We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

6,900
Open access books available

185,000
International authors and editors

200M
Downloads

154
Countries delivered to

Our authors are among the

TOP 1%
most cited scientists

12.2%
Contributors from top 500 universities

BOOK CITATION INDEX
CLARIVATE ANALYTICS
INDEXED

WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Computational Analysis of Nanostructures for Li-Ion Batteries

Jameela Fatheema and Syed Rizwan

Abstract

Due to the energy crisis, the focus on the study of new materials has increased vastly. For the increasing demand of renewable energy, there are different ways suggested to attain that, which include the rechargeable batteries and the need to achieve them at smaller costs and for longtime use. Lithium ion batteries have gained a lot of attention for that specific reason. Along with the experiments, the easier way to understand and increase the efficiency of these materials for LIBs is to study them through simulations and theoretically. Density functional theory (DFT)-based study gives us an insight into the internal workings of the compounds used in lithium ion batteries (LIBs). In this chapter, an analysis of different structures is presented for use in LIBs, which mainly includes carbon nanostructures or nanotubes as well as 2D material graphene. The various ways in which the carbon-based structure is enhanced include doping into the structure, heterostructure of graphene with other 2D materials, and adsorption of atoms like Si onto the surface. The adsorption of Li on these various structures and the varying binding energies and capacity with the changing structure along with the understanding at atomic and nanoscale are mentioned.

Keywords: density functional theory, lithium ion battery, nanostructures, graphene, nanocarbons, adsorption, doping, computational

1. Introduction

We live in a world where most of the daily tasks in our life are dependent on energy like transport and communication over large distances. To satisfy the need for energy we have various sources, some of which are wind energy, solar energy, fossil fuel, nuclear energy, and so much more. For all of these, storage of energy in a device is an important part for which we have several kinds depending on the usage and need. Examples include capacitors, supercapacitors, batteries, fuel cells, flywheel, etc. A battery consists of one or more electrochemical cells and is connected externally to provide power to different appliances such as smartphones, electric car, laptop, etc. the electrochemical cell provides with electrical energy from a chemical reaction [1]. Now, batteries have two main types depending on the fact of rechargeable and non-rechargeable as illustrated in **Figure 1**. Primary batteries are nonrechargeable and provide electricity as soon as the connection is made with an electrical device's electrodes. Primary cell can only be used one time, and once they are discharged, they cannot be charged again and are discarded. Some of the examples of primary batteries are Daniel cell, dry cell, zinc air battery, mercury battery, etc. The usage of primary cell includes a wide range of devices like remote controls,

pacemakers, toys, and clocks [1], whereas secondary battery is rechargeable and needs to be charged first for providence of energy. Secondary batteries can be used for longer time than primary cells, due to their recharging capability as they can go from 100 to 1000 cycles of charge and discharge. There are numerous examples of secondary batteries, which are magnesium ion battery, nickel zinc battery, sodium ion battery, lithium ion battery, etc. [2]. Lithium ion battery has a higher amount of importance in the industry for a number of reasons. The light weight of Li element, that is, density = 0.53 g/cm^3 and the highest electropositive nature in the periodic table has helped in the arranging of battery with high energy density. Still, there are many issues to be addressed for improving the performance [3, 4].

1.1 Lithium-ion battery (LIB)

Lithium-ion battery (LIB) is a type of rechargeable battery in which Li ion moves during discharge from the negative electrode (cathode) to the positive electrode (anode) and then during charging Li ions move back from the anode to the cathode. There are four important components: anode, cathode, electrolyte, and separator [3, 4, 7]. Separator has the main role of keeping the electrodes apart, and, to allow the transport of only the charge carriers which in this case are lithium ions [8, 9]. Electrolyte has an important role in the transport as well and is usually made of lithium salts. Whereas, cathodes are made of lithium compounds like lithium cobaltates and lithium phosphates, and anode materials are usually made of 2D materials and their respective compounds. **Figure 2** shows a schematic representation of LIBs. When a source is supplied for charging of LIB, Li ions travel from the cathode through the electrolyte and separator to the anode and are intercalated into the 2D material. After fully charged, the source can be removed and the discharging starts in which the Li ions are desorbed from the anode and are transported back to the cathode [10]. The 2D materials that are preferred are graphene and carbon-based compounds because of their high conductivity and Li storage capability, not only on defect-free sites but defective as well [9, 11].

1.2 Simulations for LIBS

For a long time, the development and creation of new materials have been due to the experimental procedures, which were based entirely upon the intuition and judgment of the experimental researchers, depending upon the facilities as well as
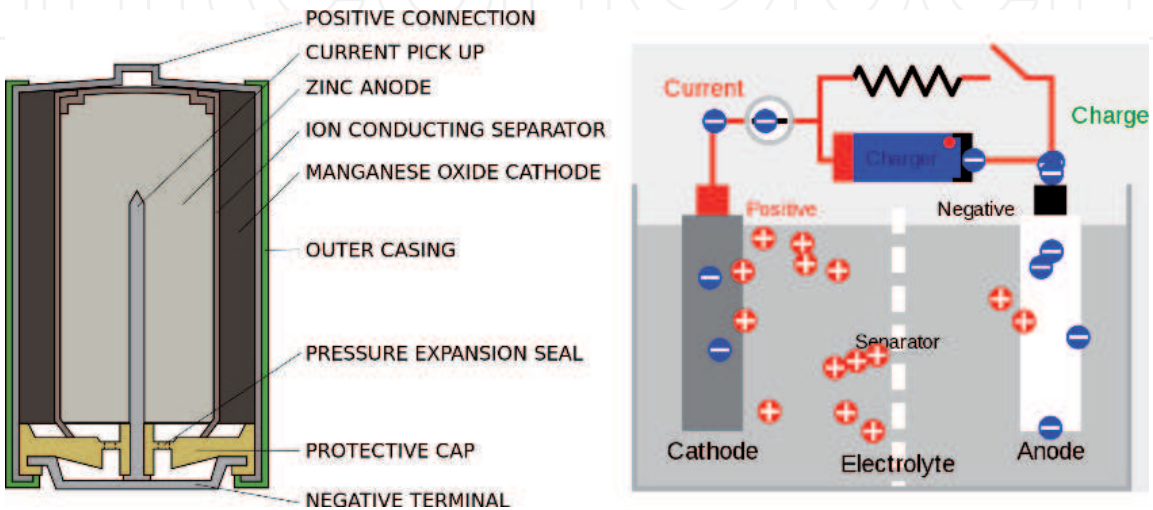

Figure 1.
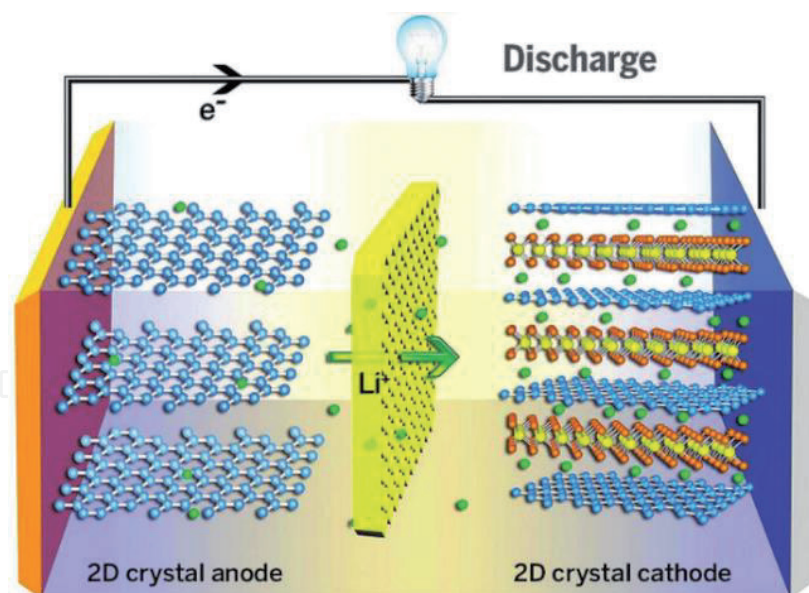*Illustration of (a) alkaline battery as an example of primary battery [5] and (b) general secondary battery [6].*

Figure 2.
A schematic reperesentation of lithium ion battery [10].

the availability of compounds and materials needed for conduction of an experiment. With the passing of time, we have developed computational techniques and codes for investigation of different aspects of a material and how to improve those materials. While the experimental methods are a complete hit in a dark room and waiting for the results to turn out for the best, we can simulate different structures, materials and compounds and alter them to our requirements and desire and then work on how to perform an experiment to get those results. Another way to think is that, when an experiment goes a specific way and we are unable to comprehend the reason, the theoretical calculations and modeling can help us understand on nano and atomic level about the hows and whys. Regarding the lithium ion batteries, there has been a lot of work done to improve its working by studying different materials to be used as a cathode along with studies for improvement of the anode and electrolyte. In this chapter, a brief review of studies made theoretically on nanocarbons for lithium-ion batteries is discussed.

2. Analysis of nanostructures

For the analysis of nanostructures, first, a brief general idea of the computational methods is necessary. There are several computational codes and different theoretical backgrounds that are used for these studies. The two main theories are potential-based methods and density functional theory. Here, we will focus on the DFT-based studies and the understanding of the electronic structure. Density functional theory (DFT) is a quantum mechanical approach to the study of the properties of matter on a microscopic basis that is most prevalent and effective [12]. The fundamental principle of DFT is that the total energy of the system is an exclusive functional of the electron density as given by Kohn-Sham equations [13]. The exchange-correlation potential that is introduced into a system helps to calculate the values accurately for which there are several formalisms, like local spin density approximation (LSDA) and generalized gradient approximation (GGA) [14, 15]. Moreover, including the Hubbard potential increases the accuracy of the system as it accounts for the columbic repulsions of the system [16].

The most important part is the simulation of a structure that will complement the experimental procedures. Then, we proceed to see the movement of electrons in these structures and analyze some of the important characteristics, like voltage

profile, formation energy, density of states, and diffusion of lithium ion. Here, our focus is on carbon-based compounds, which are mainly used as anodes in LIBs, more specifically graphene structures. Following this the doping, adsorption, heterostructures, cluster systems, composites, and other such possibilities used for enhancement of anode materials are conversed.

2.1 Doping mechanisms

One of the important ways to improve the performance of a material is the doping process. Graphene and carbon nanostructures have been doped through various procedures with different elements and studied for use in LIBs. For instance, Yang et al. have done a study on doping of germanium in graphene sheets, resulting in germagraphene and proceeded with observing the adsorption of lithium on different sites. The amount of Li adsorption is shown to be enhanced by doping germanium [17].

Ullah et al. have reported a large capacity anode material for LIBs by doping Be onto the graphene structure and studying the adsorption properties using the SIESTA code [18]. They have simulated single vacancy beryllium doped and double vacancy Be doped graphene structures and then proceeded to study the adsorption of different amounts of Li atoms on top side of the surface as well as bottom side of the surface (**Figure 3**). The doping of Beryllium makes it an electron-deficient system and the adsorption energy goes to −2.53 eV/Li atom and the rise in the capacity up to 2303.295 mAh/g for the Li_8BeC_7 structure. The reason for the huge capacitance is that in mono vacancy structure and divacancy structure the Li atoms get attached easily as the doping of Beryllium reduces the electrons and for divacancy the Li adsorption amount is more than mono vacancy.

Proceeding with Be doping, Ullah et al. have done the dual doping of graphene by modeling boron and beryllium, N and Be, and O and Be co-doped structures [19]. Doping of N and O increases the n-type characteristic while doping of B is for p-type characteristic. As Li is adsorbed onto the structures, it is indicated that the BeB doped structure shows good adsorption as the adsorption is ~3.1 times increased. The specification is that B addition increases the p-type nature of the
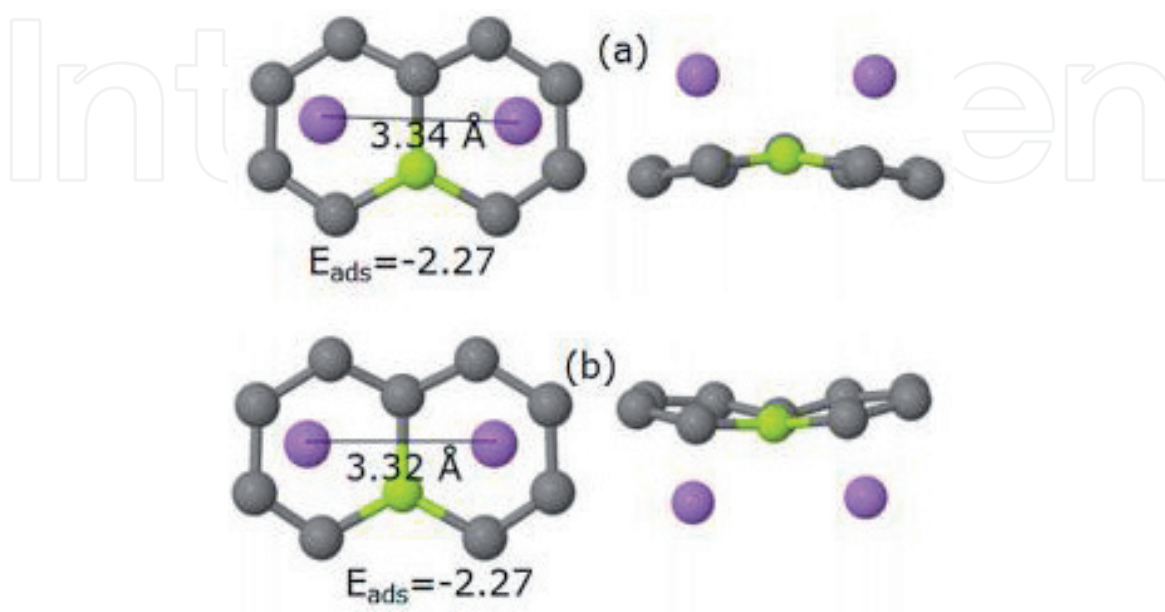

Figure 3.
Li adsorption on Be-doped graphene (top view on left and side view on right): (a) 2 Li atoms with up orientation and (b) 2 Li atoms with down orientation [18].

compound that already contains Be and C and hence the Li ion is adsorbed to the dual doped graphene sheet.

A different morphology-based structure was studied recently, in which graphene nanoribbons doped by B and undoped structures were simulated. The adsorption of Li on both the structures was observed which indicated that the capacity increases from 52 to 783 mAh/g when doped with B. The significance of this study is the fact that boron doping in graphene nanoribbons is more effective than the doping into pristine graphene structures [20].

The adsorption of lithium on undoped graphene and N or B doped graphene was studied indicating that the energy of adsorption is highest for Boron-doped graphene and lowest for Nitrogen-doped graphene [21]. The study was performed using the nudged elastic band method and the concentration for doping of both N and B was 12.5 at%, respectively, as shown in **Figure 4**. The conclusion was that N-doped graphene has better diffusion and desorption qualities than that of pristine graphene and boron doped graphene.

The doping of pyridinic and graphitic nitrogen in a double vacancy graphene structure, that is, 5-8-5 graphene vacancy is studied and the different structures are illustrated in **Figure 5** [22]. The potential surfaces, adsorption of 1 Li, adsorption of more than one lithium, and the diffusion of Li across the structure are investigated. Kong et al. have suggested that 4 pyridinic N doped graphene has good adsorption characteristic for Li as well as the diffusion, and hence it will be useful to synthesize for use as anode in LIBs.

Another point of importance is the amount of nitrogen doping that will be sufficient and what kind of doping will be useful, that is, the sites that are occupied by nitrogen. Yang has studied the nitrogen doping extensively along with the presence of defects and the adsorption of lithium on different structure shown in **Figure 6** [23]. The structures include pristine graphene, single N doping, two nitrogen doped at different sites, single nitrogen with single vacancy, and pyridinic structure with single and double vacancy and pyrrolic structure with single and double vacancy. On all these structures the electrical, magnetic, and adsorption properties are studied. The adsorption energy is more for the pristine graphene and single N doped structure while the energy is in negative for all the structures containing vacancies. Furthermore, the magnetic moment is shown to decrease with the adsorption of Li atom by the formation of a bond between free electrons with the electron in Li. Insert figure of structure.

Moreover, Watanabe et al. studied the upper limit for the nitrogen in carbon materials both theoretically and experimentally [24]. In the experimental study, they have concluded that with any increase in the carbonization temperature, the limit for nitrogen content in N doped carbon structures is decreasing. Moreover, the upper limits of N were found to be 14.32 and 21.66 wt% at 1000 and 900,
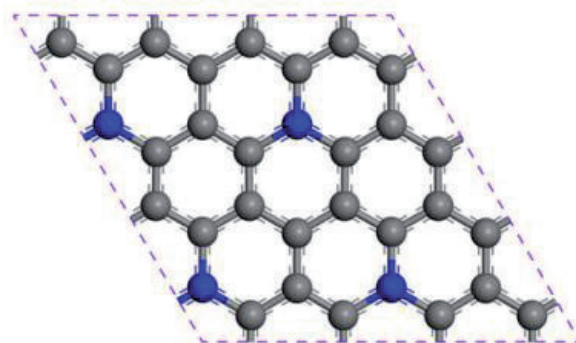

Figure 4.
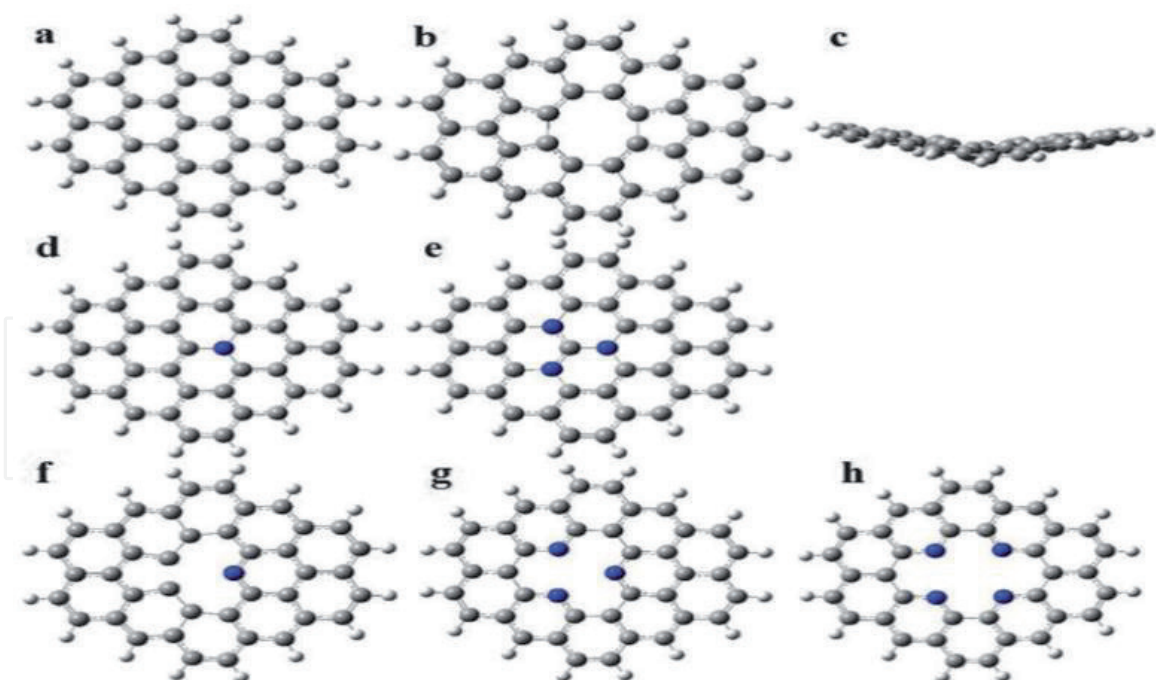*Doped graphene structure (gray color atoms = C and blue color atoms = B or N) [21].*

Figure 5.
(a) Pure graphene, (b) top view of 5-8-5 divacancy graphene, (c) side view of 5-8-5 divacancy graphene, (d) single graphitic N doped graphene, (e) 3 graphitic N doped graphene, (f) 1 pyridinic N doped graphene, (g) 3 pyridinic N doped graphene, and (h) 4 pyridinic N doped graphene [22].
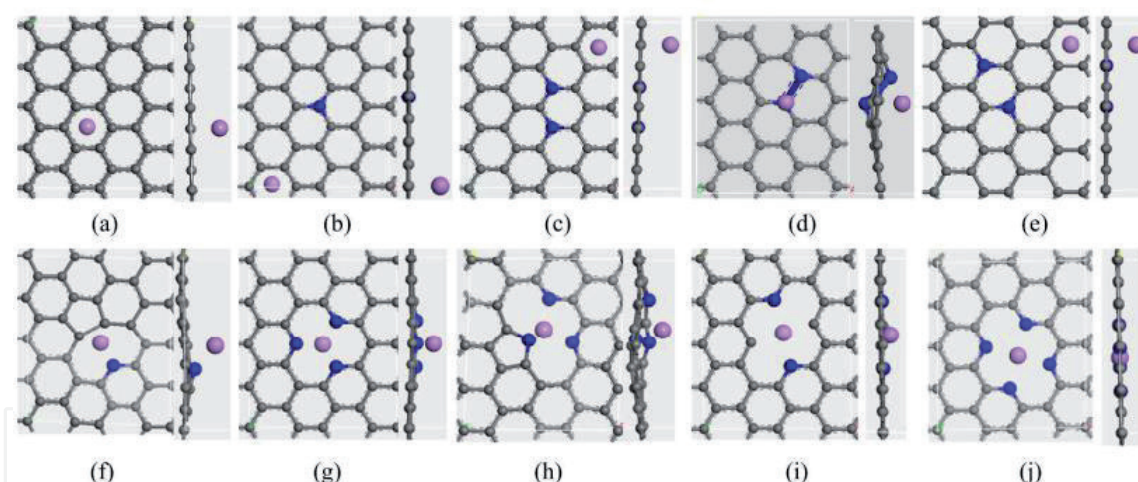

Figure 6.
Top and side view of Li adsorbed structures: (a) pristine graphene, (b) single N doped graphene, (c–e) double N doped graphene with diffent sites, (f) single N doped structure with single vacancy, (g–i) three nitrogen doped and single vacancy graphene, (j) double N doped divacancy graphene, and (j) 4 N doped and single vacancy structure [23].

respectively (**Figure 7**). Then they proceeded with studying the energetically favored structures at 1000 by doping N into C structure. The results they found were in close agreement with their experiment indicating that the existence of doped N in these structures is graphitic.

Agrawal et al. studied nanocarbon balls and microcarbon balls with and without nitrogen doping, both experimentally and theoretically [25]. Nitrogen doped porous carbon balls had been synthesized in the micro and nano range using the hydrothermal synthesis. According to their work, the nitrogen doped compounds had more electrical conductivity then undoped compounds. Their experimental results showed a similar situation as the charging capacity of N doped structures is more than the undoped micro and nano carbon balls. More recently, N and S co-doped graphene
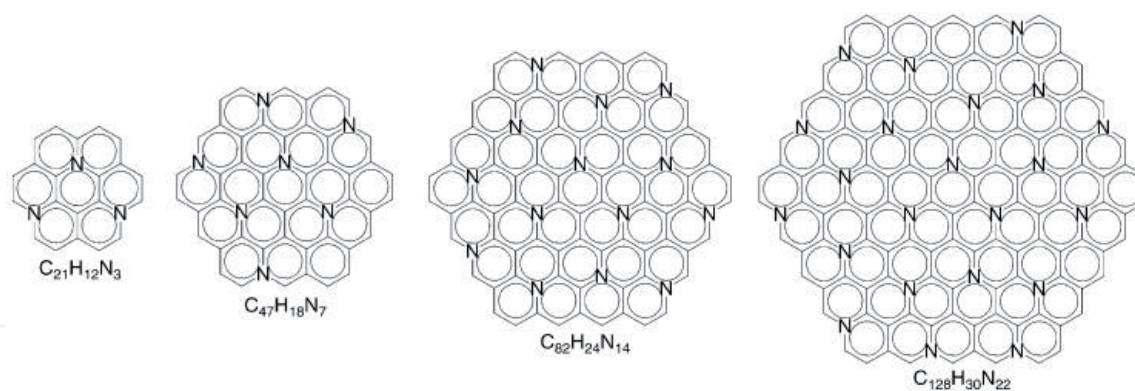
Figure 7.
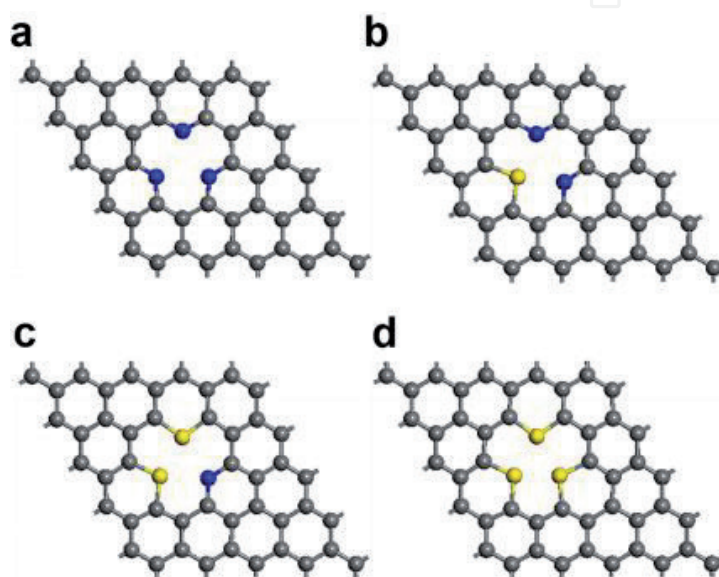*Graphene structure with varying N/C ratio [24].*

Figure 8.
Single vacancy graphene structures with (a) 3 N, (b) 2 N and 1 S, (c) 2 S and 1 N, and (d) 3 S doping [26].

structures were studied theoretically using VASP code [26]. 3N doped graphene, 2N and 1S doped graphene, 1 N and 2 S doped graphene, and 3 S doped graphene structure were simulated with single vacancy site near the doped atoms as shown in **Figure 8**. It was concluded that the bandgap goes from 0.4473 to 0.255 eV for 3N doped structure and 3S doped structure and that the N on the sited has a negative nature compared to s-doped structure which has a positive structure. With the increasing amount of S atoms, the charge on s decreases and we can tune the properties of graphene from this co-doping for electronic devices like Li-ion batteries.

The theoretical study of Yun et al. on doping of sulfur in graphene nanosheets is a good example of connecting the experiment with calculations and simulations to understand the possibility of sites that are being occupied by a dopant [27]. They have simulated three structures for doping of sulfur in graphene nanosheets as demonstrated in **Figure 9**. **Figure 9a** is the adsorption of sulfur on the graphene nanosheet, (**b**) is the substitution of sulfur in the graphene nanosheet, that is, replacing a carbon, and (c) is the placement of S_2 in a divacancy defect graphene nanosheet. The binding energies for adsorbed sulphur, substitutional sulfur, and S_2 divacancy sulfur are 0.85, 7.25, and 4.89 eV, respectively, whereas the bulk sulfur cohesive energy is 2.45 eV. They suggest that substitutional sulfur-doped structure is most likely possibility and that the doping of sulfur contributes to the increase of conductivity in sulfur-doped graphene nanosheet.
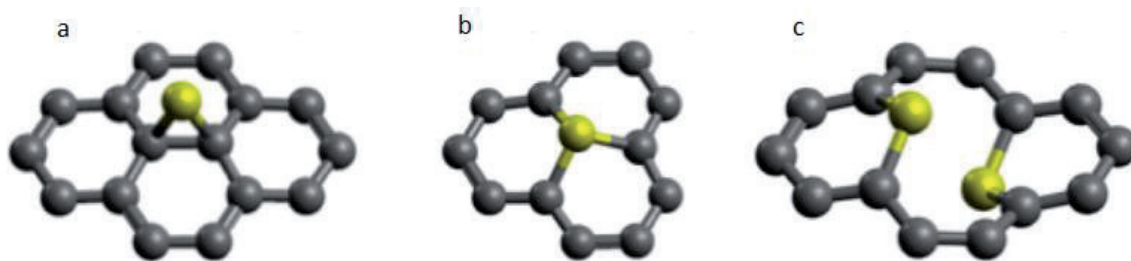
Figure 9.
Structure of (a) adsorbed S on graphene, (b) substitution of S in graphene, and (c) dimer S_2 on divacancy graphene.

2.2 Adsorption and diffusion

Besides the other properties of graphene and carbon nanostructure, it is important for LIBs that the extraction and reinsertion of lithium ion happen smoothly and the resultant is a long-lasting battery. The ionic mobility is an important characteristic; as the material capacitance and other properties improve, for the use of a material as an anode, it is necessary to see the mechanism that is happening in the structure. Adsorption plays an important role along with the doping of the structure.

Zheng et al. provide insight, which shows that in interaction between positive Li ion and graphene, Li ion favors the center of ring position [28]. Their study is based on VASP code and GGA functional. Vacancy-induced structure is also discussed, showing that the vacancy defects decrease the diffusion of positive lithium ion on the surface of the structure. Furthermore, the mechanism of lithiation in pristine graphene and defective graphene was studied by Vivek et al. [29]. They had concluded that the adsorption of Li onto the pristine graphene surface is highly unlikely whereas as the presence of the divacancy and Stone-Wales defects increases the chances of lithiation. As the defects are created, the potential around the defective zone increases which in turn increases the capability of adsorption of Li onto the surface as an adatom. The highest capacity (1675 mAh/g) is seen for the 25% divacancy defect, whereas the highest possibility for Stone-Wales defect at 100% ~1100 mAh/g where the defective structures are shown in **Figure 10**. A further insight is provided by Zhou et al. who claim that the divacancy defect is more attractive to the Li than the SW defect [30].

The effect of defects generated in graphene on Li adsorption has been studied in detail with different structure simulations [11, 31]. The formation of lithium clusters on the single vacancy and divacancy defective site was studied by Chen et al. [32]. They have shown the high amount of lithium storage in these defective sites.
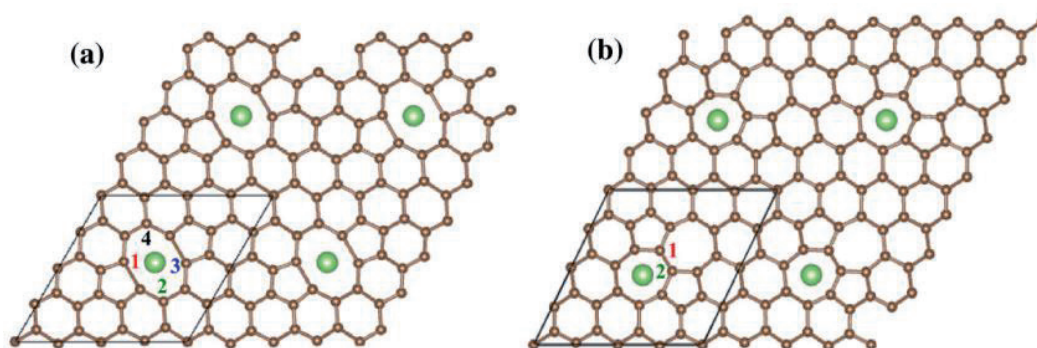

Figure 10.
(a) Divacancy defect graohene structure and (b) Stone-Wales defect graphene structure [29].

Mukherjee et al. studied the defective graphene experimentally and theoretically by synthesizing the porous graphene network and simulating it in different divacancy defect percentages [33]. They found their studies to be in agreement and that the Li adsorption had increased around the divacancy defect sites as well as the increasing divacancy defect percentage resulting in increasing lithium storage capacity [33].

The formation of lithium clusters on the (0 0 1) terminated surface suggested that the binding energy is less than that of Li on Li metal [34]. Fan et al. also studied the adsorption of single Li on to the pristine graphene structure and the different possibilities when more than one Li was adsorbed onto the surface that results into a cluster formation. The Li_4 is the most stable configuration; as the atoms were placed farther apart, the energy also increases, which is unfavorable. **Figure 11** shows the four possible configurations in which **Figure 8a** is the visualization of the stable state.

Modification of graphene to form zigzag edges is explored, which shows that the zigzag edges offer sites for the adsorption of Li and increases the adsorption as compared to pristine graphene or graphite [35, 36]. Furthermore, termination group adsorption onto edge modified graphene and graphite structure was simulated and then the diffusion of Li across these structures had been studied [37]. The termination groups included –O, –H and –OH. **Figure 9** shows the charge distribution on the edge modified graphene structure along with the presence of the termination groups on the edge-modified structure. The edge-modification increases the diffusion of lithium across the structure as compared to the pristine graphene. In
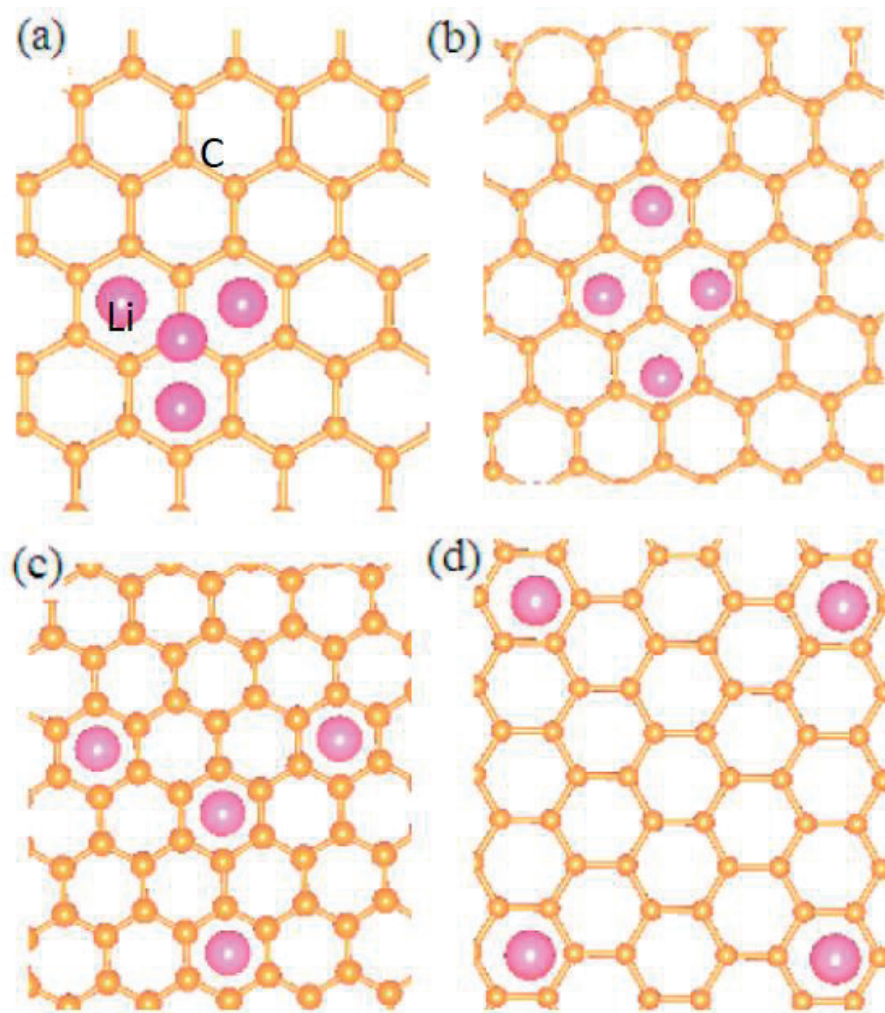

Figure 11.
Structure of Li adsorbed on graphene (a) Li_4 adsorption, (b) single Li at short distance, (c) single Li at slightly more distance, and (d) single Li at the corners of the structure [34].

the terminated structures, the –OH and –H termination decreases the diffusion as compared to the oxygen terminated structure, and from **Figure 12** we can see that oxygen has the highest charge contribution.

Recently, Si clusters have gained the attention of both experimental and theoretical researchers for different applications. The capability of Si for high Li adsorption when combined with the stability of the graphene or carbon-based materials increases the overall performance of silicon graphene composites [38, 39]. Hu et al. studied the adsorption of Li on a defective graphene surface with silicon cluster already adsorbed [40]. They had simulated various N-doped structures including graphitic graphene, pyridinic graphene, and pyrrolic graphene. After that they proceeded with the different possible configurations of Si adsorptions as shown in **Figure 13**. Then, Si_6 adsorbed structure were observed with Li adsorption, where Li forms bond with Si as along with C. Their study gives a detailed insight about the adsorption of structures where the N-doped defective sites have an important role. Si clusters move towards the defective site, where the volume expansion was decreased because of the defects and makes the adsorption of Li easier.

Liou et al. studied the different configurations for adsorption of lithium into a silicon graphene composite and concluded that in graphene silicon composite, intercalation of lithium happening in the interlayer of these two is more stable than the outside [41]. Furthermore, they proceeded with increasing the concentration of graphene layers and silicon percentage and observed that the structures are more stable with the increased concentration of Si [42]. This provides a good insight into the use of Si-incorporated graphitic structures to be used as anodes in LIBs.

2D planar carbon known as popgraphene which is composed of a network of 5-8-5 C rings was shown to be a low energy structure by the bottom-up design [43]. It was reported as an excellent material based on its high adsorption capacity, low diffusion barriers, and its metallic structure because of the attachment of CNTs. **Figure 14** shows the adsorption of 12 Li atoms on the popgraphene structure.
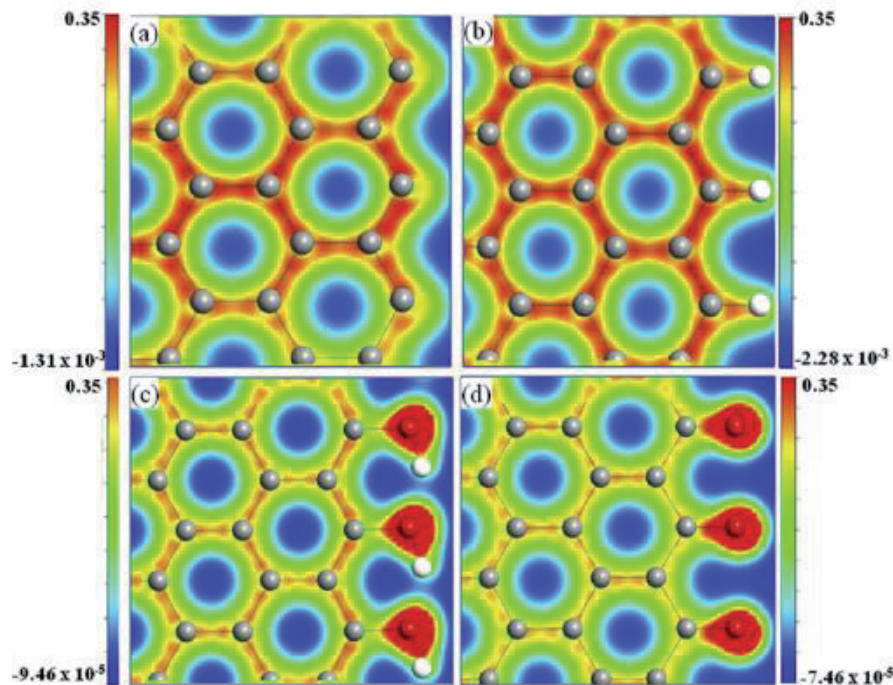

Figure 12.
Charge distribution in edge modified structure: (a) graphene, (b) −H terminations, (c) -OH terminations, and (d) −O terminations [37].
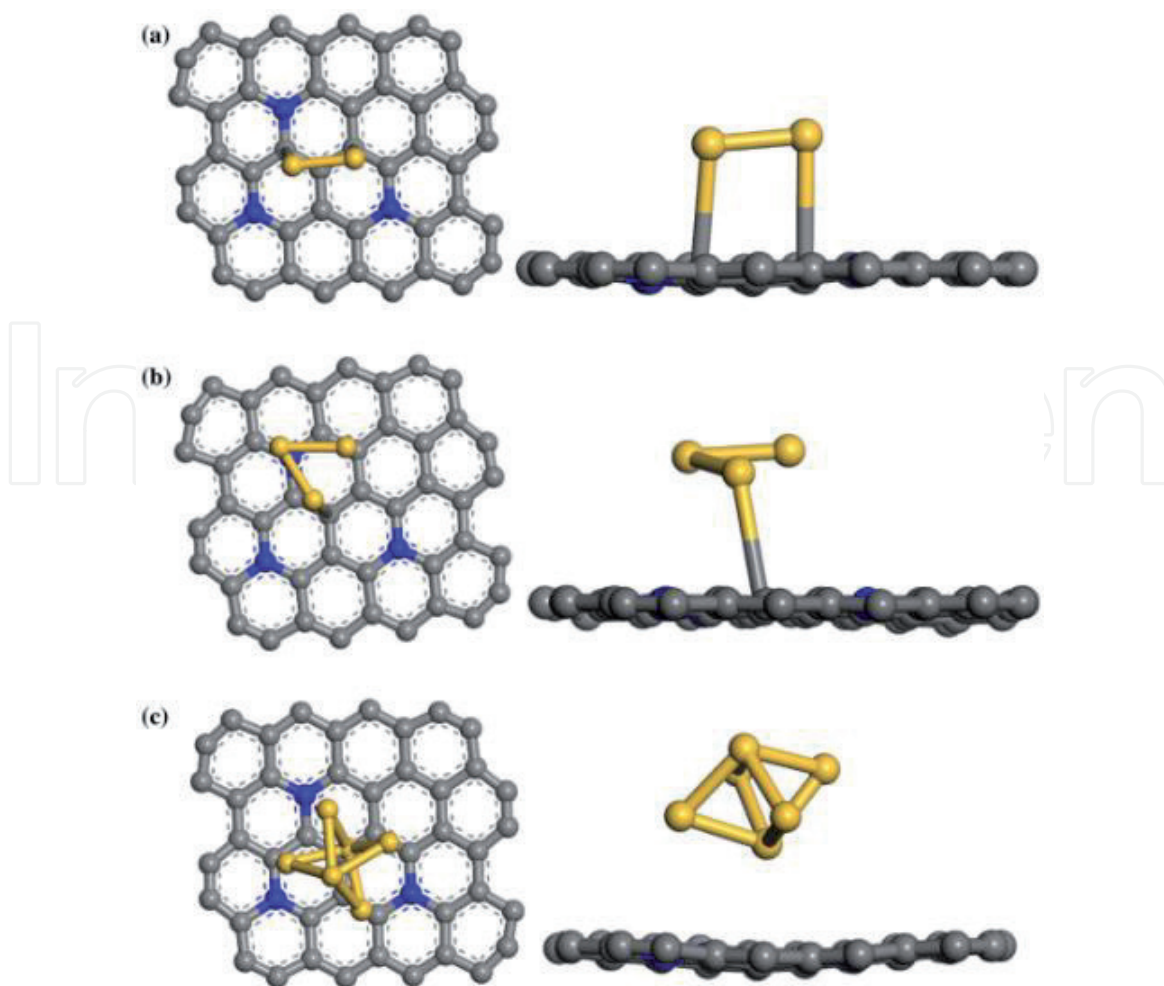
Figure 13.
(a) Si_2 cluster adorption on graphitic graphene, (b) Si_3 cluster adsorption on graphitic graphene, and (c) Si_6 cluster adorption on graphitic graphene [40].

2.3 Heterostructures of 2D compounds with graphene

The formation of heterostructures between carbon-based 2D material graphene and other 2D materials has also been studied for anode applications specifically in the LIB industry. 2D molybdenum oxide MoO_2 and graphene heterostructure were studied using the VASP code with GGA [44]. It shows a high theoretical capacity ~1400 mAh/g and high energy density for lithiation and fast charge and discharge rate. Rao et al. studied in detail the monolayer of C_2N and the bilayer heterostructure of C_2N/graphene [45]. Their results show that the diffusion coefficient for the heterostructure was better than the monolayer after the diffusion of lithium, whereas the capacity of monolayer was 220% the bilayered heterostructure.

The heterostructure of phosphorene and graphene was studied by Wang et al. and showed that the Li intercalation into the phosphorene/graphene heterostructure is better than the pristine phosphorene and pristine graphene [46]. However, there is a small band gap, which indicates the semimetal nature of the phosphorene/graphene heterostructure. Blue phosphorene and graphene heterostructure also shows a similar behavior and high theoretical capacity for lithium intercalation [47]. A bilayer hybrid structure of molybdenum sulfide 2D material with graphene was studied by experimentation as well as simulation [48]. Their purpose was to present a hybrid of these two compounds for lithium storage and concluded that their experimentation is in agreement with the simulation.
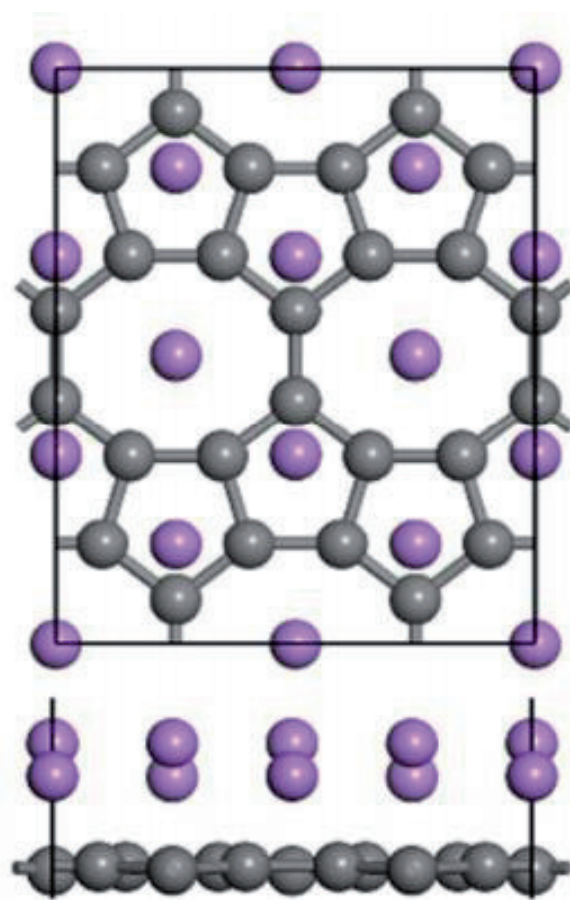
Figure 14.
Top and side view of pop graphene sheet with Li adsorption (purple = Li atom and gray = C atom) [43].

A new two-dimensional family of transition metal compounds called MXene and graphene heterostructure were simulated for lithium battery applications [49]. The study includes the intercalation of lithium into many different compounds of MXene as well as MXene and graphene heterostructure in the presence of the functional groups which are −O and −OH terminations attached to MXene as shown in **Figure 15**. They have established that the stability of the compound is maintained as the lattice parameter and interlayer separation remain almost the same after the intercalation of Li.

2.4 Carbon-based structures for cathode

Mainly for cathode in LIBs, the compounds used are lithium-based salts, phosphates, etc. Wang et al. have done an extensive study based on simulations as well as experimentations and have proposed structures containing $LiFePO_4$ (LFP) and carbon nanotubes (CNTs) [50]. Their DFT calculations provide a profound understanding of the electrochemical processes. For the DFT study, the structure of CNTs is attached at the (010) interface of LFP and the valence electron cloud charge for the structure is shown in **Figure 16**. Pure LFP structure has less density of states compared to the structure with CNTs, showing that the electrochemical activity of LFP was enhanced by the attachment of CNTs.

Jiang et al. studied the composite of vanadium oxide with vertically aligned CNT by the synthesis and characterization and then for the mechanism at atomic level the structures were simulated as well [51]. They have simulated CNT, pure vanadium oxide, and then the combination of these two with possible Li adsorption sites as shown in **Figure 17**. They have concluded that the vanadium oxide inclusion
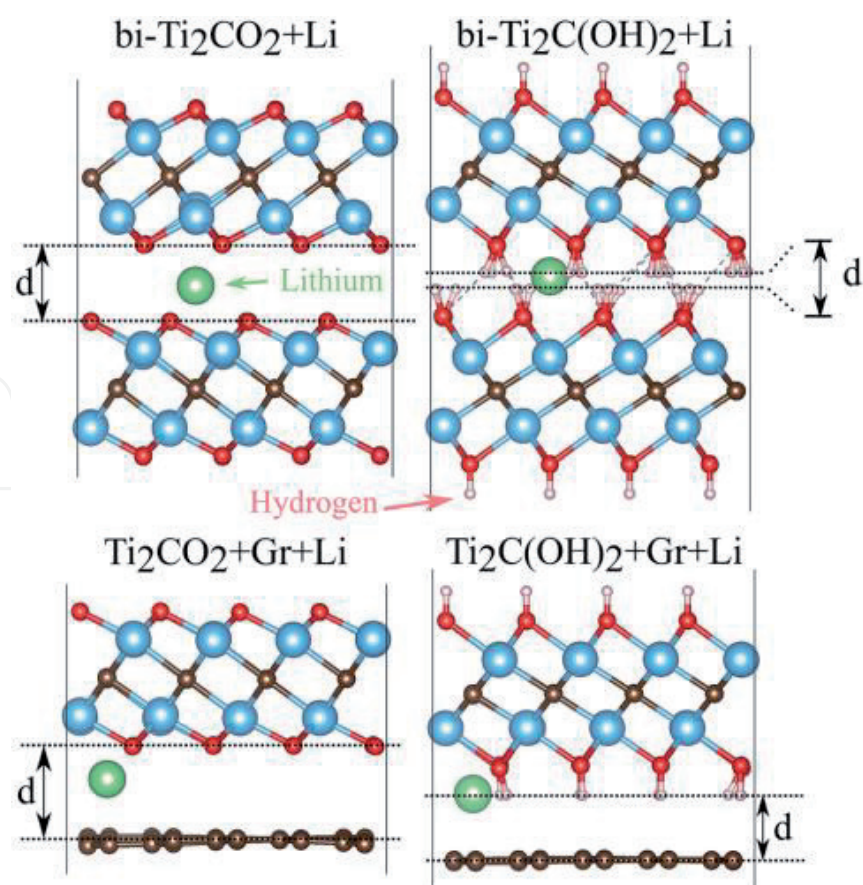
Figure 15.
(a) and (b) Bi-layer MXene Ti₂CTₓ with intercalated lithium adsorbed (c) and (d) MXene Ti₂CTₓ and graphene with intercalated lithium [49].
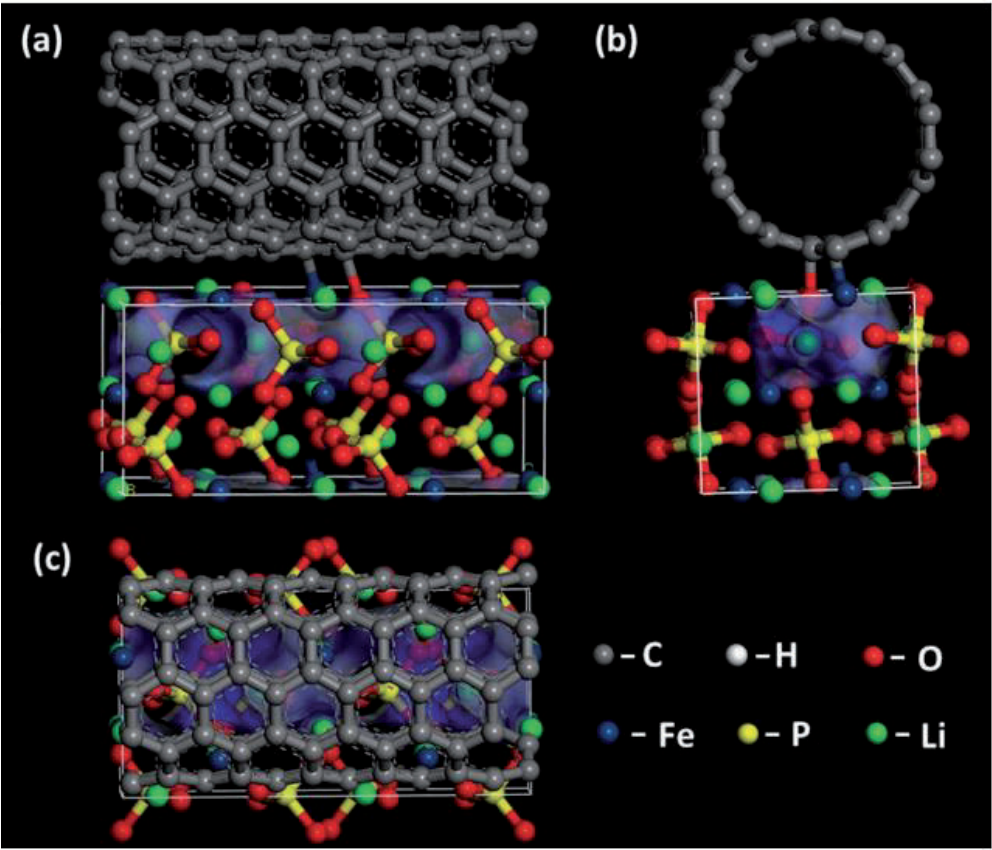

Figure 16.
(a) Front-view, (b) side-view, and (c) top-view, for compound interface of LFP and CNTs showing the valence electron cloud distribution [50].
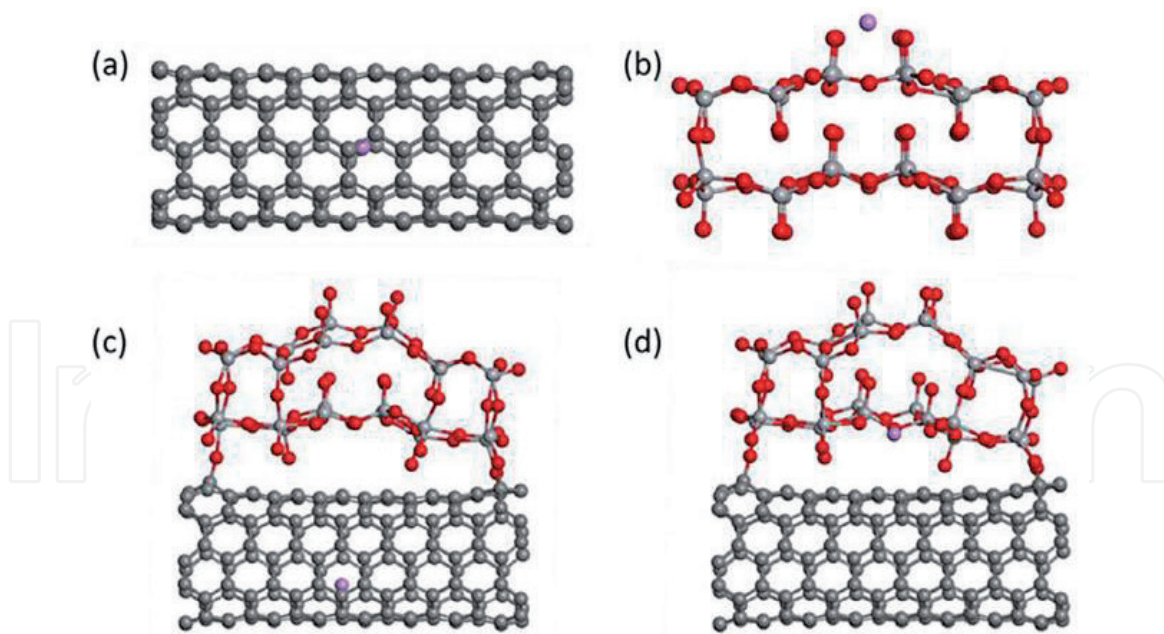
Figure 17.
Li adsorption on (a) CNT, (b) vanadium oxide, (c) and (d) composite of vanadium oxide on vertically aligned CNT [51].

onto the vertically aligned CNT decreases the path for diffusion of Li and aids the adsorption of Li.

Cui et al. presented the composite of orthorhombic MoO_3 and graphene as a cathode in LIBs with higher conductivity and adsorption of lithium. They studied the structure in bulk form as well as the monolayer structure. They have established that the Li charge and discharge rate have increased in the composite structure along with the capacity of lithium [52].

3. Conclusion

In conclusion, we can say that the carbon nanostructures are of great importance for use in the LIBs especially as anodes. Nitrogen doping and the various ways in which that is achieved showed very good results. The doping of C-based structures with beryllium, boron, and the co-doping of nitrogen and sulfur gave a different view on the possibilities. The adsorption mechanism of lithium was discussed which gave us a theoretical viewpoint of the procedures that goes on inside the LIBs. Also, the effect of defective sites in graphene structures as well as doped graphene structures on Li adsorption shows that these enhance the lithiation and de-lithiation of Li ion. The heterostructures of graphene with other 2D materials show the many possibilities for experimentation to improve the anode materials.

Acknowledgements

Conflict of interest

There are no conflicts of interest.

List of acronyms/abbreviations

LIB	lithium ion battery
DFT	density functional theory
GGA	generalized gradient approximation
LSDA	local spin density approximation
SIESTA	Spanish Initiative for Electronic Simulations with Thousands of Atoms
VASP	Vienna ab initio simulation package
SW	Stone-Wales
CNT	carbon nanotube

Author details

Jameela Fatheema and Syed Rizwan*
Physics Characterization and Simulations Lab (PCSL), School of Natural Sciences, National University of Sciences and Technology (NUST), Islamabad, Pakistan

*Address all correspondence to: syedrizwanh83@gmail.com

IntechOpen

15

References

[1] Crompton TPJ. Battery Reference Book. Elsevier; 2000

[2] Linden D, Reddy TB, editors. Handbook of Batteries. 3rd ed. New York: McGraw-Hill; 2002

[3] Nitta N, Wu F, Lee JT, Yushin G. Li-ion battery materials: Present and future. Materials Today. 2015;**18**:252-264. DOI: 10.1016/j.mattod.2014.10.040

[4] Tarascon J-M, Armand M. Issues and challenges facing rechargeable lithium batteries. In: Materials for Sustainable Energy: A Collection of Peer-Reviewed Research and Review Articles from Nature Publishing Group. World Scientific; 2011. pp. 171-179

[5] Wikipedia. Alkaline-battery-English. Alkaline battery. Wikipedia [Internet]. 5/20/2019. Available from: https://en.wikipedia.org/w/index.php?oldid=898014065 [Accessed 2019-05-22]

[6] Wikipedia. Secondary Cell Diagram. Rechargeable battery. Wikipedia [Internet]. 5/16/2019. Available from: https://en.wikipedia.org/w/index.php?oldid=896056453 [Accessed 2019-05-22]

[7] Landi BJ, Ganter MJ, Cress CD, DiLeo RA, Raffaelle RP. Carbon nanotubes for lithium ion batteries. Energy & Environmental Science. 2009;**2**:638. DOI: 10.1039/b904116h

[8] Ji L, Meduri P, Agubra V, Xiao X, Alcoutlabi M. Graphene-based nanocomposites for energy storage. Advanced Energy Materials. 2016;**6**:1502159. DOI: 10.1002/aenm.201502159

[9] Ji L, Lin Z, Alcoutlabi M, Zhang X. Recent developments in nanostructured anode materials for rechargeable lithium-ion batteries.

Energy & Environmental Science. 2011;**4**:2682-2699

[10] Bonaccorso F, Colombo L, Yu G, Stoller M, Tozzini V, Ferrari AC, et al. Graphene, related two-dimensional crystals, and hybrid systems for energy conversion and storage. Science. 2015;**347**:1246501

[11] Okamoto Y. Density functional theory calculations of lithium adsorption and insertion to defect-free and defective graphene. The Journal of Physical Chemistry C. 2016;**120**:14009-14014. DOI: 10.1021/acs.jpcc.6b05458

[12] Fiolhais C, Nogueira F, Marques MAL. A Primer in Density Functional Theory. Springer Science & Business Media; 2003

[13] Burke K, Wagner LO. DFT in a nutshell. International Journal of Quantum Chemistry. 2013;**113**:96-101

[14] Perdew JP, Burke K, Ernzerhof M. Generalized gradient approximation made simple. Physical Review Letters. 1996;**77**:3865

[15] Oliver GL, Perdew JP. Spin-density gradient expansion for the kinetic energy. Physical Review A. 1979;**20**:397

[16] von Barth U, Hedin L. A local exchange-correlation potential for the spin polarized case. I. Journal of Physics C: Solid State Physics. 1972;**5**:1629

[17] Hu J, Ouyang C, Yang SA, Yang HY. Germagraphene as a promising anode material for lithium-ion batteries predicted from first-principles calculations. Nanoscale Horizons. 2019;**4**:457-463. DOI: 10.1039/C8NH00333E

[18] Ullah S, Denis PA, Sato F. Beryllium doped graphene as an efficient anode material for lithium-ion batteries

with significantly huge capacity: A DFT study. Applied Materials Today. 2017;**9**:333-340. DOI: 10.1016/j. apmt.2017.08.013

[19] Ullah S, Denis PA, Sato F. First-principles study of dual-doped graphene: Towards promising anode materials for Li/Na-ion batteries. New Journal of Chemistry. 2018;**42**:10842-10851. DOI: 10.1039/C8NJ01098F

[20] Liu H, Dong H, Ji Y, Wang L, Hou T, Li Y. The adsorption, diffusion and capacity of lithium on novel boron-doped graphene nanoribbon: A density functional theory study. Applied Surface Science. 2019;**466**:737-745. DOI: 10.1016/j.apsusc.2018.10.107

[21] Wu DH, Li YF, Zhou Z. First-principles studies on doped graphene as anode materials in lithium-ion batteries. Theoretical Chemistry Accounts. 2011;**130**:209-213. DOI: 10.1007/s00214-011-0961-5

[22] Kong X-K, Chen Q-W. Improved performance of graphene doped with pyridinic N for Li-ion battery: A density functional theory model. Physical Chemistry Chemical Physics. 2013;**15**:12982-12987. DOI: 10.1039/c3cp51987b

[23] Yu Y-X. Can all nitrogen-doped defects improve the performance of graphene anode materials for lithium-ion batteries? Physical Chemistry Chemical Physics. 2013;**15**:16819-16827. DOI: 10.1039/c3cp51689j

[24] Zhang S, Tsuzuki S, Ueno K, Dokko K, Watanabe M. Upper limit of nitrogen content in carbon materials. Angewandte Chemie (International ed. in English). 2015;**54**:1302-1306. DOI: 10.1002/anie.201410234

[25] Agrawal A, Biswas K, Srivastava SK, Ghosh S. Effect of N-doping on hard carbon nano-balls as anode for Li-ion battery: Improved hydrothermal

synthesis and volume expansion study. Journal of Solid State Electrochemistry. 2018;**22**:3443-3455. DOI: 10.1007/s10008-018-4044-6

[26] Lee JH, Kwon SH, Kwon S, Cho M, Kim KH, Han TH, et al. Tunable electronic properties of nitrogen and sulfur doped graphene: Density functional theory approach. Nanomaterials (Basel, Switzerland). DOI: 10.3390/nano9020268

[27] Yun YS, Le V-D, Kim H, Chang S-J, Baek SJ, Park S, et al. Effects of sulfur doping on graphene-based nanosheets for use as anode materials in lithium-ion batteries. Journal of Power Sources. 2014;**262**:79-85. DOI: 10.1016/j.jpowsour.2014.03.084

[28] Zheng J, Ren Z, Guo P, Fang L, Fan J. Diffusion of Li+ ion on graphene: A DFT study. Applied Surface Science. 2011;**258**:1651-1655. DOI: 10.1016/j.apsusc.2011.09.007

[29] Datta D, Li J, Koratkar N, Shenoy VB. Enhanced lithiation in defective graphene. Carbon. 2014;**80**:305-310. DOI: 10.1016/j.carbon.2014.08.068

[30] Zhou L-J, Hou ZF, Wu L-M. First-principles study of lithium adsorption and diffusion on graphene with point defects. The Journal of Physical Chemistry C. 2012;**116**:21780-21787. DOI: 10.1021/jp304861d

[31] Yu Y-Z, Guo J-G, Zhou L-J. Theoretical investigation on the adsorption and diffusion of lithium-ion on and between graphene layers with size and defect effects. Adsorption Science & Technology. 2016;**34**:212-226. DOI: 10.1177/0263617415623429

[32] Huo L, Su F, Yi Z, Cui G, Zhang C, Dong N, et al. First-principles studies of Li nucleation on double-layered defective graphene. ChemElectroChem.

2019;**6**:810-817. DOI: 10.1002/celc.201801187

[33] Mukherjee R, Thomas AV, Datta D, Singh E, Li J, Eksik O, et al. Defect-induced plating of lithium metal within porous graphene networks. Nature Communications. 2014;**5**:3710. DOI: 10.1038/ncomms4710

[34] Fan X, Zheng WT, Kuo J-L, Singh DJ. Adsorption of single Li and the formation of small Li clusters on graphene for the anode of lithium-ion batteries. ACS Applied Materials & Interfaces. 2013;**5**:7793-7797. DOI: 10.1021/am401548c

[35] Jiao J, Xiao R, Tian M, Wang Z, Chen L. First-principles calculations on lithium and sodium adsorption on graphene edges. Electrochimica Acta. 2018;**282**:205-212. DOI: 10.1016/j.electacta.2018.05.200

[36] Uthaisar C, Barone V. Edge effects on the characteristics of Li diffusion in graphene. Nano Letters. 2010;**10**:2838-2842. DOI: 10.1021/nl100865a

[37] Leggesse EG, Chen C-L, Jiang J-C. Lithium diffusion in graphene and graphite: Effect of edge morphology. Carbon. 2016;**103**:209-216. DOI: 10.1016/j.carbon.2016.03.016

[38] Wang G, Xu B, Shi J, Lei X, Ouyang C. Confined Li ion migration in the silicon-graphene complex system: An ab initio investigation. Applied Surface Science. 2018;**436**:505-510. DOI: 10.1016/j.apsusc.2017.11.237

[39] Wang H, Wu M, Lei X, Tian Z, Xu B, Huang K, et al. Siligraphene as a promising anode material for lithium-ion batteries predicted from first-principles calculations. Nano Energy. 2018;**49**:67-76. DOI: 10.1016/j.nanoen.2018.04.038

[40] Hu R, Zhou J. A DFT study of Li adsorption on surface of Si clusters

anchored N-doped defective graphene composite. Applied Surface Science. 2018;**457**:789-796. DOI: 10.1016/j.apsusc.2018.07.004

[41] Zhou F, Liao N, Zhang M, Xue W. Lithiation behavior of graphene-silicon composite as high performance anode for lithium-ion battery: A first principles study. Applied Surface Science. 2019;**463**:610-615. DOI: 10.1016/j.apsusc.2018.08.258

[42] Zhou F, Liao N, Zhou H, Xue W. Atomic investigation on reversible and irreversible lithium storage in silicon incorporated with multi-layered graphene. Materials Letters. 2019;**244**:108-110. DOI: 10.1016/j.matlet.2019.02.068

[43] Wang S, Yang B, Chen H, Ruckenstein E. Popgraphene: A new 2D planar carbon allotrope composed of 5-8-5 carbon rings for high-performance lithium-ion battery anodes from bottom-up programming. Journal of Materials Chemistry A. 2018;**6**:6815-6821. DOI: 10.1039/C8TA00438B

[44] Ma J, Fu J, Niu M, Quhe R. MoO2 and graphene heterostructure as promising flexible anodes for lithium-ion batteries. Carbon. 2019;**147**:357-363. DOI: 10.1016/j.carbon.2019.03.006

[45] Ding Y, Xiao B, Li J, Deng Q, Xu Y, Wang H, et al. Improved transport properties and novel Li diffusion dynamics in van der Waals C 2 N/graphene heterostructure as anode materials for lithium-ion batteries: A first-principles investigation. The Journal of Physical Chemistry C. 2019;**123**:3353-3367. DOI: 10.1021/acs.jpcc.8b11044

[46] Guo G-C, Wang D, Wei X-L, Zhang Q, Liu H, Lau W-M, et al. First-principles study of phosphorene and graphene heterostructure as anode materials for rechargeable Li batteries. The Journal of Physical Chemistry

Letters. 2015;**6**:5002-5008. DOI:
10.1021/acs.jpclett.5b02513

[47] Li Y, Wu W, Ma F. Blue phosphorene/
graphene heterostructure as a promising
anode for lithium-ion batteries: A
first-principles study with vibrational
analysis techniques. Journal of Materials
Chemistry A. 2019;**7**:611-620. DOI:
10.1039/C8TA09423C

[48] Jing Y, Ortiz-Quiles EO,
Cabrera CR, Chen Z, Zhou Z. Layer-
by-layer hybrids of MoS2 and reduced
graphene oxide for lithium ion batteries.
Electrochimica Acta. 2014;**147**:392-400.
DOI: 10.1016/j.electacta.2014.09.132

[49] Aierken Y, Sevik C, Gülseren O,
Peeters FM, Çakır D. MXenes/graphene
heterostructures for Li battery
applications: A first principles
study. Journal of Materials
Chemistry A. 2018;**6**:2337-2345. DOI:
10.1039/C7TA09001C

[50] Wang B, Liu T, Liu A, Liu G,
Wang L, Gao T, et al. A hierarchical
porous C@LiFePO$_4$/carbon nanotubes
microsphere composite for high-rate
lithium-ion batteries: Combined
experimental and theoretical
study. Advanced Energy Materials.
2016;**6**:1600426. DOI: 10.1002/
aenm.201600426

[51] Jiang H, Wei Z, Cai X, Lai L, Ma J,
Huang W. A cathode for Li-ion batteries
made of vanadium oxide on vertically
aligned carbon nanotube arrays/
graphene foam. Chemical Engineering
Journal. 2019;**359**:1668-1676. DOI:
10.1016/j.cej.2018.10.223

[52] Cui Y, Zhao Y, Chen H, Wei K, Ni S,
Cui Y, et al. First-principles study of
MoO$_3$/graphene composite as cathode
material for high-performance lithium-
ion batteries. Applied Surface Science.
2018;**433**:1083-1093. DOI: 10.1016/j.
apsusc.2017.10.147