

Exploring the interaction between lithium ion and defective graphene surface using DFT studies

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The interaction between charged surface (i.e. an electrode) and ionic species (i.e. an electrolyte) is the basic science that drives various energy storage systems ranging from lithium batteries to supercapacitors. Consequently, overall performance of such energy storage system heavily depends on chemical and physical properties of materials that constitute the interfacial region. Graphene, with a very high surface area (~2675 m²/g) and high electronic conductivity, is a promising candidate for the electrode material for modern energy storage devices such as lithium-ion battery technology [1, 2]. However, wide range of performance (i.e. final specific capacity varying from 1200 mAh/g to 180 mAh/g) is reported for graphene synthesized by various methods [3]. For example, specially prepared graphene sheets with high concentration of structural defects shows mixed performance in lithium battery. These fickle performances of graphene based lithium batteries can be related to the purity and structural homogeneity of the graphene material which heavily depend on their synthesis method [3]. Therefore, understanding the chemistry behind these graphene defects and their interaction with lithium can facilitate the efficient tailoring of graphene surface to have optimal performance in lithium battery.

We carried out dispersion corrected DFT studies to understand the nature of Li⁺ interaction with graphene containing common surface defects. The Li⁺ ion adsorption energy is relatively higher at defect sites compared with pure graphene layer. It is also clear that, Li⁺ interacts profoundly with the delocalized π orbital electron cloud of pure graphene layers. For defective graphene, the single vacancy type defect group can also interact with Li⁺ through its chemical binding with carbon dangling bonds. Similarly the oxygen containing functional groups mainly interacts by forming Li-O ionic bond. In either case, the Li⁺ adsorption energy is higher for the defective sites indicating the possible resistance for reversible lithium intercalation with defective graphene. With this understanding, we will discuss the possible reasons behind the fickle graphene performances reported in the literature.

References

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