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Grain boundary and curvature enhanced lithium adsorption on carbon

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ABSTRACT

While the speculation that graphene may owe double or even higher capacity of lithium adsorption than graphite does remains speculative, there is growing evidence that defects and edges may promote lithium adsorption on graphene and other nanostructured carbon. Here we report a first-principles study on how grain boundary defects in graphene may influence the adsorption of lithium. The adsorption energy for Li atoms trapping in 5-, 7-, and 8-rings is much lower than the counter-part of Li atoms and pristine graphene. Such defective graphene could adsorb more Li atoms, and may reach the speculated ratio of 1:1 for C-Li adsorption. In a contrast study of lithium on fullerenes of different size, we find that the adsorption energy decreases with increasing size of fullerenes, but does not approach the energy when Li atoms adsorb on flat graphene. The energy in carbon nanotubes, however, converges to the adsorption energy between Li atoms and flat graphene if the radius of carbon nanotubes is sufficiently large. It hence indicates that while curvature plays a role in the enhanced adsorption in fullerenes, the twelve 5 rings in a fullerene ball is the primary factor accounting for the enhanced lithium adsorption.

1. Introduction

As the lithium ion batteries widely utilized in various fields as a type of clean energy, the enhancement of lithium storage in electrode materials becomes a key issue in the design and synthesis of battery with high capacity [1]. It is known that the lithium storage capacity is 372 mA h/g for graphite [2] and 784 mA h/g for graphene due to the capture of lithium ions on both surfaces [3]. Carbon nanotubes (CNTs) also owe large specific surface area and are proposed for suitable lithium storage materials as well [4–6]. It was shown that the maximum capacity of CNTs can be as high as 1000 mA h/g (in the form of $Li_{2.7}C_6$) by chemical etching [7] or ball-milling [8], which facilitates Li ions to diffuse freely inside the CNTs. To further improve the three key characteristics of lithium ion battery performance – capacity, voltage and energy density – other routines were also explored to tune lithium adsorption in carbon. The essence is to manipulate the chemistry, microstructure and shape of an electrode, hence changes the electronic properties of Li–C interaction [9], to improve binding between lithium ions and the electrode material. Typical routines involve the following three strategies.

(1) Chemical engineering by doping: Recently, Koh et al. investigated Li atoms embedded in the graphene-fullerene hybrid system [10] and fullerene-CNTs hybrid system [11–13] by first-principle calculations. Heterogeneous structure composed of ultrathin MoS2/nitrogen-doped graphene nanosheets also exhibits highly reversible lithium storage [14]. Alternatively, Wang et al. found that doping boron on graphene can be an effective method to enhance the lithium storage capacity, in which every boron atom can absorb 6 Li ions [15]. Wu et al. followed this line to investigate Li adsorption on nitrogen doped and boron doped graphenes [16], while Zhou et al. study the Li adsorption on nitrogen doped and boron doped CNTs [17]. Liu et al. also explored the feasibility of lithium storage on graphene and Its derivatives and they reported that certain structural defects in graphene can bind Li stably, yet a more efficacious approach is through substitution doping with boron (B) [18]. Substitutional doping with nitrogen in graphene is revealed to influence the electronic and adsorption properties of graphene

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significantly as well [19]. A very recent work demonstrated that hydrogen could enhance the capacity of graphene anode materials for lithium-ion batteries [20].

(2) Defect engineering: By functionalizing graphene sheets with hierarchical arrangement of pore structures and hence a high number of reactive sites for electrochemical reactions, Xiao et al. realized an exceptionally high capacity electrode—15,000 mA h/g [21]. Both the work by Zhou et al. [22] and Fan et al. [23] Investigated the effect of point defects on the Li adsorption on graphene and reported that the presence of point defects can significantly increase the adsorption of Li on graphene. Meanwhile, Kazume and Nishidate investigated Li adsorption and diffusion on defective CNTs [24]. Recently, Datta et al. [25] further explored the adsorption of Li on graphene with divacancy and Stone–Wales defects. Their results confirmed enhanced Li adsorption on defective graphene because of the increased charge transfer between adatom and underlying defective sheet. At the microscopic level, Mukherjee et al. [26] showed that photoflash and laser-reduced free-standing graphene paper could be high-rate capable anodes for lithium-ion batteries as photothermal reduction of graphene oxide yields an expanded structure with micrometer-scale pores, cracks, and intersheet voids. Their recent experiments illustrated that defect may induce plating of lithium metal within porous graphene networks [27]. Experiments by Lee et al. [28] demonstrated that by controlling defect concentration in graphene sheets, we may attain a high charge capacity of 2310 mA h/g in lithium-ion batteries, as a resultant of additional lithium storage sites such as defects and edges.

(3) Morphology manipulation. In addition to chemical engineering and microstructure control, morphology is another factor to influence binding between lithium ions and the electrode material [18,29].

Despite the substantial progress on tuning the chemistry, microstructure and shape of an electrode for better binding between lithium ions and the electrode material, how the grain-boundary (GB) defects and curvature of carbon structures influencing the Li adsorption remains elusive. For example, 5–7 rings are the most commonly seen grain boundary defects in polycrystalline graphene for engineering practice but their influencing on Li adsorption on graphene is missing. In the morphology side, how curvature affects Li-C binding remains unknown. In this paper, we make a thorough comparison among the binding capability of Li atoms with different GB defects in graphene. In addition, by examining the evolution of binding energy of Li-C in fullerene and CNTs with different size, we demonstrate clearly how the curvature affects the lithium adsorption in those nanostructured carbon. Our results may provide theoretical basis for defect engineering and morphology manipulation to realize high-capacity of graphene anode materials for lithium ion batteries.

2. Methods

Density functional theory (DFT) implemented in the Vienna ab initio simulation package (VASP) [30,31] is used in all our calculations. The parameterization by Perdew-Burke-Ernzerhof (PBE) [32] is used for exchange and correlation interaction in the generalized gradient approximation (GGA). We had tested the validity of PBE calculations by examining its predictability for the lattice constant of graphene. The result from PBE calculation is in good agreement with the experiments [33]. A 3 × 3 rhombus supercell is used to investigate the interaction of Li atoms with pristine graphene. The z-direction lattice constant is fixed at 20 Å to avoid the layers interaction. The Brillouin zone is sampled by a 15 × 15 × 1 Monkhorst and Pack [34] grid. For (33)–(66) and (77)–(99) CNTs, the x- and y-direction lattice constants are 20 × 20 Å and 25 × 25 Å, respectively. The Brillouin zone is sampled by a 1 × 1 × 12 Monkhorst and Pack grid. The xyz-direction lattice constant of fullerene is 20 × 20 × 20 Å. The cutoff energy in our calculation is 520 eV. All the calculation are relaxed to minimize the total energy of the system until a precision of 1 meV was reached. Following the common way about the definition of adsorption energy [35], we calculate the adsorption energy per Li atom (E_{ad}) as following

$$E_{ad} = \frac{(E_{G+nLi} - E_G - nE_{Li})}{n}$$

where E_{G+nLi}, E_G and E_{Li} represent the energy of Li-carbon, nanostructured carbon and one lithium atom, respectively, n is the number of Li atoms. The calculated adsorption energy include two parts: one is the interaction between Lithium ions and carbon atoms and the other comes from the interaction among Li ions. To understand the interaction between the Li and the graphene, we define the pure adsorption energy per Li atoms (E_{atom}) as follows

$$E_{atom} = \frac{(E_{G+nLi} - E_G - E_{nLi})}{n}$$

where (E_{nLi}) represents the energy of all lithium atoms including the interaction themselves and (E_G) represents the energy of deformed nanostructured carbon. It is noted that all adsorption energy obtained here is negative. For convenience, we use the absolute values in all following plots. In general, the larger adsorption energy of Li atoms on graphene implies higher lithium storage capacity.

3. Results and discussion

As mentioned above, we are interested in how grain boundary defects and curvature influence the binding between lithium ions and the carbon structures. Hence the binding energy of lithium adsorbed on different carbon structure is examined, including a single Li adsorbed on graphene with GB defects of different type, Li atoms adsorbed on carbon nanotubes, and binding between Li and fullerene.

3.1. Li adsorbed on defective graphene

We first show the adsorption energy for a single Li adsorbed on different position of pentagon–heptagon defects (Fig. 1a) in grain boundary of tilt angle 27.79° [36] and a grain boundary (GB) composed of pentagon-octagon defects (Fig. 1b) and discrete vacancies. It is seen that the pure adsorption energy of Li atoms is effectively enhanced even in hexagonal rings near the defect (Table 1). The adsorption energy for Li in hexagonal rings decreases as they stay far away from the defective region, and finally approaches to a constant value of −1.584 eV. The approximate range subjected to the influence of defect is about 7.48 Å. A structure full of pentagon-octagon defects are shown in Fig. 1c, where the binding energy is extremely high even if each ring binds to one atom. We also try to add Li atoms on the GB of different angles [36], as shown in Fig. 1d and e. It is seen that Li atoms prefer to adsorb on pentagon-heptagon defects. Comparing the pure adsorption energy of Li on GBs with different angles seen in Fig. 1f, there is a very slight difference. It is mainly when Li atoms are trapped in pentagon-heptagon rings to give rise to the high binding energy between Li-C system.

We further calculate the density of states (DOS) of graphene