Applied Surface Science 463 (2019) 610–615

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Full Length Article

Lithiation behavior of graphene-silicon composite as high performance anode for lithium-ion battery: A first principles study

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ARTICLE INFO

Keywords:
Lithium-ion battery
Graphene-silicon composite
Anode material
First principles calculation
Lithiation behavior

ABSTRACT

Graphene is superior as a contact with silicon active materials and their composite show very small volume expansion during charge processes. However, further study on atomistic-scale mechanism of the interaction between Li and Graphene-Silicon (Gra/Si) system is very challenging for current experimental technologies. In this work, the mechanism of Li adsorption on a Gra/Si system is investigated using density functional theory. Based on the calculated results of binding energies, charge transfer, charge density difference, mean squared displacement and diffusion constant, it concluded that the incorporation of graphene can significantly enhance the electrochemical performance of silicon as high performance anode material, which consists with the experimental results. A theoretical capacity of 2896 $mAhg^{-1}$ is obtained, it is closed to the first cycle capacity of 2634 $mAhg^{-1}$ in experiment. Moreover, the origin of irreversible capacity of Gra/Si system is investigated. The shorter bond lengths Li—S and Li—C are related to strong Li—C and Li—Si connections and irreversible capacity loss during lithiation. Then a reversible capacity of 2383 $mAhg^{-1}$ is obtained by excluding the Li atoms with shorter bond lengths, and is comparable to the reversible capacity of 2497 $mAhg^{-1}$ in experiment. The proposed computational frame can be used to evaluate and design nanocomposite anode materials for lithium-ion batteries.

1. Introduction

As a naturally abundant element, silicon is a promising anode material for lithium-ion batteries (LIBs) with very high theoretical specific capacity of 4200 $mAhg^{-1}$ [1,2]. However, large volume change during charging/discharging cycles is still the primary problem for practical application of silicon anode. The volume change will lead to rupture of Si and breaking away from electric contacts, and make it difficult to maintain a stable solid electrolyte interphase (SEI), finally resulting in quick fading of capacity and short cycle life [3,4]. Various approaches have been employed to overcome this issue and improve the overall electrochemical performance of silicon-based anodes [5,6]. Preparation of nano-scale silicon-based materials such as nanoparticles, nanowires and thin film is their major solution, while buffer layers are generally needed to make the structures stable during charging/discharging cycles.

Graphene is a new class of monolayer of carbon atoms densely packed in a honeycomb crystal lattice. Graphene has attracted enormous attention because of its two-dimensional (2D) crystal structure with atomic thickness, unique electronic structure, high intrinsic mechanical strength, high surface area and superior electronic conductivity [7–10]. Recently, silicon core-hollow carbon shell structure (also called yolk-shell structure) was prepared and demonstrated in various degree of performance improvement [11–14]. Graphene is superior as a contact with Si active materials and their composite show very small volume expansion during charge processes [15–22]. However, atomistic-scale electrochemical mechanism related to the interaction between Li and Gra/Si system is still not clear, which could be very challenging for current experimental technologies.

Atomistic simulation is a powerful tool for investigating various properties of materials, and was successfully used in modeling and simulation of SiC-based anode materials in our previous studies [23–26]. In this work, Li adsorption and diffusion properties on the Gra/Si are investigated by first principle calculations. The electrochemical characteristics include Li adsorption energies, charge transfer, band structure, density of states (DOS) are analyzed and discussed. Moreover, diffusion of Li in the Gra/Si systems and volume change under lithiation are also studied. To the best of our knowledge, this is the first study in which theoretical method is employed to study the lithiation behavior of Gra/Si composite.

2. Computational method

For the first principles calculations, generalized gradient approximation

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https://doi.org/10.1016/j.apsusc.2018.08.258
Received 3 July 2018; Received in revised form 20 August 2018; Accepted 30 August 2018
Available online 30 August 2018
0169-4332/

(GGA) [27] Perdew-Burke-Ernzerhof (PBE) [28] functional were used to accurately describe the interactions between an adsorbate and various surface. Ultrasoft pseudopotentials are used for the description of electron-ion interactions. An energy cut off of 400 eV was used for the expansion of plane waves. G-point sampling was used with 3 × 3 × 1 K-point mesh for integration of Brillouin zone. The dimensions of unit cell were 7.53 Å × 7.53 Å × 28.9 Å, a vacuum space with a height of 15 Å was added between silicon and graphene. Periodic boundary conditions were employed in all three directions. Geometry optimizations were performed by using the conjugate gradient method for the structures until the residual force were less than 10^{-2} eV/Å and the convergence of energy change per atom were less than 10^{-5} eV. By Ab intio molecular dynamics (AIMD) simulations with Canonical ensemble (NVT), Nosé-Hoover thermostat for temperature controlling and a time step of 1 fs, the structures were annealed at 500 K to obtain sufficient atomic rearrangement. The diffusion properties of Li in Gra/Si system were calculated by NVT simulations and a temperature of 800 K. All the calculations were carried out with the CASTEP module [29] of Materials Studio.

The binding energy per atom for adsorption of Li atoms is defined by:

$$E_{\text{binding}} = (E_{\text{Gra/Si+Li}} - E_{\text{Gra/Si}} - E_{\text{Li}})/n \quad (1)$$

where n is the total number of absorbed Li atoms, $E_{\text{Gra/Si+Li}}$ is the total energy of the composite structure containing Li atoms, $E_{\text{Gra/Si}}$ is the total energy of Gra/Si system without Li atom, and E_{Li} is the energy of the Li atoms.

To better describe the ion bond of Li incorporation at the different sites, the charge density difference was calculated by:

$$\Delta\rho = \rho_{\text{Gra/Si+Li}} - \rho_{\text{Gra/Si}} - \rho_{\text{Li}} \quad (2)$$

where $\rho_{\text{Gra/Si+Li}}$ is the charge density of Li incorporated Gra/Si system, $\rho_{\text{Gra/Si}}$ is the charge density of Gra/Si system, and ρ_{Li} is the charge density of isolated Li atoms with the same positions in the lithiated structure.

The formation energy per Si atom (E_f) of Li_xSi-Gra (x is the number of lithium atoms per silicon atom) can be calculated by:

$$E_f = E_{Li_xSi-Gra} - (xE_{Li} + E_{Gra/Si}) \quad (3)$$

where $E_{Li_xSi-Gra}$ and $E_{Si/Gra}$ are the total energies per Si atom for Li_xSi-Gra and Gra/Si respectively, and E_{Li} is per-atom energy of Li.

Based on the calculated E_f profile, the voltage-composition (V − x) curve for the lithiated system was obtained by [30]:

$$V_{(x)} = -\frac{d(E_f)}{dx} \quad (4)$$

To investigate the influence of graphene on diffusion properties of Li, the diffusion coefficient of Li near graphene were calculated based on Einstein relation:

$$D = \frac{<|R_i(t) - R_i(0)|^2>}{6t} \quad (5)$$

where $R_i(t)$ is the position of atom $i$at time of t, the angular bracket denotes a thermal average.

3. Results and discussions

The adsorption properties of Li in the Gra/Si system are investigated firstly. Two typical adsorption sites are selected, as shown in Fig. 1(b): (1) Adsorption of Li on the outside surface of graphene (Li/Gra/Si), including the center of the hexagon of C atoms (H_e site) and the top of the C atom (H_t site); (2) Adsorption of Li in the interlayer of Gra/Si (Gra/Li/Si), including the top of the central Si atom (H_c) and the top of the Si atom which is beside the central Si atom (H_b). The band structures of graphene and Gra/Si system are shown in Fig. 1(c–d). The Fermi levels are shifted to 0 eV. Since the Gra/Si system is maintained through dispersion interactions, the hybrid system retains the characteristics of its components. The overall features on band structure of the system are a composite of graphene and silicon.

The calculated binding energies and charge transfer results for the Li adsorption sites are shown in Table1. The most stable adsorption site of Li for Li/Gra/Si is similar to that of pristine monolayer (Li/Gra), and Li atoms can feel the presence of graphene in Li/Gra/Si and Gra/Li/Si systems. Based on the binding energies, Gra/Li/Si system ($E_b = -3.80$ eV) is energetically more stable than Li/Si ($E_b = -3.04$ eV), Li/Gra/Si ($E_b = -1.94$ eV) and Li/Gra ($E_b = -1.30$ eV). It indicates that Li atoms are more likely to adsorbed into the interlayer of Gra/Si rather than the outside surface of graphene in Gra/Si composite. The incorporation of graphene can significantly enhance adsorption performance of Li, which is attributed to synergistic effect.

The amount of charge transfer between adsorbed Li and Gra/Si system is quantitatively estimated by Hirshfeld analysis. When Li atom adsorbs on the outside surface of graphene (Li/Gra/Si), the

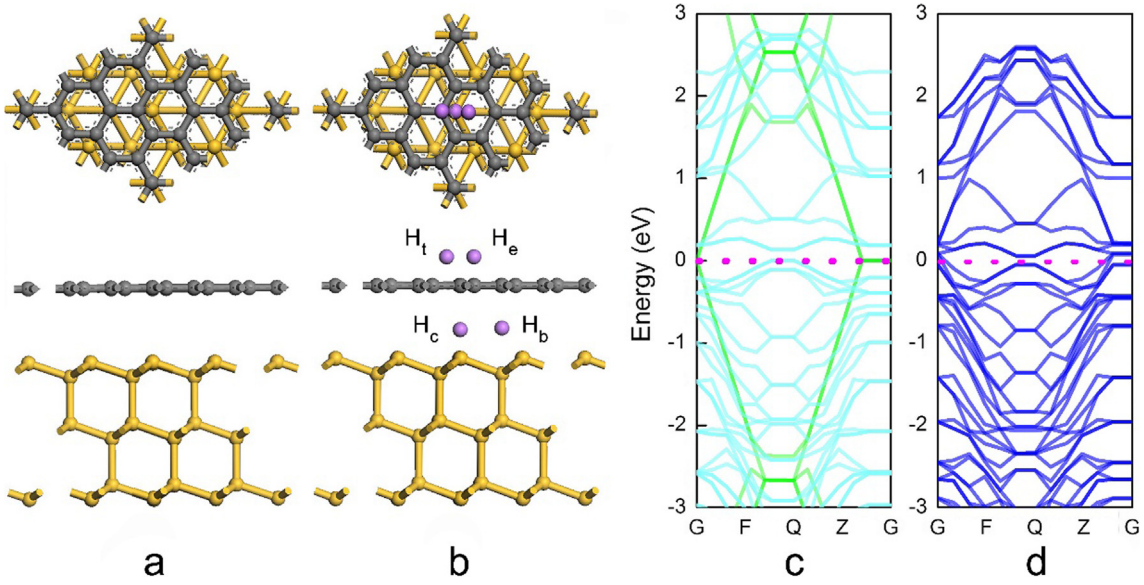

Fig. 1. Top and side views of Gra/Si (a) and Li adsorption sites in Gra/Si (b). Band structures of (a) graphene (green) and Si (blue) and (b) Gra/Si. The black, yellow, and violet spheres represent the C atom, Si atom and Li atom respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)