



First-Principles studies of silicon underpotential deposition on defective graphene and its relevance for lithium-ion battery materials



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ABSTRACT

First-principles calculations are undertaken to analyze the properties of carbon-silicon hybrid materials consisting of silicon modified graphene and defective graphene to evaluate the stability of the structure and their interactions with lithium. Underpotential shifts are determined for the different structures on defective surfaces, showing that decoration of graphene defects with a small number of silicon atoms should occur at underpotentials. Nucleation overpotentials are also determined using a thermodynamic formalism, showing that the formation of nuclei should be hindered with respect to free standing Si clusters. These results analyze the possibility of using underpotential deposition of silicon on graphene to obtain high capacity and cycling stable material for anodes of lithium batteries.

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1. Introduction

In terms of sustainable development and environmental issues, the use of efficient storage systems is an increasingly critical point. The world has undergone a great technological revolution in the past 20 years led by lithium ion batteries, due to their relatively high energy density. However, in order to meet the energy demand of our modern life, a new generation of lithium batteries, more powerful, efficient and cheaper, is desirable. The challenge lays in choosing electrochemically active, light, abundant and environmentally friendly materials that achieve high density energy [1–4], long life cycle and when possible, a high power density. Silicon has shown to be a very promising anode material to fulfill the needs of a lithium-ion battery. It has a high theoretical capacity, of around 3579 mAh/g [5], low cost and natural abundance. However this material runs with the great disadvantage that during the formation of a Si-Li alloy corresponding to the insertion of Li in the anode for the charging process, it suffers a change of volume that can reach 380% [6–8]. This expansion, followed by contraction of the material upon battery discharge, quickly leads to irreversible damage of the electrode, causing a rapid decrease in capacity

during cycling [9–11]. Furthermore, Si usually has a low electrical conductivity. In this regard, some current studies propose the combination of Si with graphene sheets to improve conductivity [12–15]. Even more, the combination of Si-based materials with carbonaceous materials as graphene can substantially relieve the mechanical stress suffered by the electrode [16]. Graphene has been proposed as one of the best candidate matrices for anodes due to its mechanical strength, high surface area, porous structure, and the capacity to provide a high flexibility to tolerate volume changes [17–19]. On the basis of these considerations, an appealing option appears to be the generation of graphene/Si multilayer structures at the nanometer scale, as proposed in the article of Ji et al. [15]. These authors have used a repeated process of filtering liquid-phase exfoliated graphene film and a subsequent coating of amorphous Si film via plasma-enhanced chemical vapor deposition method to get graphene/Si multilayer structures. However, the cycling performance did not fill the expectations that this material awakened. The SEM pictures of these compounds show that while the desired structures have been successfully obtained, the adhesion between the Si and C materials is relatively weak. These features can be understood in terms of the weak interaction between Si nanostructures and graphitic structures, as shown by first principles calculations. While the minimum binding energy of a single Si atom to a (0001) graphite surface is $E_{gr}^{Si} = -1.768$ eV, the binding energy of Si clusters to the surface denotes a dramatically

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weaker interaction of Si with the graphite surface as cluster size increases. For example, the binding energy is -0.13 eV/atom for Si_3 and -0.055 eV/atom for Si_7 . If we compare the E_{gr}^{Si} value given above with the experimental bulk cohesive energy of Si, $E_{coh}^{Si} = -4.97$ eV, we can understand the progressively weaker Si-graphite interaction in bond-order terms: as a Si atom finds more and more Si neighbors, its bond with the graphite surface becomes progressively weaker. This weak interaction between silicon nanostructures and graphite has been also confirmed by STM experiments [20]. A possible remedy to this weakened interaction could be sought by functionalizing the carbonaceous surface. Kulish et al. [21] have shown that functionalization with carboxyl groups of carbon nanotubes improved considerably the bonding of the Si clusters to the carbonaceous nanostructure. In fact, the presence of the $-\text{COOH}$ groups was found to be able to strengthen the Si_6 -(5,5) nanotube interaction in -0.6 eV. Another way to improve the adhesivity between silicon and carbon could be the generation of silicon carbide at this interface through intermixing induced by Ar-ion beam [22]. We analyze here a different alternative to improve the stability the Si adsorbed structures: the introduction of surface defects.

In the present work we perform first-principle studies of carbon-Silicon hybrid materials consisting of silicon modified graphene and defective graphene to evaluate the stability of the structures and their interactions with lithium. We evaluate the effect of the presence of simple and double vacancy defects in the interaction with silicon and the interaction of these hybrids structures with lithium. We discuss this information in the context of underpotential deposition, which could be relevant to seek an electrochemical alternative for the controlled decoration of graphenic surfaces.

2. Calculations Methods and Modeling

2.1. Calculation details

The ab initio calculations were performed with the Quantum Espresso package [23], which is based on plane waves bases, setting up a kinetic energy cutoff of 680 eV. For the calculations we used ultrasoft pseudopotentials within the Perdew-Wang approximation for the exchange correlation functional in the PW91 functional [24,25]. The simulation box consisted in a 4×4 graphene supercell containing 32C atoms with periodic boundary conditions in all directions. The cell size was kept constant during optimization. In the z direction we leave a 10 Å vacuum to avoid interaction among the graphene layers. In the case of larger clusters of silicon we used as a control a graphene supercell containing 60C atoms observing no significant differences with the

results obtained for the one with 32C atoms. We evaluated pristine and defective graphene considering simple and double vacancy defects. The Brillouin zone was sampled in a $4 \times 4 \times 1$ irreducible Monkhorst-Pack k point grid [26]. The convergence threshold for the total energy at each electronic calculation was set to 1×10^{-5} eV, taking into account Van der Waals interactions using the DFT-D method, since results for similar systems [27] have shown that is important to consider dispersion interactions to get a good accuracy in the energy values. Geometry optimizations were performed employing the Broyden-Fletcher-Goldfarb-Shanno (BFGS) algorithm (for stress minimization).

2.2. Model for defective graphene and its decoration with Si atoms. Thermodynamic analysis

The interaction of a silicon atom and silicon clusters with a pristine and a defective graphene surface was analyzed by the calculation of different energy-related quantities that are relevant to the present problem.

In order to analyze the stability of adsorbed Si atoms with respect to isolated Si atoms in the gas phase, it is useful to define a cluster formation energy referred to the atomic state as:

$$\Delta E_{for}^{at} = E_{Si_nGr} - E_{Gr} - NE_{Si} \quad (1)$$

where E_{Si_nGr} is the energy of the optimized hybrid structure (pristine or defective graphene, modified with N silicon atoms), E_{Gr} is the energy of pristine or defective graphene and E_{Si} is the energy of a silicon atom in vacuum. Thus, a negative value of ΔE_{for}^{at} indicates that the Si adatoms are more stable in the nanostructure than in the gas phase.

Alternatively, in order to determine the relative stability of the surface Si nanostructures with respect to the bulk Si material it is useful to define the following cluster formation energy from the bulk material, denoted with:

$$\Delta E_{for}^{bulk} = E_{Si_nGr} - E_{Gr} - NE_{SiBulk} \quad (2)$$

where E_{SiBulk} is the cohesive energy of Si in diamond structure and N the number of silicon atoms in the nanostructure. In this case, a negative value of the formation energy ΔE_{for}^{bulk} indicates a favorable formation of the hybrid structure from the bulk materials. As found below, the quantity ΔE_{for}^{bulk} is particularly useful in the case of electrochemistry, since it is closely related to the free energy of formation of the corresponding nanostructure, which can be used to predict its electrochemical stability. With this purpose, we shortly revisit the modeling developed by some of us with the purpose of analyzing the stability of metallic nanostructures deposited in a cavity of a foreign substrate[28]. Similar modeling

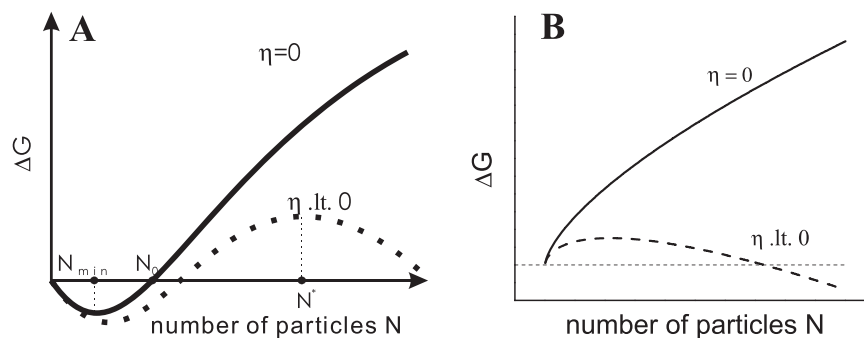


Fig. 1. A) Scheme of the excess of free energy as function of the number of deposited atoms for the case of metal growth in a nanocavity of a foreign substrate, for the case where the interaction of the deposited atoms with the concave substrate is stronger than the interaction of the adsorbate atoms among themselves. It is also assumed that further wetting of the flat substrate is less favourable than the interaction between adatoms, so that cluster growth occurs. B) Scheme of the excess of free energy of an isolated metal cluster as function of the number of atoms at two different overpotentials.

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