intercalation in a DMPI-AlCl₄ 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 4.3. The highest calculated voltage is 5.25 V, which is obtained from the combination of stage-2 DMPI - stage-4 AlCl₄ intercalated system. Experimental evidence suggests that the voltage plateaus range within 3.1-4.3 V with cut-off charging voltage at 4.4 V [25] 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 AlCl₄ is more feasible compared to the other stages during the initial charging process. The combination of stage-3 DMPI stage-4 AlCl₄ and stage-4 DMPI - stage-4 AlCl₄ 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 AlCl₄ 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.*[25,59]* Thus we propose that during initial charging process, the stage-1 DMPI - stage-4 AlCl₄ intercalation occurs. However, when the charging process approaches completion, both DMPI and AlCl₄ ions are expected to follow stage-1 type of intercalation into graphite system. Considering the combination of stage-1 DMPI - stage-1 AlCl₄ 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.*[25]*

DMPI AlCl4	Stage-1	Stage-2	Stage-3	Stage-4
Stage-1	1.61	3.12	3.17	3.03
Stage-2	2.10	3.61	3.66	3.52
Stage-3	3.25	4.76	4.80	4.67
Stage-4	3.74	5.25	5.23	5.16

Table 4.3: Calculated theoretical voltage (V) with different stages ofDMPI cations and AlCl4 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,[54]

$$C_{cathode} = C_{anode} = \frac{nxF}{M_f}$$
(4.7)

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_{cathode} and C_{anode} are the capacity of the cathode and anode, respectively. The total cell capacity (C_{total}) can be expressed as a combination of the individual capacity of both cathode and anode.[63]

$$C_{total} = \frac{1}{\frac{1}{c_{anode}} + \frac{1}{c_{cathode}} + \frac{1}{c_M}}$$
(4.8)

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,

$$C_{total} = \frac{C_{anode} \times C_{cathode}}{C_{anode} + C_{cathode}}$$
(4.9)

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-AlCl₄ DIB, initial gravimetric capacity was reported to be 27 mAh/g which could further be increased upto 82 mAh/g at higher current density with subsequent loss in coulombic efficiency of the cell.[25] During the initial charging process by considering four ions intercalation, as the DMPI cations follow stage-1 and AlCl₄ 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 AlCl₄ 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 AlCl₄⁻ ions only (~2.0 V).[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 AlCl₄ intercalation in graphite system (150-160%).[54] However, the reported cycle life values (1000 cycles) are less for DMPI-graphite system which could be due to the strong interaction between aromatic DMPI cation and graphite, hindering repeated intercalation/deintercalation cycle.

4.3.6. 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 4.9a represents the total DOS (TDOS) and projected DOS (PDOS) for the DMPI intercalated graphite system. Graphite is known to show good inplane electronic conductivity because of presence of the pz 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 4.9a. 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,

$$\rho_{CDD} = \rho^{total} - \sum_{i} \rho_{i}^{fragments}$$
(4.10)

Where, ρ^{total} is the total charge density of the DMPI-graphite system and $\rho_i^{fragments}$ is the charge density of the individual fragments. The CDD plot has been shown in Figure 4.9b, 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 p-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 s-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 4.9: (a) TDOS and PDOS of the DMPI cation intercalated graphite. The Fermi level is set to zero. (b) Isosurface (0.0008 $|e|^{A^{-3}}$) for the CDD plot of DMPI intercalated system, where yellow colour indicates the electron density accumulation and cyan colour indicates electron density depletion.

4.3.7. 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 4.10a.[52] The MEPs have been shown in the Figure 4.10b. 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).[64,65] 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. Recently, both experimental and computational results have found that high diffusion barrier of the ions have tendency to form the dendrite which reduce the crystallinity nature of the electrode and also reduce the overall cycle life of the battery.[66-68]



Figure 4.10: 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.

4.4. 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 π - π 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 AlCl₄ 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 AlCl₄ anion intercalation in cathodes to achieve better electrochemical

performance compared to DIBs using metal anodes along with AlCl₄ 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 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. Overall, this study 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.

4.5. References

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Importance of Non-aromatic Ionic Liquid for Dual-Ion Batteries

5.1. Introduction

Climate change is becoming the most critical global issue in the current scenario. Shift from non-renewable and polluting sources like fossil fuel to renewable energy sources, is crucial to maintain the high-tech growth in geopolitics. [1] On the other hand, batteries are frontrunner among energy storage technologies to facilitate uninterrupted electricity. [2] Since the last few decades, researchers have developed different types of metal-ions based batteries such as Li-ion, [3-5] Na-ion, [6-8] Al-ion, [9-11] and Mgion batteries. [12,13] Among them, Li-ion batteries have seen the most commercialization due to their high voltage and capacity/14,15] However, Li-ion batteries are not a suitable option for long term energy storage due to the limited resources of Li metal anode in the earth's crust and use of expensive transition metal (Ni and Co) oxides as cathode. [16] Moreover, the safety concerns and thermal runaway events are not properly solved.[17] In this contrast, Na-ion batteries would perform as better energy storage devices on the basis of high abundance of Na metal and potentially low cost compared to Li.[18] However, Na-ion batteries technology faces several challenges like low gravimetric and volumetric capacity and hard to achieve broader voltage window./19] Therefore, it is necessary to build low cost, but highly efficient energy storage devices using the most abundant materials.

The graphite electrode based low-cost dual graphite batteries (DGBs) have recently been conceptualized owing to their redox amphoteric nature where it can be reduced and oxidized in electrochemical reaction in proper cation/anion uptake and release process.[20-22] Hence, dual graphite batteries are also known as dual ion batteries (DIBs) where intercalation/deintercalation of cations and anions occur at both the graphite cathode and anode, respectively, in terms of charging/discharging cycle of battery.[23-25] The research in DIBs have been started with the finding of the acceptor type graphite intercalation compounds (GICs). Anion acceptor graphite cathodes are well established in DIBs

study. [10,26] The DIBs and LIBs follow different mechanistic pathways. LIBs follow the rocking chair style mechanism *i.e.*, only Li^+ ions are shuttling between the electrodes for charge/discharge cycle.[4,5] In DIBs case, cations and anions are reversibly intercalated to anode and cathode electrodes in the charging process, and in discharge process ions revert to electrolytes. [27,28] Furthermore, the DIBs generally use lithiumcontaining salts (LiPF₆, LiTFSI) with highly volatile carbonate based organic solvent electrolytes which undergo decomposition at a high working voltage of >4.5 V.[29] Thus, electrolytes with high stability are mandatory for DIBs. Previous studies have focused on non-aqueous solvents such as cyclic/linear carbonates, dimethylformamide, dimethyl sulfoxide, and sulfones which can be used as electrolytes upon mixing with salts.[30,31] However, these solvents have shown relatively poor oxidative stability which leads to the lowering of Coulombic efficiency and decrease in reversibility. Carlin et al. and Placke et al. introduced room temperature ionic liquids (RTILs) electrolyte as a better alternative to traditional organic solvents. [25,32]

Ionic Liquids (ILs) have played an important role in designing a new class of electrolytes, due to their possessing certain interesting properties such as higher ionic conductivity, low vapor pressure and broad electrochemical window, which are important in the development of battery technology.[33-35] The electrochemical reaction has mainly been focused due to possessing high oxidative and reductive stability of ILs electrolyte which results in higher electrochemical stability window, thus accepting the high cut-off charging voltage (4.0-5.0 V).[14,24,36] Carlin *et al.* have studied different metal free ILs based cations such as 2,3-dimethyl-1-propyl imidazolium (DMPI⁺),1-ethyl-3-methyl imidazolium (EMI⁺), N-butyl-N-methyl pyrrolidinium (BMP⁺) coupled with anions like $AlCl_4^-$, $CF_3SO_3^-$, PF_6^- and BF_4^- as electrolytes in DIBs.[30,37-39] Our previous computational study has demonstrated DGB with DMPI-AlCl4 ionic liquid-based electrolyte where the natural graphite-based battery

shows a higher discharge voltage of 3.74 V, which is in good accordance with the experimental voltages. [21] Owing to the large size of the organic DMPI cation, the interlayer distance of graphite anode is expanded from 3.4 to 7.8 Å in the charging process. However, the constant expansion/contraction of the graphite anode due to intercalation/deintercalation of large cations during charge/discharge process tends to exfoliate the graphite anode resulting in poor cycling performance, lower capacity, and reducing the reversibility of the DIBs. [40] Therefore, it is important to explore the DIB anode suitable for room temperature ionic liquid electrolytes which accomplish the superior cyclic performance and high reversible capacity. Redox active organic materials are the encouraging alternative anode electrode due to easy availability, high theoretical capacity, and easy preparation. Thus, various organic compounds have been tested as anode materials, which can reversibly interact with a cation such as BMP providing good specific capacity and moderate voltage. Several redox active organic electrodes are reported such 1,4,5,8-napthalenetetra carboxylic as dianhydride (NTCDA), polyparaphenylene, and conjugated-carbonyl compounds.[38,41,42] Furthermore, polycyclic aromatic hydrocarbons (PAHs) have been developed as potential cathode materials due to the availability of the intercalation space for the guest ions and redox active nature.[43] Besides, many reports on PAHs have shown that using of coronene as an electrode material is an economic, flexible and environmentally safe.[44-46] Our previous report has studied with different PAHs based cathode electrodes such as pyrene, perylene, triphenylene and coronene for Al DIBs.[47] Among these, coronene has shown better electrochemical properties compared to other PAHs. Furthermore, the previous reports have shown that coronene has low solubility in IL electrolyte and there is no loss of active electrode material. [43,48] Recently, Fang et al. have designed a novel organic DIB using coronene as anode with BMP-TFSI electrolyte.[48]

Inspired from these experimental studies and attractive features of PAHs as anode, here we have modelled two DIB systems computationally, coronene anode used with graphite cathode and graphite employed as both anode and cathode in the other case. We have considered pyrrolidiniumbased IL, N-butyl-N-methyl pyrrolidinium chloride (BMP-Cl) with AlCl₃ at a 1:1 molar ratio as the electrolyte. We have explored the intercalation mechanism of organic BMP cation into the coronene as well as graphite anode. Using the first principles calculations, we have performed the systematic study of the structure, stability, electronic properties, and electrochemical properties of the electrodes for the development of organic batteries. Further to this, we have calculated the average voltage of BMP cation intercalated graphite coronene dual-ion battery (GCDIB) and dual graphite battery (DGB), respectively. Moreover, we have calculated the diffusion pathway of BMP cations inside the coronene as well as graphite. Based on obtained theoretical results, we believe that the polycyclic aromatic hydrocarbon based coronene can be used as potential anode material for DIBs technology to accomplish the better electrochemical features compared to metal anode-based DIBs, and this study would encourage further developments of low-cost and high voltage DIBs.

5.2. Computational Details

All the calculations have been performed using first principles method in the Vienna *ab initio* simulation package (VASP.5.4.4).[49,50] The generalized gradient approximation of the Perdew-Burke-Ernzerhof (GGA-PBE) exchange correlation functional has been used for all ground state relaxation and other respective calculation.[51] The valence electron and core ion interactions are considered by implementing the projected augmented wave (PAW) method[52] and the plane wave cut-off energy set to 470 eV. The DFT-D3 approach has been considered for taking account of van der Waals correction in our calculation.[53] All the structures have been optimized with the energy criterion of 10^{-5} eVÅ⁻¹ and Hellmann-Feynman force criterion of $\leq 0.01 \text{ eV}\text{Å}^{-1}$ for all the atoms to obtain the fully relaxed structure between atomic and lattice position. For the calculation of the BMP cation intercalation inside the coronene unit cell, we have chosen Γ -centered k-point mesh of $3 \times 5 \times 3$ for Brillouin zone sampling. Similarly, for the graphite anode we have considered $4 \times 4 \times 1$ supercell with Γ -centered k-point mesh of $2 \times 2 \times 1$ for Brillioun zone sampling. We have considered the three different stages for the both BMP cation and AlCl₄ anion intercalation of graphite anode and cathode, respectively, where a $6 \times 6 \times 2$ supercell of graphite containing 288 carbon atoms for the stage-1, stage-2 and stage-4 systems. Due to different supercell model of stage-3, we have not considered them in our calculation. For the density of states calculation, the Brilloun zone is sampled with k-point mesh of $11 \times 13 \times 11$ and $9 \times 9 \times 1$ for coronene and graphite anodes, respectively. Bader charge analysis has been performed using the Henkelman program to quantify and understand the charge transfer process between intercalant species (BMP cation) and host anodes. [54-56] Ab initio molecular dynamics (AIMD) simulations have been carried out in broad range of temperature 300-600 K for 5 picosecond (ps) timestep using Nosé-Hoover thermostat [57] with a Nosé mass of 0.01 to control the temperature fluctuation in NVT ensemble. The diffusion energy barrier of BMP cation has been calculated using the climbing image nudged elastic band method (Cl-NEB)/58/ by considering six and four images for the graphite and coronene anodes, respectively.

5.3. Results and Discussion

5.3.1. Different Orientations and Stable Binding Sites of BMP Cation

In the DIBs, the cation and anions are reversibly intercalated/ deintercalated from the cathode and anode with respect to charge/ discharge cycle, respectively. So, it is essential to understand the exact orientation of the BMP cation intercalation inside the anodes. Here, we have chosen the two different orientations of the BMP cation where the methyl (Me) group of BMP cation is placed parallel and perpendicular towards the graphite layer (Figure 5.1a and b). Among these the perpendicular orientation is more stable by 0.14 eV compared to the parallel orientation. It is believed that the C-H··· π interaction in perpendicular orientation is more because the 3H of Me group are situated as the tridentate binding mode towards the one carbon atom of central C-C bond of aromatic graphene and therefore, it is more stable compared to the parallel orientation Me group as they cannot directly interact with graphitic layers. [59] Furthermore, we have considered the four different binding sites with respect to the N atom of BMP cation inside the graphite layers, such as (i) B1 (Bridge 1), (ii) B2 (Bridge 2), (iii) T (Top), and (iv) H (Hollow), as shown in Figure 5.1c-f. The reason behind the consideration of N atom, is the presence of localized positive charge on the N atom of BMP cation which suggests that the substantial interaction would occur between N atom and graphite layers. In the Bridge 1 site, the N atom occupies the bridging position between two bonded carbon atoms, whereas in the Bridge 2 site the N atom occupies the bridging position of the two non-bonded carbon atoms of graphite layers. Similarly, in the T site where N atom of BMP cation occupies the top position of a carbon atom of graphite layers and Hollow site N atom occupies the center of hexagons (C6) of the graphite layers.



Figure 5.1: BMP cation intercalated graphite anode with (a) parallel orientation, (b) perpendicular orientation of methyl group of BMP. Optimized structures of different binding sites of BMP cation (c) Bridge 1 (B1), (d) Bridge 2 (B2), (e) Hollow (H), and (f) Top (T). The Blue, cyan, magenta and brown colours stand for N, C, H of BMP cation and graphite layers carbon, respectively.

From the relative energy calculation, Bridge 2 binding site is more stable compared to other binding sites (Table 5.1). However, these relative energy values are very small, suggesting that all four possible sites are thermodynamically accessible upon intercalation of the BMP cation inside the graphite anode.

 cation intercalated graphite anode.

 Sites
 Relative Energy (eV)

Table 5.1: Relative energy of the different binding sites of the BMP

Sites	Relative Energy (eV)
Bridge 1	0.038
Bridge 2	0.000
Тор	0.036
Hollow	0.035

To identify the most stable binding site for the BMP cation into the coronene anode, three possible intercalation orientations are investigated, namely S1, S2 and S3 (Figure 5.2). Due to unsymmetrical special arrangement of polycyclic aromatic ring of the coronene, the binding sites are not regular as it is in graphite case. These orientations are described with the consideration of different position of the long alkyl chain (butyl group) and methyl group of BMP cation inside the coronene anode. In the S1 site, the butyl and methyl groups occupy the c-direction and negative a-

direction of coronene unit cell, respectively. Similarly, for the S3 site, the butyl and methyl groups occupy the negative a-direction and c-direction of



Figure 5.2: Optimized structures of different orientation of BMP cation intercalated coronene anode (a) S1, (b) S2, and (c) S3. The blue, cyan colours stand for N, C of BMP cation and brown colours represent the coronene carbons and magenta for hydrogen of the system.

coronene unit cell, respectively. The S2 site is similar with the S3, with the methyl group slightly tilted towards the positive b-direction of unit cell. From our relative energy calculation, the S1 orientation is more stable compared to other two orientations (Table 5.2), as the BMP cation is placed on the vacant site of the coronene cell. Whereas, in S3 binding site the BMP cation orientation is the highly unstable by 4.96 eV (relative to S1), due to the intramolecular repulsion between hydrogen atoms of BMP and the hydrogen of polycyclic aromatic rings.

Sites	Relative Energy (eV)
S1	0.00
S2	1.24
S 3	4.96

Table 5.2: Relative energy of different binding sites of coronene-BMP.

Moreover, to check the thermal stability, we have performed AIMD simulation of the range of 300-600 K temperature for both BMP cation intercalated anodes: graphite and coronene. In the simulation, the

individual polycyclic aromatic rings remained intact with the unit cell of coronene, and no significant change has been observed in AB stacked graphite layers even in higher temperature. Small change has been observed for bond lengths and bond angles of the BMP cation at high temperature of 600 K. Therefore, we can say from the AIMD simulation that in temperature range of (300-600 K) the geometrical orientation of BMP cation is stable enough.

5.3.2. Model System and Binding Properties

In DIBs, formation of graphite intercalation compounds (GICs) is well established phenomena where both cations and anions are intercalated into the graphite layers. The GICs formation follows the staging mechanism of intercalant insertion based on different competing interaction between the intercalate and intercalant species. During the intercalation process, BMP cation needs to overcome the van der Waals attraction of the parallelly stacked graphite layers as well as the intermolecular repulsive forces between themselves. Hence, the intercalation phenomena can be continued by maintaining a balance between two competing forces. Based on this, we have considered the various stages of intercalation mechanism during the charge/discharge process.[10] In this fashion, we have chosen three most favourable stages, stage-1, stage-2 and stage-4 with a fixed number of four BMP cation molecules (Figure 5.3). Stage-1 corresponds to intercalation occurring in every graphite gallery. Similarly in stage-2 and stage-4, intercalation can occur in alternate two and four galleries of graphite bulk, respectively. Our calculated relative energy trends have shown the stage-4 intercalation process is most stable followed by stage-2 and stage-1. Opening of each of the four galleries of the graphite in stage-1 requires more energy, which is not balanced by the energy released in binding of BMP cation inserted in each gallery of graphite. However, in the case of stage-4, the energy released upon insertion of four BMP cations into a graphite layer is high compared to energy required in

opening one gallery of graphite. Similarly, the competition between energy released due to BMP binding and the energy required for gallery opening must be intermediate in stage-2 compared to stage-1 and stage-4 processes.



Figure 5.3: Schematic representation of (a) graphite and staging process of BMP cation intercalation into the graphite anode (b) stage-4, (c) stage-2, and (d) stage-1. The magenta, cyan, blue and brown colours stand for H, C, N of BMP cation and graphite layers carbon, respectively.

To further investigate the stability of the individual model stages, we have calculated the binding energy for BMP cation intercalated anodes using the following equation.

$$E_{Binding} = \frac{E_{[(BMP)_{\chi}host]} - E_{host} - xE_{BMP}}{x}$$
(5.1)

Where, $E_{[(BMP)_xhost]}$, E_{host} and E_{BMP} stand for the total energy of BMP cation intercalated host materials, individual energy of bulk host materials and energy of free BMP cation, respectively. Here, host signifies the coronene and graphite anodes and x is the number of BMP cations. Thus, more negative binding energy implies more feasible intercalation of BMP cations into considered anode systems. The binding energy of different

stages for a fixed concentration of four BMP cation intercalated graphite anode has been presented in Table 5.3. The low binding energy (-0.49 eV) for the stage-1 is due to the activation barrier that must be overcome against the van der Waals interaction among the graphite layers during the

Table 5.3: Binding energy of BMP cation intercalated graphite (fixed concentration of four BMP cations) and coronene systems (increasing concentration of BMP cations).

Graphite System		Coronene System		
Stages	Binding Energy (eV)	Average Interlayer Distance	No. of BMP cation	Binding Energy (eV)
		(Å)	1	-0.90
1	-0.49	7.9	2	-1.32
2	-1.87	5.8	3	-1.35
4	-2.36	4.7	4	-1.71

gallery opening. The stage-4 formation is more favourable in BMP cations intercalation process in graphite anode among other two stages because of higher binding energy of -2.36 eV. The binding energy of non-aromatic BMP cation intercalated graphite (-2.36 eV) is less compared to imidazolium based aromatic cation (DMPI) intercalated graphite system (-3.5 eV) calculated in our previous report.[21] The high binding energy of aromatic cation (DMPI) is because of strong $\pi - \pi$ interaction with graphite layers which is absent in non-aromatic BMP cation. Thus, we believe that due to lower binding energy in case of BMP, the faster reversibility of the BMP cation intercalation/deintercalation into/from graphite will be maintained compared to DMPI cation during charging/discharging process of battery. Moreover, our calculated binding energy (-2.36 eV) of BMP is found to be neither high nor low compared to other commonly used anions (PF_6^- : -2.9 eV, $AlCl_4^-$: -1.5 eV) binding in graphite electrode.[10,60] For the coronene anode, we have considered the $1 \times 1 \times 2$ supercell with enough vacant space for intercalating up to four BMP cation. From the equation 5.1, we have computed the binding energy of BMP cation intercalated coronene system as shown in Table 5.3. Our calculated binding energy shows that upon increasing the BMP cations the binding energy values increases. Consequently, four BMP cation intercalated coronene becomes more stable (Figure 5.4). The more available vacant space and highly flexible nature of coronene anode can easily accommodate the BMP cation. The less binding energy value of -0.90 eV for one BMP intercalation, could also be the reason of experimentally observed poor Coulombic efficiency (60%) for the early stages of charging process.[48] Subsequent intercalation of BMP cations leads to increase in the binding energy value up to 1.71 eV. This as well gets reflected in the increase of overall columbic efficiency to (80-90%), observed experimentally. Moreover, our calculated average binding energy matches with the other anion such as AlCl₄ (-1.79 eV) intercalated to PAH cathodes.[47] The optimum binding energy is required as a criterion for the battery study to maintain the overall reversibility of the ions.



Figure 5.4: Optimized structure of BMP intercalated coronene, where (a) 1 BMP; (b) 2 BMP; (c) 3 BMP; and (d) 4 BMP cations. The blue, cyan

colors stand for N, C of BMP cation and brown colors represent the coronene carbons and magenta for hydrogen of the system.

Upon the intercalation of the BMP cation into the graphite the average interlayer distance of the graphite increases from 3.4 to 7.9 Å as shown in Table 5.3. The average interlayer distance (d_i) can be calculated as follows,

Average Interlayer Distance $(d_i) = \frac{\text{Total height of the different stages}}{\text{number of gallery}}$

The increased interlayer distance is directly reflected on the volume expansion of the electrode. Meanwhile, a lack of proper synchronization of the volume expansion and contraction of electrode has been observed upon charging/discharging process which can lead to the severe exfoliation of the electrode. Whereas in coronene electrode structure, due to the unique spatial arrangement of individual coronene molecules and available vacant sites, the volume expansion is less compared to the graphite anode. Thus, the volume expansion in maximum BMP intercalated graphite anode (stage-1) is higher (148%) compared to coronene anode (53%), (Figure 5.5). Overall, from the binding energy and volume expansion calculations, we can conclude that the BMP cation has moderate binding strength with both the considered anodes which is essential in DIBs. Coronene has better prospects as a potential anode material over graphite due to less volume expansion.



Figure 5.5: Volume expansion plot of both coronene and graphite anodes.

5.3.3. Electrochemical Properties

Here we have discussed the electrochemical properties of both dual graphite battery (DGB) and graphite coronene dual-ion battery (GCDIB), where the BMP cations are paired up with the AlCl₄ anions. In the charging, the AlCl₄ anions and BMP cations are intercalated into the graphite cathode and anode in DGB, respectively. In the GCDIB, BMP cations are intercalated into coronene anode and AlCl₄ anions are intercalated into the graphite cathode. To investigate electrochemical properties of full DIB, it is necessary to study the AlCl₄ intercalation inside the graphite cathode as well. Previously, our group has carried out extensive study on AlCl₄ anion intercalation in the graphite cathode.*[10]* Here, we have considered different stages such as stage-1, stage-2 and stage-4 of AlCl₄ anions intercalation into graphite electrode and suggesting that stage-4 is more stable followed by stage-2 and stage-1 (Figure 4.8, chapter 4). Besides low cost and safety concerns, the open

circuit voltage (OCV) and charge capacity are the most important criterion for the practical feasibility of the considered DIBs. In the DIB, BMP-AlCl₄ is not only used as an IL but also as the active charge carrier in terms of the electrochemical activity. From the cathodic and anodic reaction, we could calculate the OCV of DIB. Firstly, we have considered the following discharge voltage equations for the DGB systematically.

Cathodic Reaction:
$$C_n(AlCl_4)_y + ye^- \leftrightarrow yAlCl_4^- + C_n$$
 (5.2)

Anodic Reaction:
$$C_m(BMP)_x \leftrightarrow xBMP^+ + C_m + xe^-$$
 (5.3)

When the equal number (x = y) of BMP cations and AlCl₄ anions are intercalated into graphite cathode and anode, the overall reaction would be as follows,

Overall Reaction:
$$C_n(AlCl_4)_y + C_m(BMP)_x \leftrightarrow xBMP^+ + yAlCl_4^- + C_n + C_m$$
(5.4)

where, C_m and C_n are the anode and cathode, respectively and x is the number of BMP cations and y is the numbers of AlCl₄ anions. The cell voltage can be calculated using the following Nernst equation, $V = \frac{-\Delta G_{cell}}{zF}$, where F and z are the Faraday constant and number of electrons transferred, respectively. Due to negligible contribution from change of volume and entropy as all the calculations have been performed in 0 K temperature, so the change of free energy can be equated with the change of internal energy of the BMP intercalated systems. Therefore, the change of internal energy for the overall reaction would be,

$$\Delta E = x E_{BMP^+} + y E_{AlCl_4^-} + E_{C_m} + E_{C_n} - \{E_{[C_n(AlCl_4)_y]} + E_{[C_m(BMP)_x]}\}$$
(5.5)

Where, $E_{[C_m(BMP)_x]}$, $E_{[C_n(AlCl_4)_y]}$, E_{BMP^+} and $E_{AlCl_4^-}$ are the total energy of the BMP cation intercalated graphite system and AlCl₄ intercalated graphite system, and the individual fragments of BMP cation and AlCl₄ anion, respectively. E_{C_m} and E_{C_n} are the total energy of graphite electrodes. E_{BMP^+} and $E_{AlCl_4^-}$ are the calculated optimizing energy of the individual molecule of BMP cation and AlCl₄ anion, respectively due to unavailability of their crystal structure. Thus, the average voltage can be formulated as follows,

$$V = \frac{\{E_{[C_n(AlCl_4)_y]} + E_{[C_m(BMP)_x]}\} - \{xE_{BMP} + yE_{AlCl_4} + E_{Cm} + E_{Cn}\}}{z}$$
(5.6)

In GCDIB, the cathodic reaction is same as DGB, and anodic reaction can be given as follows,

Anodic Reaction:
$$Coro(BMP)_x \leftrightarrow xBMP^+ + Coro + xe^-$$
 (5.7)

Thus, the average voltage equation for GCDIB would now be,

$$V = \frac{\{E_{[C_n(AlCl_4)_y]} + E_{[Coro(BMP)_x]}\} - \{xE_{BMP} + yE_{AlCl_4} + E_{Coro} + E_{C_n}\}}{z}$$
(5.8)

where, $E_{[Coro(BMP)_x]}$ and E_{Coro} are the total energy of the BMP cation intercalated coronene anode and free coronene materials, respectively. To investigate the exact mechanism of the charging/discharging process, we have studied the different staging intercalation behaviour of both BMP cations and AlCl₄ anions at the initial and final state of charge in DGB. Therefore, based on our model we have calculated all possible value of average voltage as shown in Table 5.4, by intercalating four cations and anions to replicates the initial state of charging in DGB. The combinations of stage-1 BMP–stage-1 AlCl₄, and stage-1 BMP–stage-2 AlCl₄ have provided the lower voltage values of 0.13 and 0.10 V, respectively. This may be due to the activation of electrode by the ions intercalation which agrees with our calculated lower binding energy values in stage-1 process of both BMP and AlCl₄ intercalated graphite systems. The highest calculated voltage is 3.79 V, which is obtained in the stage-4 BMP–stage-4 AlCl₄ intercalated system. Owing to lack of exact experimental evidence of the BMP-AlCl₄ DGB, we have compared our calculated voltage values with the BMP-TFSI, DGB, where both AlCl₄ and TFSI are used as an active intercalant anion species in DIB study. The experimental voltage window was observed in the range of 1.0-4.6 V for the BMP-TFSI with a very high voltage discharge plateau achieved at 3.7 V.*[48]* However, this observation is also reflected with our calculated voltage trends of BMP-AlCl₄ DGB, where the highest discharge voltage values is found to be 3.79 V. Furthermore, our calculated relative energy and literature study have suggested that the formation of stage-4 is feasible in the case of both BMP

Table 5.4: Calculated theoretical voltage of different stages of BMP-AlCl₄ in DGB.

BMP AlCl4	Stage-1	Stage-2	Stage-4
Stage-1	0.13	1.25	1.75
Stage-2	0.10	1.45	1.98
Stage-4	1.94	3.29	3.79

The average voltage of the stage-2 BMP-stage-4 AlCl₄ is calculated to be 3.29 V which lies in the range of experimental voltage window. However, the BMP stage-2 is less stable compared to the stage-4 of BMP cation intercalation into the graphite as discussed earlier. Thus, we have proposed that in the initial state of charging process in DGB, both BMP cations and AlCl₄ anions prefer to follow the stage-4 intercalation process over other stages. In addition to this we have considered the fully charged states,

where all the BMP cations and AlCl₄ anions are expected to follow the stage-1 type of intercalation into the graphite. However, the stage-1 BMP-stage-1 AlCl₄ results in an OCV of 3.05 V with the maximum intercalation (16 ion pairs) at both the electrodes in DGB, which follows the experimental reported range of voltage value. Similarly, applying the equation 5.8, we have calculated the discharge voltage (Table 5.5) for the four BMP cations intercalated into the coronene and four AlCl₄ anions intercalated into graphite system to replicate the initial state of charging. From the Table 5.5, the stage-4 AlCl₄ intercalation has shown the highest voltage of 3.14 V in GCDIB. Besides, the combination of stage-1 and stage-2 AlCl₄ with coronene gives the less average voltages of 1.09 V and 1.33 V, respectively, due to the activation of electrode at the initial state of charging. Our calculated highest voltage value of 3.14 V matches with the experimental voltage window of 3.0-3.9 V for the coronene-TFSI dual-ion battery. [48] To replicate the fully charged state, we have considered the maximum sixteen ion pairs intercalation, where BMP cations are intercalated into the $2 \times 2 \times 2$ supercell of coronene, and stage-1 type intercalation is followed for AlCl₄ anions intercalation into graphite. Consequently, the calculated OCV of 3.1 V falls in the experimental voltage range of 3.0-3.9 V.

 Table 5.5: Theoretical calculated voltage of GCDIB system with different

 stages of AlCl₄ intercalated graphite cathode.

AlCl ₄	Stage-1	Stage-2	Stage-4
Coronene	1.09	1.33	3.14

Moreover, we have measured the gravimetric capacity using equation 4.9 (from chapter 4) for our considered DIBs. In the fully charged state, we have obtained the maximum capacity of 130 $mAhg^{-1}$ for our BMP-AlCl₄ DGB system. Whereas in case of BMP-TFSI DGB the maximum capacity is reported to be 90-100 $mAhg^{-1}$, which is less than BMP-AlCl₄ DGB

system, due to high molar mass of TFSI anions than the AlCl₄ anions. Cycle numbers of 200 only have been observed for the BMP-TFSI DGB, because of exfoliation in the electrodes during intercalation of large size cations and anions.*[48]* We believe that the cycle number will increase for the BMP-AlCl₄ DGB due to the smaller volume of the intercalating AlCl₄ anions compared to the TFSI anions.

Furthermore, our calculated gravimetric capacity of BMP-AlCl₄ GCDIB upon maximum ion intercalation is 116 $mAhg^{-1}$, which is much higher than experimental capacity range of 55-80 $mAhg^{-1}$ reported for BMP-TFSI GCDIB. The less volume expansion nature of BMP intercalated coronene results in the maximum cycle number of 450 for the BMP-TFSI graphite coronene dual-ion battery.[48] Hence, we predict that the cycle number may also increase for BMP-AlCl₄ GCDIB, because of less exfoliation of graphite electrodes due to the smaller size of AlCl₄ anion compared to TFSI anion. Thus, the use of AlCl₄ anion is vastly superior over the TFSI anion because of higher capacity and longer cycle number of DIBs. Thus, in our GCDIB, the choice of coronene anode will lead to lower volume expansion than graphite anode. Also, the choice of smaller size AlCl₄ anion can help in decreasing the exfoliation at cathodic part. Such informed choices can result in a higher cycle life for our considered GCDIB.

5.3.4. Electronic Properties

In this section, we have studied the electronic contribution of the BMP cations intercalated graphite as well as the coronene anode. It is important to understand the direction of charge transferred of less familiar organic (BMP) cation intercalated carbon-based anodes compared to more commonly anions intercalated layered like graphite cathode. In the charging process, the electrons flow from cathode to anode direction through the external circuit, which permit the intercalation/adsorption of cations and anions inside the anode and cathode, respectively. Equally, the

reverse phenomena happen in the discharge process where all ions revert to the electrolyte. Therefore, a constant electric conductivity of the electrode is essential to maintain the reversibility nature of the ions in battery. The electronic conductivity can be explained from the DOS (density of states) configuration in terms of the Fermi region. In Figure 4a and b has shown the total DOS and projected DOS for the BMP cation intercalated graphite and coronene anodes, respectively. It is well known that the graphite has a good in-plane electronic conductivity due to presence of p_z electronic state at the Fermi level. In Figure 5.6a, the Fermi level of BMP cation intercalated graphite has shifted towards the conduction band with respect the pristine graphite, because of charge transfer from BMP cation to graphite. Due to unsymmetrical arrangement of the coronene, the p states of carbon in coronene are appeared irregularly as compared to the pristine graphite in the DOS structure as shown in Figure 5.6b. The Fermi level of BMP intercalated coronene has slightly moved to the conduction band with respect to the free coronene. This observation suggest that the amount of charge has transferred from BMP cation to coronene electrode resulting the reduction of coronene electrode.



Figure 5.6: TDOS and PDOS of BMP cation intercalated (a) graphite anode, and (b) Coronene anode. Here the Fermi level is set to zero.

Furthermore, we have investigated the charge density difference (CDD) study to visualize the charge transfer mechanism with help of following equation.

$$\rho_{CDD} = \rho^{total} - \sum_{i} \rho_{i}^{fragments}$$
(5.12)

Where, ρ^{total} and $\rho^{fragments}$ are the total charge density of the BMP cation intercalated host materials and the charge density of the individual fragments, respectively. The CDD plot of the BMP intercalated graphite anode and coronene anodes has shown in the Figure 5.7a and b, respectively. Where the yellow and blue colours represent the electron density accumulation and depletion, respectively. The mainly σ electrons are transferred from the C-H bond of the BMP cation to the aromatic ring (C-H $\cdots \pi$ interaction) of host materials of graphite and coronene. From the Figure 5.7a, it is indicating that the electron density accumulation is more (*i.e.*, high portion of yellow colour on the graphene sheet) in BMP intercalated graphite compared to that in the coronene electrode. Furthermore, the Bader charge analysis is done to understand the process quantitatively. Quantitatively, +0.85 |e| and +0.80 |e| charge has transferred from the BMP cation to the graphite and coronene anodes, respectively. Overall, the higher charge transfer from the BMP cation to the graphite as interpreted from CDD plot and Bader charge analysis, is responsible for the higher binding energy of BMP-graphite (2.36 eV) compared to the BMP-coronene (1.71 eV). Therefore, based on our DOS and CDD study, we can conclude that both electrodes can be used as potential anode for the BMP cation intercalation due to presence of a constant electronic conductivity during charging/discharging process which is highly required in DIBs technology.[45,59]



Figure 5.7: The CDD plot of BMP intercalated (a) graphite with isosurface of 0.0008 $|e| Å^{-3}$ and (b) coronene with isosurface of 0.0009 $|e| Å^{-3}$ systems, where the yellow and cyan colours represent the electron density accumulation and depletion, respectively.

5.3.5. Diffusion Pathway

The fast charging/discharging rate can be explained based on the mobility of the BMP cations inside the anode material. The mobility can be implemented by calculating the diffusion barriers of the BMP cation intercalated graphite as well as coronene anodes. The trouble-free diffusion and high mobility are the prerequisite for the BMP cations to improve the overall performance of the considered DIBs. To calculate the diffusion barrier of the BMP cations inside the graphite layer using the CI-NEB method, we have considered three minimum energy pathways (MEPs) for diffusion starting from most stable site (Bridge 2) of the BMP cation to second most stable sites of the AB stacked graphite layers as shown in Figure 5.8a. All the three possible MEPs have shown in Figure 5.8b, where the path 1, path 2 and path 3 have shown diffusion barrier of 0.1, 0.26 and 0.13 eV. Among these, path 1 shows the lowest diffusion barrier (0.1 eV) which is relatively less compared to the others metal cations such as Li or Na (0.2-0.4 eV) intercalated graphite layers.*[62,63]*



Figure 5.8: Schematic representation of BMP cation intercalated graphite representing (a) three diffusion pathways which are shown by brown, red and violet colour arrows, and (b) the energy profile diagram of the three diffusion pathways.

Similarly, we have studied the diffusion energy barrier of BMP cations intercalated coronene anode. We have chosen the two MEPs starting from most stable site of b and c-direction of one unit cell to next unit cell, respectively as shown in Figure 5.9a. We have not considered the diffusion of BMP cation in the a-direction, due to presence of large aromatic ring of coronene, which creates the blockage for the free movement of BMP cation inside the coronene unit cell. Among of two MEPs, the c-direction diffusion barrier is less (1.16 eV) than the bdirection diffusion barrier of 1.8 eV. Consequently, the BMP cations transport in c-direction is much easier compared to b-direction because of low diffusion barrier of 1.16 eV. Whereas the coronene BMP cation diffusion barrier is high compared to the diffusion barrier of BMP cation inside the graphite layers. This observation indicates that the ions intercalation/deintercalation rate can be easy upon the high charging voltage of the GCDIB system. [48] Overall, from the diffusion pathway study, we can conclude that the organic BMP cation intercalated graphite anode can be used for fast charging rate DIBs in future.



Figure 5.9: (a) Schematic representation of the diffusion energy barrier for BMP cation intercalated coronene, (b) and (c) are the diffusion pathways BMP cation in b and c-directions of coronene, respectively.

5.4. Conclusion

In this study, we have demonstrated the applicability of coronene, a polycyclic aromatic hydrocarbon (PAH), as a n-type redox active anode in DIB. To get the better comparison we have considered the layer like graphite anode along with coronene for BMP cation intercalation study. Based on our dispersion-corrected DFT calculations, we have investigated the staging mechanism of BMP cation intercalation inside the graphite anode, along with this charge transfer mechanism, diffusion barrier, electrochemical properties such as voltage and capacity for BMP cation intercalated coronene as well as graphite anodes. We have modelled three staging mechanisms (stage-1, stage-2 and stage-4) for the BMP cation intercalated graphite anode to investigate the electrochemical and thermodynamic properties. To verify the stability, we have calculated the binding energy of BMP cation intercalated graphite as well as coronene systems. Our calculated relative energy values of the different stages of the BMP cation intercalated graphite systems suggest the stability in the following order: stage-4 > stage-2 > stage-1. The BMP cations are strongly interacting with the graphite layer due to having higher binding energy of 2.36 eV compared to the coronene binding energy of 1.71 eV.

Upon intercalation of BMP cation into the graphite anode in charging process the interlayer distance has increased to 3.4 to 7.9 Å, which leads to increase of volume expansion of the electrode. In the fully charged state of DIB, the percent of volume expansion of graphite anode is higher of (148 %) than coronene anode of (53%), which indicates that the graphite anode is more prone to exfoliation in nature over the coronene. So, we can assume that the cycle number may increase in the GCDIB system than that in the DGB for the BMP-AlCl₄ system. Our calculated average voltage of DGB is found to be 3.79 V when stage-4 mechanisms of both BMP cations and AlCl₄ anions are considered, which is in good agreement with the experimental high discharge voltage of 3.7 V. The theoretical voltage of GCDIB is calculated to be 3.1 V which again very much in agreement with the experimental voltage range of 3.1-3.9 V. Moreover, our calculated gravimetric capacity of DGB and GCDIB are 130 and 116 $mAhg^{-1}$, respectively for the maximum ions intercalated system. From the DOS structure, the Fermi level of both BMP intercalated graphite and coronene systems are shifted towards the conduction bands, indicating the considered electrode can behaves as anode materials. The Bader charge analysis has also confirmed the electrochemical reduction of the electrode materials which is consistent with the experimental findings. Despite, the coronene having higher diffusion barrier, it can be a promising organic electrode for DIBs because of the less volume expansion and comparable voltage/capacity with respect to the graphite anode. The high diffusion barrier of coronene indicates the BMP cations is more restricted inside the coronene compared to graphite anode. So, from the perspective of state of charge, GCDIB might take a little more time compared to the DGB to get fully charged. On the other hand, the cycle life of GCDIB is expected to be almost twice to that of DGB. Hence, the little increase in charging time can be compensated by the higher cycle number, meaning high cycle stability of GCDIB. Overall, our findings provide the in-depth understanding of interaction between BMP cation and coronene anode,

which helps to explain the usage of nonaromatic organic cation of BMP. We propose that the polycyclic aromatic hydrocarbons can be used as an organic anode for various organic cations for the development of low-cost high performance-based DIBs.

5.5. References

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Optimization of Voltage for Dual-Ion Batteries

6.1. Introduction

The rapid growth in human population has resulted in increased reliance on non-renewable energy sources, such as coal and crude oil. As nonrenewable energy consumption escalates, it drives up living costs and exacerbates climate change vulnerabilities. Recognizing the urgency to transition from fossil fuels to renewable sources, significant efforts have been made in recent decades.[1,2] Renewable energy sources, while promising, present challenges due to their intermittent nature and geographical limitations. To address this, researchers have focused on energy storage solutions, particularly batteries, to ensure an uninterrupted electricity supply. Lithium-ion batteries (LIBs) have dominated the current energy market, serving a wide range of applications from portable electronic devices to grid storage and electric vehicles, owing to their high energy density. [3-5] However, LIBs have their own set of challenges, including the thermal runaway effect and the use of costly transition metal-based cathodes. [6,7] In light of the substantial costs and safety concerns associated with LIBs, there is a growing preference to seek alternative solutions for environmentally friendly energy storage devices. This pursuit has led to the exploration of novel materials, such as graphite, with the aim of developing more cost-effective, high-performance batteries. Owing to its redox-amphoteric properties and layered structure, graphite exhibits both reduction and oxidation through electrochemical reactions involving the uptake and release of cations and anions. This concept has given rise to dual graphite batteries, often referred to as dualion batteries (DIBs), in which both the graphite anode and cathode play essential roles in the intercalation and deintercalation of cations and anions throughout the charge and discharge cycles of the battery. [8-10] Unlike shuttle-style mechanism in LIBs, DIBs demonstrate distinct the mechanistic behaviours, where both cations and anions are simultaneously intercalated into graphite cathode and anode in charging process.[11-13] DIBs offer several advantages, including a high working voltage of 4.5 V,

enhanced safety, and lower cost and ultra-fast charging capability compared to conventional LIBs.[14-16] As a result, DIBs are gaining as a significant energy storage system in the post-LIBs era, driven by their cost-effectiveness and environmentally friendly characteristics.

The first reported use of graphite-based dual-ion batteries (DIBs) dates back to 1989 when McCullough and co-workers employed a nonaqueous electrolyte containing ClO_4^- .[17] Since then, DIBs have typically relied on lithium salts like LiPF₆, LiTFSI, and LiFSI, dissolved in organic carbonate-based solvents such as ethylene carbonate and ethyl methyl carbonate.[18,19] However, these traditional DIBs encounter significant challenges during cyclic processes. At high working voltages (>4.5 V), the electrolytes may decompose, leading to electrolyte degradation and performance issues. Additionally, solvent molecules may co-intercalate, resulting in the exfoliation of the graphite electrode.[15,20] To undertake these crucial challenges, Carlin and co-workers have introduced a promising alternative: room temperature ionic liquids (RTILs) as electrolytes.[21] In contrast to volatile carbonate-based electrolytes, RTILs offer enhanced stability and reduced decomposition, rendering them more suitable for DIB applications.

Ionic liquids (ILs) are a remarkable class of low melting point salts, remaining in liquid state at room temperature, and possessing exceptional properties like low vapor pressure, good thermal and chemical stability, high ionic conductivity, and a wide electrochemical window.[22-25] Due to these unique attributes, ILs have emerged as potential alternatives to traditional carbonate-based electrolytes, finding applications in DIBs as well as in LIBs. IL-based electrolytes have been used in LIBs, however higher viscosity of ILs and lower lithium mobility reduces the overall performance of LIBs compared to the traditional electrolytes-based LIBs.[26,27] A high throughput ML screening of ionic liquids may be helpful towards the development of the LIBs. ILs are composed of different organic moieties of cations and their counter anions. These are

not only used as electrolytes in DIBs but also, they are revealed as active intercalant species. Recent studies have shown that the organic moieties of imidazolium and pyrrolidinium based cations and counter anions such as OTf (CF₃SO₃), AlCl₄, PF₆ and BF₄ of ILs are intercalated into the graphite anode and cathode, respectively during charging process. [28-31] These DIBs show the higher cut-off changing voltage of 4.0-5.0 V, due to the broad electrochemical window of ILs. However, there is limited research on DIBs using organic moieties of imidazolium- (1-ethyl-3-methyl imidazolium and 2,3-dimethyl-1-propyl imidazolium) and pyrrolidiniumbased (N-butyl-N-methyl pyrrolidinium) cations in the graphite anode. [30,32] Exploring DIBs with other organic moieties-based cations, like morpholium, piperidinium, and thiazolium, is challenging both computationally and experimentally due to the complexities of the ion intercalation process and the sensitivity of ILs. The intercalation of ions into the graphite electrode follows a proper staging mechanism, making computational studies time-consuming and costly. Additionally, ILs are highly sensitive to both water and air, therefore difficult to handle in experiments.[33,34]

To overcome these issues, we have considered a high throughput data driven machine learning (ML) approach in this work to predict the binding energies (BEs) of cations of different stages of graphite anode. For this, we have adopted 10 organic cation moieties and 9 anions as shown in Figure 6.1. The relevant input features have been considered to train the machine for the predictions of BEs of cations for the different stages. Our predicted BEs of cations are validated with DFT calculated values. To assess the generalization and stability of our ML model, we employed the cross-validation technique. Furthermore, we have calculated the anions BEs of different stages. Upon coupling of both cations and anions BEs, we have successfully designed and calculated voltages for dual graphite batteries (DGBs). Nevertheless, we have used interpretable ML library to

understand the features importance towards the prediction of BEs of cations.



Figure 6.1: Various organic cation and anion-based structures were employed to represent the ionic liquids. The numbers in parenthesis represent the cations having different alkyl substitutions (R1 to R4) and the corresponding structure and substitutions details are given in Table 6.1.

Organic Moieties	Cations ID	Alkyl Groups					
	0	$R_1=C_4H_9$ (Butyl), $R_2=R_3=CH_3$ (Methyl)					
Pyrazolium	1	$R_1 = C_4 H_9, R_2 = R_3 = H$					
	2	$R_1=C_3H_7$ (Propyl), $R_2=R_3=H$					
	3	$R_1 = C_2 H_5$ (Ethyl), $R_2 = R_3 = H$					
Piperidinium	4	$R_1 = C_4 H_9$					

Table 6.1: Different alkyl groups are presented for each cation.

	5 R ₁ =C ₃ F					
	6	R ₁ =C ₂ H ₅				
	7	R ₁ =CH ₂ OCH ₃				
	8	R ₁ =C ₂ H ₅ OCH ₃				
	9	$R_1 = C_2 H_5 O C_2 H_5$				
	10	$R_1 = C_4 H_9, R_2 = R_3 = R_4 = H$				
	11	$R_1 = C_3 H_7, R_2 = R_3 = R_4 = H$				
Pyridinium	12	$R_1 = C_2 H_5, R_2 = R_3 = R_4 = H$				
Fyndiniuni	13	$R_1 = C_4 H_9, R_2 = CH_3, R_3 = R_4 = H$				
	14	R ₁ =C ₄ H ₉ , R ₃ =CH ₃ , R ₂ =R ₄ =H				
	15	R ₁ =C ₄ H ₉ , R ₄ =CH ₃ , R ₂ =R ₃ =H				
	16	$R_1=C_4H_9$				
Pyrrolidinium	17	R1=C3H7				
	18	R ₁ =C ₂ H ₅				
	19	$R_1 = C_4 H_9, R_2 = C H_3$				
Thiozolium	20	$R_1 = C_2 H_5, R_2 = C H_3$				
Tinazonum	21	$R_1 = C_4 H_9, R_2 = H$				
	22	$R_1 = C_2 H_5, R_2 = H$				
	23	R ₁ =CH ₃ , R ₂ =R ₃ =C ₂ H ₅ , R ₄ =C ₂ H ₅ OCH ₃				
	24	$R_1 = R_2 = R_3 = CH_3, R_4 = C_4H_9$				
	25	$R_1 = R_2 = R_3 = R_4 = C_4 H_9$				
A	26	$R_1 = R_2 = R_3 = R_4 = C_3 H_7$				
Ammonium	27	$R_1 = R_2 = R_3 = R_4 = C_2 H_5$				
	28	$R_1 = R_2 = R_3 = R_4 = CH_3$				
	29	$R_1 = R_2 = R_3 = CH_3, R_4 = CH_2CN$				
	30	$R_1 = CH_3, R_2 = R_3 = R_4 = C_4H_9$				
	31	$R_1 = R_2 = R_3 = R_4 = C_4 H_9$				
Phoenhonium	32	$R_1 = R_2 = R_3 = R_4 = C_3 H_7$				
rnospholinum	33	$R_1 = R_2 = R_3 = R_4 = C_2 H_5$				
	34	$R_1 = R_2 = R_3 = C_2 H_5, R_4 = C_4 H_9$				

	35	$R_1 = CH_3, R_2 = R_3 = R_4 = C_4H_9$
	36	R ₁ =R ₂ =R ₃ =C ₂ H ₅ , R ₄ =CH ₂ OCH ₃
	37	$R_1 = R_2 = R_3 = C_2 H_5, R_4 = C_2 H_5 OC H_3$
	38	$R_1 = R_2 = C_2 H_5, R_3 = C H_3$
	39	$R_1 = R_2 = R_3 = C_2 H_5$
Sulfonium Morpholium	40	$R_1 = R_2 = C_2 H_5, R_3 = C_3 H_7$
Sunomum	35 $R_1=CH_3, R_2=R_3=R_4=C$ 36 $R_1=R_2=R_3=C_2H_5, R_4=CH_2$ 37 $R_1=R_2=R_3=C_2H_5, R_4=C_2H$ 38 $R_1=R_2=C_2H_5, R_3=C_2H_5$ 39 $R_1=R_2=R_3=C_2H_5$ 40 $R_1=R_2=R_3=C_2H_5$ 41 $R_1=R_2=R_3=C_3H_7$ 42 $R_1=R_2=R_3=C_3H_7$ 43 $R_1=R_2=R_3=C_4H_9$ 44 $R_1=R_2=R_3=C_4H_9$ 45 $R_1=C_3H_7$ 46 $R_1=C_2H_5OC_2H_5$ 48 $R_1=C_2H_5OC_2H_5$ 49 $R_1=C_2H_5, R_2=H$ 50 $R_1=C_3H_7, R_2=CH_3$ 51 $R_1=C_3H_7, R_2=CH_3$ 52 $R_1=C_4H_9, R_2=H$ 53 $R_1=C_6H_{13}$ (Hexyl), R_2	$R_1 = R_2 = R_3 = C_3 H_7$
	42	$R_1 = R_2 = C_4 H_9, R_3 = C H_3$
	43	$R_1 = R_2 = R_3 = C_4 H_9$
	44	$R_1=C_4H_9$
	45	R1=C3H7
Morpholium	46	$R_1 = C_2 H_5 OC H_3$
	47	$R_1 = C_2 H_5 O C_2 H_5$
	48	R ₁ =CH ₂ OCH ₃
	49	$R_1 = C_2 H_5, R_2 = H$
	50	$R_1 = C_3 H_7, R_2 = H$
Imidazolium	51	$R_1 = C_3 H_7, R_2 = C H_3$
midazonum	52	$R_1 = C_4 H_9, R_2 = H$
	53	R ₁ =C ₆ H ₁₃ (Hexyl), R ₂ =H
	54	$R_1 = C_8 H_{17}$ (Octyl), $R_2 = H$

6.2. Methods

6.2.1. DFT Details

In machine learning studies, the quality of the data holds paramount importance. In the context of BEs of cations, the available data is quite limited. Therefore, it is essential to calculate BEs of some of these cations for the training. To achieve this, the first principles calculations have been employed using the Vienna *Ab initio* Simulation Package (VASP).[35,36] The calculations involve geometry optimizations and utilize the generalized gradient approximation of the Perdew-Burke-Ernzerhof (GGA-PBE) functional.[37] Additionally, the projected augmented wave

(PAW) method is employed to account for the interaction between valence and core electrons (further details in section 4.2, chapter 4).[38] The workflow related to the calculations of binding energies of cations and anions has been shown in scheme 6.1. The concept of BE stands as a pivotal criterion in comprehending the stability and feasibility of the intricate intercalation process. All the structures are optimized to calculate the BEs. Hence, binding energies of cations ($(E_B)_{Cation}$) and anions ($(E_B)_{Anion}$) can be calculated using the following equations.

$$(E_B)_{Cation} = \frac{E_{[G(cation)_x]} - E_G - x E_{cation}}{x}$$
(6.1)

$$(E_B)_{Anion} = \frac{E_{[G(anion)y]} - E_G - yE_{anion}}{y}$$
(6.2)

Where, the $E_{[G(cation)_x]}$ is the total energy of the x numbers of cation intercalated graphite anode and $E_{[G(anion)_y]}$ is the total energy of the y numbers of anion intercalated graphite cathode. E_{cation} and E_{anion} are the total energies of the individual cation and anion, respectively, and E_G is the total energies of the graphite electrode.



Scheme 6.1: The workflow involves assessing the binding energies of cations and anions across various stages of graphite electrodes and subsequently utilizing these values for voltage calculations.

6.2.2. ML Models

The input binding energy (BE) values serve as pivotal markers for the training of our supervised machine learning (ML) model. As there are large numbers of cations, we calculated binding energies of some cations and predicted the binding energies of the remaining cations using the ML

model. The comprehensive workflow, encompassing data set division to user comprehension, has been meticulously presented in Scheme 6.2. In our supervised ML framework, we partitioned the known BEs into an 80:20 ratio, designating them as the training and test data sets.[39,40] The training data set was harnessed to train the model, while individual errors were assessed by contrasting them against the test data set. For this purpose, we explored eight diverse supervised regression algorithms, namely Kernel Ridge Regression (KRR), eXtreme Gradient Boosting Regression (XGBR), Extra Trees Regression (ETR), Random Forest Regression (RFR), Adaptive Boosting Regression (ABR), Decision Tree Regression (DTR), Gradient Boosting Regression (GBR), and Light Gradient Boosting Machine (LGBM) regression (more details in section 1.6.6, chapter 1) employing the Scikit-learn package version 0.23.1 within Python 3.8.2.[41-43]



Scheme 6.2: ML work flowcharts for the prediction of cation binding energy.

These algorithms are conveniently accessible through open-source libraries, replete with default parameters that can be tailored to meet specific user requirements. To identify the most aptly suited ML model, we employed randomized search cross-validation (RandomizedSearchCV) for hyperparameter tuning across the various algorithms. The predictive efficacy of each model was assessed using the mean absolute error (MAE) and root mean squared error (RMSE), quantified through the following equations.

$$MAE = \frac{1}{n} \sum_{i=1}^{n} (Y_i - y_i)$$
(6.3)

$$RMSE = \sqrt{\frac{1}{n} \sum_{i=1}^{n} (Y_i - y_i)^2}$$
(6.4)

Where, n is the total data point, the Y_i , and y_i are the ML and DFT calculated BEs, respectively. Subsequently, we subjected our randomly partitioned dataset through various cross-validation methods to ascertain the stability and generalizability of our optimized model. Additionally, we harnessed the interpretative potential of SHapley Additive exPlanations (SHAP) library rooted in game theory. This enabled us to unravel the intricate interplay between features and the target output (binding energy), both on a global and local scale. The game theory based Shapely value aims to fairly distribute the player's contribution when they achieve a certain prediction jointly.[44] Moreover, we have extracted the waterfall and force plots upon implementing the waterfall and force functions on the SHAP value in python library to understand the local interpretation for a certain prediction. In the realm of machine learning, SHAP values ($\phi(i)$) quantify the impact of each feature within the model, which collectively shapes the prediction.[45] The Shapley values are calculated for the feature *i* in the model is:

$$\phi(i) = \sum_{k \subseteq M\{i\}} \frac{k!(N-k-1)!}{k!} [f_x(k \cup \{i\}) - f_x(k)]$$
(6.5)

$$f_x(k) = E[f(x)|x_k] \tag{6.6}$$

Where, N is a subset of the features (inputs). M{i} is the set of all possible combinations of features other than *i*. $E[f(x)|x_k]$ represents the expected value of the function on the subset k.

6.3. Results and Discussion

6.3.1. Different Types of Cations and Staging Mechanisms

We have examined various combinations of cations and anions, forming a range of ionic liquid-based electrolytes. Specifically, we have explored alkyl groups spanning from methyl to butyl as shown in Table 6.1. Some of these organic moieties are commonly utilized in battery technology. Notably, we have refrained from incorporating higher-order alkyl groups (higher than butyl) due to their larger volume, which might trigger the exfoliation of the graphite electrode considerably during the charge/discharge cycle. In investigating the binding behaviour of O-alkyl groups, we have included functional cations like methoxy (OMe) and ethoxy (OEt). Furthermore, we have incorporated acyclic structures of ammonium, phosphonium, and sulfonium cations which could accommodate long chain alkyl group without steric hindrance.

Graphite intercalation compounds (GICs) typically consist of graphite layers and intercalant species, which can be cations or anions. The process of GIC formation adheres to a systematic staging mechanism, driven by interplay between attractive and repulsive forces between the intercalant molecules and the graphite. Graphene layers in graphite are held together by strong van der Waals forces, requiring the overcoming of these forces for intercalation to occur. Various experimental and computational studies have unveiled different stages of GICs during charge and discharge cycles.[46,47] Staging is quantified by the stage index, indicating the count of unintercalated graphene layers between intercalated ones. The stage-n system signifies the "n" number of graphene sheet present and "n-1" empty host gallery presents between intercalated layers. For example, stage-1 GICs involve intercalation after each graphene layer, while stage-2 corresponds to every second empty layer, and stage-3 and stage-4 consist of two and three empty galleries, respectively. Thus, we explored four staging mechanisms for ion intercalation: stage-1, stage-2, stage-3, and stage-4. These mechanisms are applied to graphite models, such as a 6×6

× 2 supercell with 288 carbon atoms for stage-n (n = 1, 2, and 4), and a 6 × 6 × 3 supercell with 432 carbon atoms for stage-3. Stoichiometry considerations allow a maximum of four ions per gallery, leading to variations in ion count among the models. Demonstrating this with BF₄ anions intercalation, the generalized formula unit [C₂₈₈(BF₄)_m] represents stage-1 (m = 4, 8, 12, 16), stage-2 (m = 2, 4, 6, 8), and stage-4 (m = 1, 2, 3, 4) as shown in Figure 6.2-6.4. For stage-3, it becomes C₄₃₂(BF₄)_m with m = 2, 4, 6, 8 (Figure 6.5). These anions are stabilized through the anion- π interaction inside the graphite electrode.[48] Similar staging models have been considered for the cation's intercalation into the graphite anode electrode as well.

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**Figure 6.2:** Pictorial representation of different BF₄ anion intercalated stage-1 graphite system, (a)  $C_{288}(BF_4)_4$ , (b)  $C_{288}(BF_4)_8$ , (c)  $C_{288}(BF_4)_{12}$ , and (d)  $C_{288}(BF_4)_{16}$ . Where, the brown color carbon represents the graphite layers, green (B), and pink (F).

(a) analysaksanalitatisais	(b)	(c) <del>。</del>	(d)		
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	0-00-00-00-00-00-0	0-40-40/40/42/42/42/42/42/40/40/40/40/40-40-0	0-09-000000000000000000-00-0		

**Figure 6.3:** Pictorial representation of different  $BF_4$  anion intercalated stage-2 graphite system, (a)  $C_{288}(BF_4)_2$ , (b)  $C_{288}(BF_4)_4$ , (c)  $C_{288}(BF_4)_6$ , and

(d)  $C_{288}(BF_4)_8$ . Where, the brown color carbon represents the graphite layers, green (B), and pink (F).



**Figure 6.4:** Pictorial representation of different  $BF_4$  anion intercalated stage-4 graphite system, (a)  $C_{288}(BF_4)_1$ , (b)  $C_{288}(BF_4)_2$ , (c)  $C_{288}(BF_4)_3$ , and (d)  $C_{288}(BF_4)_4$ . Where, the brown color carbon represents the graphite layers, green (B), and pink (F).



**Figure 6.5:** Pictorial representation of different  $BF_4$  anion intercalated stage-3 graphite system, (a)  $C_{432}(BF_4)_2$ , (b)  $C_{432}(BF_4)_4$ , (c)  $C_{432}(BF_4)_6$ , and (d)  $C_{432}(BF_4)_8$ . Where, the brown color carbon represents the graphite layers, green (B), and pink (F).

# 6.3.2. Data Pre-Processing and Features Engineering

Predicting binding energies (BEs) of different types of cations using a trained ML model presents a formidable challenge. To mitigate this complexity, we meticulously constructed a well-balanced and diverse dataset, ensuring uniformity in the training set. This approach promises that the ML predictions remain unbiased toward BEs of specific cation.[49,50] To achieve this, we introduced a combination of BEs from

different stages into the training dataset, deviating from a strictly monotonic dataset of a particular stage. For each cation we have sixteen BEs values for all the stages and we have considered 55 cations, hence we need to predict the 880 (55*16=880) BE values using ML algorithms. For that we have considered the training dataset of 169 DFT-calculated BE values. Approximately 20% of the DFT-derived dataset is used as training data points, allowing the machine to be effectively trained. Random division of our training dataset allocates 80% of the data to the train subset and the remaining 20% to the test subset.

To achieve precise BE predictions, we have meticulously incorporated both intercalant (cation) and intercalate (graphite host material) features. Our approach encompasses both molecular and elemental characteristics of cations, as highlighted in Table 6.2, to tailor BEs by modulating cations. Elemental features were sourced from the Correlated Based Features Vector (CBFV) library.[51] This holistic comprehension of feature attributes greatly accelerates the ML process. Assessing feature correlations is a potent strategy to expedite BE predictions. Several strong correlations emerged (Figure 6.6) such as between the total energy of cation and molecular weight (PCC=0.99), molecular weight and number of cations (PCC=0.94), total energy of cation and number of cations (PCC=0.92), and average polarizability and average 1st ionization potentials (PCC=0.92). Therefore, features such as total energy of cation, molecular weight, and average polarizability of cations were excluded from the dataset, retaining number of cations and average 1st ionization potentials in the training dataset. These coefficients serve as a guide for us, aiding in the decision of retaining or discarding feature-to-feature and feature-to-target relationships.

Intercalate features	Intercalant features (Cation)				
(Graphite)	Molecular features	Elemental features			
a. Stages	c. Number of cations	k. Avg. ionic radius (Å)			
b. Number of galleries	d. Molecular weight (g/mol)	1. Avg. Pauling electronegativity			
	e. HOMO energy (eV)	m. Avg. polarizability (Å ³ )			
	f. LUMO energy (eV)	n. Avg. 1 st ionization potentials (kJ/mol)			
	g. Dipole moment (D)	o. Avg. number of valence electrons			
	h. Total energy of				
	cation (eV)				
	i. Number of hetero				
	atoms				
	j. Average (avg.)				
	charge ( e ) on hetero				
	atom				

**Table 6.2:** Features of the intercalant and intercalate systems.



**Figure 6.6:** Pearson's correlation matrix between all features (features are listed in Table 6.2) and target BE (p).

The refined feature correlation plot, in Figure 6.7, depicts the postreduction scenario. While a PCC of 0.92 may not signal highly correlated features, our prediction performance distinctly improved after excluding features at this PCC value. Furthermore, positive and negative PCC values highlight linear and inverse correlations with the target variable (BE). In the correlation matrix, vivid blue and red colours represent strong positive and negative correlations, while grey denotes absence of correlation.



**Figure 6.7:** Reduced Pearson's correlation matrix for features (features are listed in Table 6.2) and target BE (p).

# 6.3.3. Machine Learning Algorithms

We applied eight ML algorithms to our training dataset for model training. To optimize the performance of the ML model, we harnessed hyperparameter tuning techniques using the RandamizedSearchCV method from the scikit-learn package.[52] Hyperparameters are unique to each ML model and were tuned accordingly. Subsequently, the optimized models were tested on our separate test dataset, and their performance was evaluated through calculation of RMSE and MAE. Smaller RMSE and MAE values were indicative of superior algorithms. Figure 6.8 illustrates the RMSE and MAE for each ML algorithm, with blue and red bars representing RMSE and MAE values, respectively. Figures 6.8 depicts the train and test errors of all considered algorithms. Among these considered

algorithms, the XGBR and GBR algorithms showcased minimal RMSEs of 0.15 and 0.14 eV, coupled with low train RMSEs of 0.02 and 0.01 eV, respectively. Other algorithms are not able to perform well for the predications of BEs of cations. The LGBM regression model has been considered as it is a powerful ensemble learning algorithm. However, the test RMSE (0.35 eV) is higher (Figure 6.8) compared to the XGBR and GBR model (0.15 and 0.14 eV). Although the RFR model's train and test RMSEs are closer at around 0.30 and 0.32 eV, indicating its potential for accurate BE prediction, however, its relatively high train RMSE may limit its overall performance. Considering all the ML models, both XGBR and GBR emerged as suitable algorithms for accurate prediction of BEs.



**Figure 6.8:** The RMSEs and MAEs of eight considered ML models for the (a) train and (b) test data set. The scatter plots of ML predicted vs. DFT calculated binding energies for (c) XGBR and (d) GBR models.

The MAEs of all algorithms follow the same trend as the RMSEs. Notably, our observed RMSE values are very close with the range of the conventional DFT error (0.09 to 0.13 eV).[53,54] Interestingly, our predicted BEs are at the DFT accuracy level, validating the robustness of our results.

In order to comprehensively assess the stability and generalizability of our model, we employed the leave-one-out cross-validation (LOOCV) technique (details provided in section 1.8.6.2, chapter 1). The computed average RMSEs ( $\overline{RMSEs}$ ) for the XGBR and GBR models were found to be 0.19 and 0.20 eV, respectively. These average RMSEs align remarkably well with the RMSEs obtained from our randomly partitioned test dataset, which were 0.15 eV for XGBR and 0.14 eV for GBR. Consequently, our meticulously evaluated ML models (XGBR and GBR) exhibit impressive stability and generalizability. These models exhibit a consistent and dependable performance even when applied to unknown datasets for the prediction of BEs of cations.

## 6.3.4. Prediction and Validation of Binding Energies of Cations

In this section, we harnessed the optimized hyperparameters from both the XGBR and GBR ML algorithms to predict the BEs of the unknown cations. Our predictions closely aligned with twenty-four DFT-calculated values covering diverse organic moieties across different stages and a variety of cation counts, as tabulated in Table 6.3.

**Table 6.3:** XGBR and GBR predicted vs. DFT calculated cations BE of different organic moieties-based cations with their various stages. The structure corresponding to the ID of the cation is given in Table 6.1.

	Organia	Cations	No. of	ML p	redicted	DFT	Error   (eV)	
Stages	Maiatian			BEs	s (eV)	calculated		
	woreties	(11)	Cations	GBR	XGBR	BEs (eV)	GBR	XGBR
	Pyrrolidinium	$P_{\rm Vr}14~(16)$	8	-1.47	-1.45	-1.68	0.21	0.23
	i ynonannann	1 y114 (10)	16	-2.20	-2.19	-2.01	0.19	0.18
			4	1.19	1.20	1.34	0.15	0.14
1	Pyridinium	N-Et (12)	8	-0.06	-0.05	0.02	0.04	0.03
1			16	-0.84	-0.93	-0.52	0.32	0.41
	Piperidinium	N1(EtOEt) (9)	4	-0.67	-0.59	-0.35	0.32	0.24
	Imidazolium	DMPI (51)	8	-3.14	-3.17	-3.58	0.44	0.41
	Pyridinium	N-Et (12)	2	1.52	1.44	1.47	0.05	0.03
			6	-0.59	-0.59	-0.56	0.03	0.03
	Piperidinium	N1(EtOEt)	2	-0.51	-0.44	-0.31	0.20	0.13
2		(9)	4	-2.18	-2.08	-1.97	0.21	0.12
	Imidazolium	DMPI (51)	2	-2.46	-2.41	-2.51	0.05	0.10
			6	-3.85	-3.81	-4.00	0.15	0.19
	Pyrrolidinium	Pyr14 (16)	6	-2.28	-2.32	-2.36	0.08	0.04
	Pyridinium	N-Et (12)	6	-0.60	-0.59	-0.52	0.08	0.07
3			8	-0.80	-0.77	-0.76	0.04	0.01
5	Imidazolium	DMPI (51)	4	-3.84	-3.88	-4.04	0.20	0.16
			6	-3.96	-3.92	-4.26	0.30	0.34
	Pyridinium	N-Et (12)	2	-0.30	-0.26	-0.16	0.14	0.10
			4	-0.69	-0.59	-0.79	0.10	0.20
4	Piperidinium	N1(EtOEt)	2	-2.72	-2.16	-2.34	0.38	0.18
	- pertaintaint	(9)	3	-2.63	-2.56	-2.56	0.07	0.00
	Pyrrolidinium	Pyr14(16)	1	-0.92	-0.65	-0.62	0.30	0.03
	,,,	·	2	-2.17	-2.11	-2.21	0.04	0.10

The absolute error (difference between ML predicted and DFT calculated values) of each algorithm are quite acceptable. Upon scrutinizing the error analysis, it emerged that the XGBR model exhibited a higher number of

entities with lower errors compared to the GBR model. While the test RMSEs of both ML models (XGBR and GBR) were comparable, the XGBR model demonstrated superior performance with respect to the DFT-calculated values. This leads us to conclude that the XGBR model emerged as the most fitting choice for predicting the BEs of cations. Using the optimized parameters of the XGBR model, we achieved successful predictions of 880 unknown BEs of cations as shown in Figure 6.9. Positive BEs are observed when fewer cations are intercalated between graphite layers, signifying the expansion of galleries between graphene sheets requiring greater forces that the cation-graphite interaction fails to balance. With an increased numbers of cations for a given stage, the predicted BE values indicate of stable binding (negative binding energies). In certain cases, such as with an ammonium-based cation (cation ID=29) bearing the CH₂CN functional group, the positive BE observed in Figure 6.9 signifies that the forces of interaction between graphite and cation are insufficient to counteract the forces between two adjacent graphite layers. Overall, 880 BEs of cations are predicted using the XGBR model for further analyses and insights.



**Figure 6.9:** The ML predicted binding energies of (a) stage-1, (b) stage-2, (c) stage-3, and (d) stage-4 intercalated cations where the bar indicates the range of average binding energy of the cation as the number of cations

changes. The structure corresponding to the ID of the cation is given in Table 6.1.

#### 6.3.5. SHAP Analysis

#### **6.3.5.1.** Global Features Importance

In this study, we employed machine learning algorithms that fall within the category of black box models. This implies that understanding the inner workings and the relationships between features and output predictions can be quite intricate. To surmount this challenge, we embraced an interpretable model that facilitates insights into both local and global patterns for specific features. We harnessed the game theorybased SHapley Additive exPlanations (SHAP) library, utilizing our bestfitting XGBR algorithm. SHAP offers a window into the global feature contributions, presenting us a clear comprehension of the elements influencing the predictions made by our ML models. The global feature importance is portrayed through the blue bars in Figure 6.10a. Notably, the number of cations, staging number, and the energy of the LUMO of cations emerge as the top three most contributing features. As observed in the broader BEs prediction, the binding energy exhibits shifts with changes in the number of cations, implying a robust relationship between cation count and binding energy. Similarly, the stage of intercalation showcases a pronounced connection with BE. Altering the loading pattern of cations systematically influences the formation of various stages, which in turn affects the BEs upon cation intercalation. These organic cations achieve stabilization within the graphite structure through charge transfer between the graphitic layer and the cations. The energies of HOMO and LUMO play a pivotal role in enabling this charge transfer process. Particularly, LUMO emerges as a stronger contributor compared to HOMO, which could be attributed to the phenomenon of charge acceptance from the graphitic layer. Other features also contribute to the prediction of BEs of cations, albeit with mean SHAP values less than 0.1.



**Figure 6.10:** (a) Visualization plots of SHAP global features importance of each feature and (b) beeswarm plot, where every dot corresponds to an individual data point associated with a specific feature.

Furthermore, we illustrate the beeswarm plot of the SHAP analysis in Figure 6.10b. The nature of global feature importance and the beeswarm plot of SHAP analysis align, while the individual feature values of each data point can be adjusted by the beeswarm plot. The vertical color-coded lines signify the dispersion of feature values, highlighting the similarity of attributed importance for a given feature. Blue and red dots indicate low and high feature values, respectively. The horizontal axis of the plot represents the positive and negative impact on model predictions. The SHAP values linked to the number of cations are influenced predominantly by a combination of lower and less median feature values. Meanwhile, SHAP values associated with stage and cation LUMO energy display broader dispersion, influenced by both low and high feature values. Overall, the insights from the global feature importance and beeswarm plot of SHAP analysis emphasize that the most influential factors affecting the BEs of cations are the number of cations, staging number, and the LUMO energy of cations.





**Figure 6.11:** (a) SHAP waterfall plot and (b) force plot for the most accurately predicted binding energy of the pyrazolium based cation of BM (1), where the cation ID referred to the Table 6.1.

Similarly, we employed SHAP to explore the individual feature contributions for a specific cation. Figure 6.11 showcases SHAP visualization plots that highlight the precise prediction of binding energy (BE) for the pyrazolium cation-based BM (1), with minimal deviation (predicted BE: -1.067 eV vs. DFT calculated BE: -1.068 eV). In Figure 6.11a and b, the SHAP waterfall and force plots respectively illustrate the instance of the pyrazolium-based BM cation. In the waterfall plot, positive contributions are represented by red bars, while negative contributions are depicted by blue bars. In this plot, the baseline (average expected value) is denoted as E[f(x)] = -1.09, and the final predicted value is f(x) = -1.067. Each row's SHAP value signifies the outcome of the interaction between the individual feature value and the final prediction value. For instance, in

the context of this specific instance, stage 1 exhibits a positive effect on the target BE, leading to an increase of 0.85 in the prediction from the baseline. Conversely, having 8 cations exerts a negative effect on the target BE, resulting in a decrease of 0.69 in the prediction from the baseline. Moreover, the cation's LUMO (eV) of -1.85 and dipole moment (D) of 5.54 influence the BE prediction positively and negatively, causing increases of 0.47 and decreases of 0.35 from the baseline, respectively. Furthermore, the significance of the stage as a feature is magnified for this instance, although it ranks as the second most impactful feature in the global feature importance plot. Quantitatively, the final predicted value f(x) can be computed as the sum of the average prediction of all observations (E[f(x)]) and the sum of all SHAP values ( $\phi_i$ ) according to equation 6.7.

$$f(x) = E[f(x)] + \sum_{i=1}^{N} (\phi_i)$$
(6.7)

Where, N is the subset of the features and  $\phi_i$  can be calculated from equation 6.5. Figure 6.11b illustrates the SHAP force plot, which qualitatively complements the information from the waterfall plot. In the force plot, blue-coloured features shift the model's prediction from higher to lower (towards the left), while red-coloured features influence the model's prediction from lower to higher (towards the right). In the case of this specific instance, both red and blue features contribute equally to predicting the model's output prediction. Moreover, the explanations of our extracted waterfall and force plots from SHAP are well followed with the previous interpretable ML reports. [55,56] Likewise, similar SHAP waterfall and force plots are presented in Figure 6.12 for the thiazoliumbased cation N-Et (22). Notably, this cation exhibited the most significant deviation in prediction (ML predicted BE: -0.647 eV vs. DFT calculated BE: -1.047 eV). From the SHAP waterfall plot, staging number of graphitic layers provides the highest negative SHAP value of 0.65 compared to others features. Whereas, in most accurately predicted system

of BM (1) cation, the staging number of graphite contributed most positive SHAP value. In the case of force plot, we observed that red colours features contributed (towards right) more compared to the blue colours (towards left) features. Overall, the SHAP waterfall and force plots provided the valuable insights of individual features for the prediction of BEs of pyrazolium and thiazolium based cations.



**Figure 6.12:** (a) SHAP waterfall plot and (b) force plot for the most deviated binding energy prediction of thiazolium based cation of N-Et (22), cation ID represented to the Table 6.1.

# 6.3.6. Voltage Calculations

It is important to understand which pairs of cations/anions combinations are suitable for the providing of better electrochemical properties. For this, we considered calculating the voltage property of the battery upon coupling between cations intercalated graphite anode and anions intercalated graphite cathode. The discharge voltage can be calculated using the following cathodic and anodic reactions.

Cathodic reaction:  $G(Anion)_{\gamma} + \gamma e^- \leftrightarrow \gamma Anion + G$  (6.8)

Anodic reaction:  $G(Cation)_x \leftrightarrow xCation + G + xe^-$  (6.9)

Where, the x and y are the number of cations and anions, respectively. G is the graphite electrode. In this case, equal numbers (x=y) of ions are intercalated into the graphite electrodes, the overall reaction would be as follows,

Overall: 
$$G(Cation)_x + G(Anion)_y \leftrightarrow xCation + yAnion + 2G$$
  
(6.10)

The cell voltage can be calculated from the Nernst equation using the Gibbs free energy change of the overall reaction (more details in section 4.3.5.2, chapter 4). Thus, the average voltage (V) would be as follows,

$$V = \frac{\{E_{[G(Anion)_{\mathcal{Y}}]} + E_{[G(Cation)_{\mathcal{X}}]}\} - \{x \in Cation + \mathcal{Y} \in Anion + 2E_G\}}{z}$$
(6.11)

However, this voltage equation 6.11, can be modified using the binding energies of both cations  $[(E_B)_{Cation})]$  and anions  $[(E_B)_{Anion})]$  from equation 1 and 2. Hence, the modified voltage equation would be as follows,

$$V = \frac{x(E_B)_{Cation} + y(E_B)_{Anion}}{z}$$
(6.12)

Where, z represents the number of electrons transfer. As the equal numbers of ions intercalated (x = y = z) then the final voltage equation can be changed as follows,

$$V = [(E_B)_{Cation} + (E_B)_{Anion}]$$
(6.13)

To solve the equation 6.13, we also need BEs of anions as calculated using the DFT (Figure 6.13). On the other hand, the ML predicted BEs (Figure 6.9) of cations are used to get the voltage. Based on these values, we have effectively computed a comprehensive set of 20,790 voltages [sum of 7,920 self-stages voltages (total of 495 ILs and each IL provided 16 selfstages voltages, hence total self-stages voltages would be (16*495=7,920) and 12,870 mixed stages voltages (each IL provide 26 mixed voltages irrespective of stages with identical number, hence total mixed-stages voltages would be (26*495=12,870)], encompassing various combinations of stages with equal numbers of ions.



**Figure 6.13:** DFT calculated anions binding energies of different stages such as (a) stage-1, (b) stage-2, (c) stage-3, (d) stage-4 with varying the number of ions.

These ML+DFT calculated voltages have been categorized into three distinct ranges: high voltage (HV), moderate voltage (MV), and low voltage (LV). Different voltage ranges considered to distinct them: high voltage (4.0 < HV < 7.0), moderate voltage ( $2.5 < MV \le 4.0$ ), and low voltage ( $0.001 < LV \le 2.5$ ). Figure 6.14 illustrates a set of parallel plots, showcasing the fluctuation of voltages in relation to variations in ion numbers and stages for all self-stages.



**Figure 6.14:** The parallel set plots display the self-stages (identical stages for both cations and anions) voltages calculated using ML+DFT for (a) stage-1, (b) stage-2, (c) stage-3, and (d) stage-4 of the considered cations and anions-based ILs electrolytes in DGBs. The cations range from 0 to 54 (refer to Table 6.1) and voltages below 2.0 V have been excluded for clarity. Moderate voltage (MV) and low voltage (LV) patterns observed in stage-1 are consistent across the other stages as well.

During the fully charged state of the batteries, the ions predominantly adhere to a stage-1 type of intercalation, as this process can accommodate a maximum number of ions. The corresponding voltages for batteries in this fully charged state are depicted in Figure 6.15. Significantly, we have effectively devised 495 distinct DGBs, each associated with specific voltage values. Among these DGBs, 69 belong to the high voltage (HV) category, 230 to moderate voltage (MV), and 196 to low voltage (LV). Notably, the HV DGBs are predominantly based on the intercalation of  $BF_4$  and  $PF_6$  anions with all possible types of cations considered (excluding pyridinium and thiazolium based cations). Imidazolium and piperidinium based cations offer moderate to high voltage when coupled with all the considered anions. In a similar vein, FSI, TFSI, FSI-CH₃, and AlCl₄ anions provide a range of low to moderate voltages when paired with diverse cations. The DCA, OTf, and sulfate anions mainly contribute to the low voltage spectrum when coupled with cations. Furthermore, mixed-stage voltages are depicted in Figure 6.16. This visualization aids experimental researchers in comprehending the precise staging intercalation mechanism adopted by individual ions, evident through their respective voltage values. From the prior reports, it has been observed that anions play a pivotal role in determining the comprehensive electrochemical properties of DIBs, a similar trend evident in our study as well.[46,47] Notably, interesting findings arise from the cationic perspective, wherein aromatic-based imidazolium cations exhibit enhanced voltage performance compared to their non-aromatic counterparts. The high voltage observed in the aromatic imidazolium cations-based system can be attributed to the presence of a robust  $\pi^+$ - $\pi$ interaction. Kim and coworkers have demonstrated that the  $\pi^+$ - $\pi$ interaction combines characteristics of both conventional  $\pi$ - $\pi$  and cation- $\pi$ 

54 53 5	2.15	2.66	0.65	1.20	1.38	0.90	0.10	0.94	1.16	-15
23	2.15	2.40	0.45	2100						
5		2.46	0.45	1.00	1.18	0.69	0.10	0.73	0.96	
N	3.05	3.36	1.35	1.90	2.08	1.59	0.80	1.63	1.86	
15	5.97	6.28	4.27	4.82	5.00	4.52	3.72	4.56	4.78	
20	3.20	3.51	1.50	2.05	2.23	1.74	0.95	1.78	2.01	
49	5.24	5.56	3.55	4.09	4.28	3.79	3.00	3.83	4.06	- 2.0
48 4	4.74	5.05	3.04	3.59	3.77	3.29	2.49	3.33	3.55	
17 4	4.88	5.20	3.18	3.73	3.91	3.43	2.64	3.47	3.70	
16 4	4.85	5.16	3.15	3.70	3.88	3.40	2.61	3.44	3.66	
5	4.42	4.75	2.72	3.27	3.45	3.08	2.17	3.10	3 35	
4	4.42	4.25	2.24	3.79	3.45	2.49	2.17	3.00	3.75	
3 42	3.93	4.24	2.23	2.78	2.96	2.48	1.68	2.52	2.74	- 2.5
41	3.82	4.13	2.12	2.67	2.85	2.37	1.57	2.41	2.63	
40	3.80	4.12	2.11	2.66	2.84	2.35	1.56	2.39	2.62	
39	3.67	3.98	1.97	2.52	2.70	2.21	1.42	2.25	2.48	
38	3.58	3.89	1.88	2.43	2.61	2.13	1.33	2.17	2.39	
37	4.21	4.52	2.51	3.06	3.24	2.75	1.96	2.79	3.02	
36	3.78	4.09	2.08	2.63	2.81	2.33	1.54	2.37	2.59	- 3.0
32	4.20	4.52	2.51	3.06	3.24	2.75	1.96	2.79	3.02	
34	4.07	4.39	2.38	2.92	3.11	2.62	1.83	2.66	2.89	
33	3.49	3.81	1.80	2.35	2.53	2.04	1.25	2.08	2.31	
32	4.13	4.44	2.43	2.98	3.16	2.68	1.88	2.72	2.94	
31 3	4.13	4.45	2.43	2.98	3.16	2.68	1.89	2.72	2.95	5.5
08	4.40	4.71	2.70	3.25	3.43	2.95	2.15	2.99	3.21	-35
6	1.43	1.74	0.27	0.28	0.46	0.03	0.82	0.01	0.24	
8	3.68	3.99	1.98	2.52	2.71	2.22	1.43	2.26	2.49	
N N	4.13	4.45	2.44	2.99	3.10	2.00	1.89	2.72	2.95	
cat ⁶ 2	4.59	4.71	2.70	2.99	3.45	2.94	1.89	2.98	2.95	
5 24	4.73	3.05	2.70	3.24	3./7	2.28	2.49	2.08	3.00	- 4.0
1S	4.69	5.01	2.99	3.54	3.72	3.24	2.45	3.28	3.51	- 4.0
	2.86	3.18	1.17	1.72	1.90	1.41	0.62	1.45	1.68	
12	3.04	3.36	1.34	1.89	2.07	1.59	0.80	1.63	1.86	
5	3.21	3.53	1.52	2.07	2.25	1.76	0.97	1.80	2.03	
1 1	3.33	3.64	1.63	2.18	2.36	1.88	1.09	1.92	2.14	
18	3.88	4.20	2.18	2.73	2.91	2.43	1.64	2.47	2.70	- 4.5
1	3.90	4.21	2.20	2.75	2.93	2.45	1.65	2.49	2.71	
16	4.57	4.89	2.88	3.42	3.61	3.12	2.33	3.16	3.39	
5	3.65	3.97	1.96	2.50	2.69	2.20	1.41	2.24	2.47	
14	3.73	4.05	2.04	2.58	2.77	2.28	1.49	2.32	2.55	
13 1	3.74	4.06	2.05	2.59	2.78	2.29	1.50	2.33	2.56	
1	3.32	3.63	1.62	2.17	2.35	1.86	1.07	1.90	2.13	- 5.0
1	3 3 3 2	3.63	1.70	2.55	2.51	1.87	1.25	1.91	2.29	
6	3.47	3.79	1.78	2 33	2.51	2.02	1.23	2.06	2.29	
00	4.66	4.97	2.96	3.51	3.69	3.21	2.42	3.25	3.47	
	4.36	4.67	2.66	3.21	3.39	2.91	2.11	2.95	3.17	
9	4.06	4.37	2.36	2.91	3.09	2.61	1.81	2.65	2.87	- 5.5
in .	4.27	4.58	2.57	3.12	3.30	2.82	2.02	2.86	3.08	
4	4.37	4.69	2.68	3.22	3.41	2.92	2.13	2.96	3.19	
m	3.44	3.76	1.74	2.29	2.47	1.99	1.20	2.03	2.26	
N	3.51	3.82	1.81	2.36	2.54	2.06	1.27	2.10	2.32	
-	3.94	4.25	2.24	2.79	2.97	2.49	1.69	2.53	2.75	
0	3.66	3.97	1.96	2.51	2.69	2.20	1.41	2.24	2.47	- 6.0

**Figure 6.15:** Voltages of different combination of cations and anions for the fully charged state of stage-1 intercalation process with maximum ions intercalation. Where the cations IDs are referred to Table 6.1.

interactions, although they have not explicitly represented their combined effect.[57,58] Importantly,  $\pi^+$ - $\pi$  interaction is significantly stronger than conventional  $\pi$ - $\pi$  interaction and notably weaker than cation- $\pi$  interaction. As a result, aromatic imidazolium cations exhibit an exceptionally strong  $\pi^+$ - $\pi$  interaction compared to their non-aromatic counterparts. Conversely, non-aromatic cations show limited interactions. While strong interactions can boost electrochemical properties, they can compromise battery reversibility and leading to reduce the cycle numbers for DIBs. Hence, selecting appropriate aromatic and non-aromatic cations is essential to balance elevated voltage and sustained cycle numbers.



**Figure 6.16:** The parallel set plots for the mixed-stages (different stages for cations and anions) voltages calculated using ML+DFT method and voltages below 2.0 V have been excluded for clarity. Cations IDs are referred to Table 6.1.

Additionally, we have conducted a comparative analysis between our ML+DFT calculated voltage data for various organic moieties-based
cations and anions and previous experimental findings (as summarized in Table 6.4). It's worth noting that direct comparisons for larger voltage values were restricted due to the limited availability of experimental voltage data. Nonetheless, our calculated results fall well within the range of experimental voltage values, reaffirming the reliability and accuracy of our predictions. Overall, the extensive collection of computed voltages presented in our study serves as a valuable roadmap for experimental researchers aiming to identify and create optimal electrolytes using ILs to improve the fabrication of electrochemical devices. We believe that our results hold significant practical implications and can be readily applied to advance the development of more efficient and cost-effective energy storage devices.

**Table 6.4:** ML+DFT calculated voltages vs. experimental voltages for the ILs electrolytes used in DGBs, where the cation's IDs are referred to the Table 6.1.

Organic	Cations (ID)-	ML+DFT	Experimental
Moieties	Anions (ILs)	Voltage (V)	Voltage (V)
Pyrrolidinium	Pyr14 (16)-TFSI	3.6	3.0-4.2[30]
Imidazolium	EMIM (49)-OTf	3.0	2.2-3.7[59]
	DMPI (51)-AlCl ₄	4.7	3.8-4.4[29]
Piperidinium	N14 (4)-TFSI	3.4	2.5-4.5[60]

## 6.4. Conclusion

In this study, we focused on a diverse set of organic cations-based ionic liquids (ILs), commonly employed as electrolytes in dual-ion battery (DIB) technology. The process of cation intercalation into graphite electrodes is intricate and characterized by distinct staging mechanisms and very few organic cations intercalation have been studied so far. Investigating broad scale organic cations intercalations are challenging due to computational complexity, time constraints, and the sensitivity of

ILs in experimental setups. To address these complexities, we harnessed a supervised machine learning (ML) approach to precisely predict the binding energies (BEs) of cations during their intercalation into graphite anodes. From a selection of eight ML algorithms, the XGBR algorithm emerged as the most suitable, as lowest RMSE of 0.15 eV for predicting BEs from an unfamiliar dataset. Our observed RMSE values are close to the conventional DFT error (0.09 to 0.13 eV). Interestingly, our predicted BEs are in good accuracy with the DFT level, indicating the robustness of our results. Using the optimized parameters of the XGBR model, we succeeded in predicting 880 BEs across a spectrum of cations, encompassing intercalation of varying stages of graphite. Our ML predictions concurred nicely with DFT-calculated outcomes for a range of organic moieties across different stages and varying cation numbers. To ensure model reliability and independent verification, we applied leaveone-out cross-validation (LOOCV) techniques. Additionally, we harnessed the game theory based SHAP library to illuminate the intricate relationships between global and local features influencing the prediction of BE. With our ML-predicted BEs of cations and DFT-calculated BEs of anions, we calculated voltages by considering cation and anion intercalation into graphite anode and cathode. This effort yielded 495 new graphite-based DIBs, featuring a spectrum of voltage ranges. Among these, 69, 230, and 196 fell within the high voltage (HV) range of 4.0 <HV < 7.0, moderate voltage (MV) range of  $2.5 < MV \le 4.0$ , and low voltage (LV) range of  $0.001 < LV \le 2.5$ , respectively. Our computed ML+DFT voltages demonstrated strong agreement with experimental findings. Notably, ILs based on BF₄ and PF₆ anions exhibited high voltage behaviour when coupled with most cations (except pyridinium and thiazolium). Similarly, other anions, including FSI, TFSI, FSI-CH₃, and AlCl₄, demonstrated a range of low to moderate voltages when combined with diverse cations. Overall, our extensive dataset of computed voltages can serve as a valuable guidepost for experimental researchers seeking to

optimize electrolytes using ILs, thus enhancing the design of electrochemical devices. We believe that our outcomes carry substantial practical implications, readily applicable to advancing the development of more efficient and cost-effective dual-ion based energy storage devices.

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## Scope for Future Works

## 7.1. Scope for Future Works

The electrochemical window (ECW) is one of the most important parameters of ionic liquids (ILs) which determines the overall stability and voltage of the batteries. This doctoral thesis is about the development of computational techniques/methods to calculate the ECW of ILs based electrolytes important for dual-ion batteries (DIBs). For this, different computational techniques have been established to calculate the ECWs of ILs accurately. Among the various techniques, we report the classical MD followed by DFT (MD+DFT) is the most suitable one to calculate the ECW values accurately. We have demonstrated that the ECW can be calculated using the cathodic  $(V_{CL})$  and anodic  $(V_{AL})$  limiting potentials of the electrolytes. Therefore, the  $V_{CL}$  and  $V_{AL}$  are crucial parameters to understand the stability of the electrolytes. We have also shown that machine learnings (ML) based techniques can be highly useful to calculate the ECW properties of a large number of ILs based electrolytes. The high throughput screening of ILs is very much possible while combining DFT with ML. The calculation of the individual potentials of  $V_{\text{CL}}$  and  $V_{\text{AL}}$  for the electrolytes using the MD+DFT as well as ML technique can be very effective. Such methods and techniques can also be used to calculate the important properties of ILs for Li-ion batteries among others. However, finding suitable forcefield is very difficult for the classical simulation for all the ILs. To overcome the challenges, the ML-based interatomic potentials can be very effective. Furthermore, AI and deep learning techniques have emerged to find the suitable non-aqueous electrolytes more rapidly, which can help to accelerate the development of high-performance energy storage devices for future energy demand.