

Synopsis

In the current scenario of global warming, pollution and the very limited resources of fossil fuels, Li ion batteries show great promises to fulfil the energy demand of modern civilization without harming the environment. Moreover, Li ion batteries are the most popular energy storage devices in the recent decades due to their smaller size and high energy density. Extension of their application to hybrid electric vehicles and portable electronics, which require a very high energy density, is not possible due to limited specific storage capacity of commercially used graphite (372 mAh/g) anode. Much effort has been focused on finding suitable high capacity anode materials. Graphitic materials are shown to be promising candidates having low diffusion barrier, low and flat voltage, high diffusivity and high specific capacity. Besides graphitic materials, silicon, having very high theoretical capacity (4200 mAh/g), also becomes suitable candidate to replace graphite. However, silicon goes through severe volume change during charging/discharging causing the breaking of contacts. Experimentally, it has been shown that by coating Si anode with graphitic materials, volume pulverization can be avoided. This coating is known as artificial solid electrolyte interface (a-SEI). Therefore, graphitic materials can be used as both anode material and a-SEI. In order to further improve the electrochemical performance, in this thesis, various pathways have been described to tune the electronic structure of these graphitic materials by introducing defects and doping, applying strain and making van der Waals (vdW) heterostructures.

This thesis has been organized as follows:

- **Chapter 1** introduces the importance of Li ion battery and current challenges. As one of the challenges is the low capacity of commercially available anode material graphite, the requirements for good anode materials and an overview of the possible replacements for anode material have been described. Various techniques by electronic structure tuning of these materials, have been proposed to further enhance the electrochemical performance, which have been carried out in this thesis.
- **Chapter 2** describes the theoretical methodology adopted in this work. It gives a brief

overview of first principles based density functional theory (DFT), which is used to obtain structural and electronic properties. Methods employed for calculation of minimum energy path and diffusion barrier, i.e, nudged elastic band method, are also discussed briefly.

- **Chapter 3** unravels that doping and defect significantly reduces the diffusion energy barrier of Li in graphene and enhances storage of Li. Moreover, the problem of Li clustering in pristine monolayered graphene due to positive adsorption energy has been shown to be avoided by introducing doping and defect. We find that N doping leads to strong adsorption of Li in divacancy graphene, while B doping consistently shows lower energy barrier and optimum adsorption energy.
- **Chapter 4** investigates the effect of B concentration in B doped graphene (BC_x) sheets on electrochemical performance as anode materials in Li ion battery. Both uniformly doped and non-uniformly doped BC_x sheets have been studied and it has been found that uniformly doped BC_2 sheet shows remarkably high capacity due to the availability of maximum empty states above the Fermi level. Furthermore, it shows low energy barrier along with low and flat voltage, making BC_2 the best candidate among B doped graphene sheets.
- **Chapter 5** describes Li diffusion in bulk FCC fullerene. Li diffuses through tetrahedral and octahedral voids alternatively with an energy barrier at octahedral void. Upon application of hydrostatic pressure, this barrier reduces upto 17.7% volume strain due to charge transfer from Li to fullerene leading to two orders of enhancement in diffusivity. Moreover, band gap of FCC fullerene reduces as the strain increases and at 17.7%, semiconductor to metal transition happens, which boosts the conductivity. Further enhancement in pressure increases energy barrier as inter-fullerene bond formation happens.
- **Chapter 6** investigates monolayered fluorinated graphene (CF_x) sheets having different F concentration as the promising candidates for cathode materials in primary lithium batteries. We found that $CF_{0.75}$ exhibits the highest capacity due to the weak bonding between Li and F upon lithiation. However, the open circuit voltage drops as a function of F concentration having the highest voltage for $CF_{0.25}$ and therefore, $CF_{0.25}$ shows the maximum energy density.
- **Chapter 7** reports a large band gap opening in graphene/graphane vdW heterostructure under normal compressive (NC) strain. Interlayer charge transfer between graphene and graphane induces intralayer charge transfer in graphene, which breaks the symmetry

between two sublattices in graphene. Under the application of NC strain, charge transfer increases leading to splitting of the Dirac cone. The enhancement of charge transfer from graphene to graphane under NC strain has also been confirmed by theoretical Raman spectra by red-shift of G peak of graphene.

- **Chapter 8** develops a band alignment method to predict the nature of band gap and the origin of band edges in vdW heterostructures using graphene Dirac cone as a unique reference point. We find that the interaction with graphene shifts the band edges of 2D material such a way that the band dispersion almost becomes similar when this 2D material would form a vdW heterostructure with other 2D materials. Therefore, the band gap and the origin of band edges for any heterostructure can be predicted well, by knowing the band dispersion of 2D materials with graphene.
- **Chapter 9** summarizes and concludes the work presented in this thesis.