Role of Interface in the Lithiation of Silicon-Graphene Composites: A First Principles Study

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ABSTRACT: We examine the lithiation behavior of silicon-graphene (Si-Gr) composites using density functional theory calculations. Our calculations demonstrate charge transfer from Li to both Si and C (in graphene); the excess electrons on graphene create an electric field, which attracts Li cations while repelling Si anions and thus results in a distinct alternative Li−Si layering structure near graphene. The interfacial Li ions exhibit substantially higher mobility along the Si/Gr interface in comparison to bulk diffusion in Si; such facile interfacial diffusion could contribute toward high performance anodes with fast charge/discharge rates. However, the presence of graphene tends to have no significant impact on the structural evolution of Si during lithiation, as Li atoms are mostly incorporated in the Si matrix rather than at the Si/Gr interface. Consequently, the theoretical capacity and voltage profile of the Si-Gr composite are predicted to be close to those of pure Si.

1. INTRODUCTION

Facing the ever-increasing demand for safer lithium (Li) ion batteries (LIBs) with high energy density, rapid charge rate, and long cycle life, there is an urgent need to find a new electrode material in replacing graphite which has a limited theoretical capacity of 372 mAh/g (LiC6). Among the alternative anode materials considered, silicon (Si) stands out the most because of its highest known theoretical capacity about 4200 mAh/g (Li4.4Si)1,2 and abundance. However, the practical use of Si as anode material is hampered by its large volume expansion, causing pulverization, loss of electrical contact, and consequently early capacity fading. For this reason, considerable efforts have been made to overcome these drawbacks, including structural modifications such as utilizing amorphous phases,3−5 nanoparticles6,7 and nanowires,8 and alloying Si with active/inactive elements.9−12

Nanostructured Si in particular has shown promising improvements, as it can accommodate larger strain and provide better mechanical integrity since its dimension would limit the size and propagation of cracks.13−15 By combining Si with carbonaceous (C) materials (Si−C), the cycling stability can be further improved with the enhanced buffering effect and electrical conductivity from carbon.16−23 Several structurally superior designs have been demonstrated by researchers, including (1) making nanosized Si−C composites in particular forms such as core−shell heterostructures,16,19 (2) depositing Si−C multilayer films,24 (3) making Si-graphene composites by coating Si on graphene,25 or encapsulating Si nanoparticles with crumpled graphene,17,26,27 and (4) putting C coating on Si nanowires or coating tubular forms of C with Si.18,20−23 As the result, excellent capacity retention was realized by composites made of Si and carbonaceous materials; nano-silicon-coated graphene granules have been reported with capacity exceeding 2000 mAh/g at the current density of 140 mA/g and excellent stability for 150 cycles,25 and near-theoretical capacity (of Si) could be achieved (3890 mAh/g) for more than 100 cycles in Si−C thin films, which is thought to be attributed to the buffering effect of intercalated C layers.24 Furthermore, nanostructured Si−C anodes have also been utilized to enhance the high-rate capabilities; previously, capacity as high as 2000 mAh/g was reported at 5C charging rate (full lithiation in 1/5 h) for Si decorated carbon nanotubes,36 and capacity in excess of 1500 mAh/g was demonstrated at 8C rate using porous Si−C composites.35 As a promising anode material for LIBs, Si−C composites exhibit many unique synergistic benefits, such as remarkable capacity retention and rate capabilities. However, in comparison to pure Si or C anodes, it is more challenging to investigate the lithiation behavior in Si−C composite anodes, especially concerning the complexities and intricate reactions at Si/C interfaces. On the theoretical side, there have been many studies employing density functional theory (DFT) to examine Li incorporation in Si (crystalline/amorphous bulks30−33 and NWs34−36), graphite,37,38 and graphene.39−43 However, to the best of our knowledge, no atomistic-scale study has been reported regarding the lithiation behavior in Si−C composites.

In this paper, based on DFT calculations we present the structural evolution and voltage profile of the lithiated Si-graphene (Si-Gr) composite, and also discuss the bonding mechanism and Li diffusivity in Li,Si-Gr systems (0 ≤ x ≤ 4.33), with particular attention to the effect of the Si/Gr interface. In reality, Si−C composites could be composed of Si
with graphite (or multiple layers of graphene) or turbostratic carbon (disordered graphite); however, most of the constituent C atoms are likely sp$^2$ bonded, so it would be reasonable to use the Si-Gr model structure for investigating the Si/C interface effect. The fundamental findings from this computational work will contribute to a better understanding of the properties and performance of Si–C nanocomposites as LIB anode materials.

2. COMPUTATIONAL METHOD

The calculations reported herein were performed based on DFT within the generalized gradient approximation (GGA-PW91), as implemented in the Vienna Ab-initio Simulation Package (VASP). The projected augmented wave (PAW) method with a plane-wave basis set was employed to describe the interaction between ion core and valence electrons. The PAW method is in principle an all-electron frozen-core approach that considers exact valence wave functions. Valence PAW method is in principle an all-electron frozen-core approach that considers exact valence wave functions. Valence configurations employed are as follows: 1s$^2$2s$^1$ for Li, 3s$^2$3p$^3$ for Si, and 2s$^2$2p$^2$ for C. An energy cutoff of 400 eV was applied for the plane-wave expansion of the electronic eigenfunctions.

As illustrated in Figure 1, each Li$_x$Si-Gr supercell consists of a 48-atom 12.8187 $\times$ 9.8680 Å$^2$ rectangular graphene sheet which is interfaced with the amorphous Li$_x$Si alloy (a-Li$_x$Si) of desired composition ($x$ varies from 0 to 4.33).

Here, we used the GGA-optimized lattice constant of 2.467 Å for graphene, which is in good agreement with the experimental value of 2.46 Å. The compositions and dimensions of the Li$_x$Si-Gr systems considered are summarized in Table 1.

The model structures for bulk a-Li$_x$Si alloys were created based on ab initio molecular dynamics (AIMD) simulations as previously described in ref 49. To simulate a Li$_x$Si-Gr system, the a-Li$_x$Si bulk alloy and graphene sheet were placed approximately 2 Å apart and fully relaxed using a conjugate gradient method until residual forces on constituent atoms became smaller than 5 $\times$ 10$^{-2}$ eV/Å. The Li$_x$Si-Gr system was then annealed at 500 K for 1 ps with a time step of 1 fs to allow sufficient atomic rearrangement (the annealing temperature was controlled via velocity rescaling), followed by geometry optimization. For geometry optimization, the Brillouin zone sampling was done with a Γ-centered (2 $\times$ 2 $\times$ 1) Monkhorst-Pack grids, and for charge analysis an increased $k$-point mesh size (6 $\times$ 6 $\times$ 1) was used to refine the calculations. Periodic boundary conditions were employed in all three directions, and for each composition three independent samples were considered. AIMD simulations of 18 ps duration with a time step of 1 fs were carried out at 800 K (temperature was controlled via Nose-Hoover thermostat) to calculate Li diffusivities in Li$_x$Si-Gr and the counter bulk a-Li$_x$Si alloy.

3. RESULTS AND DISCUSSION

3.1. Atomic Arrangement and Bonding Mechanism near the Lithiated Si/Gr Interface. First, we examined the lithiated structures of the Si-Gr composite with varying Li contents. Figure 2 shows a set of atomic structures from our simulations for selected Li$_x$Si-Gr systems ($x = 1.00, 1.67$, and 3.57).

Table 1. Compositions of the Li$_x$Si-Gr Systems Employed in This Work, Together with the z-Dimension Values which Are Averaged Based on Three Different Supercells (See Figure 1 for a Schematic of the Supercell).

<table>
<thead>
<tr>
<th>$x$ in Li$_x$Si-Gr (# Li/Si/C)</th>
<th>z-Dimension (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00 (0/64/48)</td>
<td>16.26 ± 0.32</td>
</tr>
<tr>
<td>0.13 (8/64/48)</td>
<td>16.64 ± 0.27</td>
</tr>
<tr>
<td>0.25 (16/64/48)</td>
<td>17.35 ± 0.35</td>
</tr>
<tr>
<td>0.50 (32/64/48)</td>
<td>18.52 ± 0.31</td>
</tr>
<tr>
<td>0.75 (48/64/48)</td>
<td>19.87 ± 0.31</td>
</tr>
<tr>
<td>1.00 (64/64/48)</td>
<td>21.24 ± 0.09</td>
</tr>
<tr>
<td>1.67 (80/64/48)</td>
<td>20.70 ± 0.58</td>
</tr>
<tr>
<td>2.35 (90/38/48)</td>
<td>20.65 ± 0.13</td>
</tr>
<tr>
<td>3.57 (100/28/48)</td>
<td>20.44 ± 0.21</td>
</tr>
<tr>
<td>4.33 (104/24/48)</td>
<td>20.82 ± 0.11</td>
</tr>
</tbody>
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We notice a distinct Li enrichment at the Li$_x$Si/Gr interface, but away from the graphene layer, Li and Si atoms tend to be well-mixed similar to bulk Li$_x$Si alloys. As partitioned by the vertical dashed lines, away from graphene (|z| = 0.0 Å), the first layer (|z| ≈ 1.7 to 3.0 Å) comprises only Li atoms with the average Li-Gr distance around 2.3 Å, the second layer (|z| ≈ 3.0 to 4.5 Å) is mainly composed of Si atoms while the third layer consists of a blend of Li and Si atoms but slightly richer in Li. The distinct layering near graphene tends to be pertinent within the first two to three atomic layers. Further away from graphene, the bulk-like structure is restored where Li and Si atoms are well mixed without segregation.

Figure 1. Side view of a Li$_x$Si-Gr system in which the a-Li$_x$Si alloy is interfaced with a 48-atom rectangular graphene sheet (12.8187 $\times$ 9.8680 Å$^2$). The z-dimension values are summarized in Table 1.

Figure 2. Set of atomic structures from our simulations for (a) Li$_{1.00}$Si-Gr, (b) Li$_{1.67}$Si-Gr, and (c) Li$_{3.57}$Si-Gr. The graphene position is set to zero (in z-dimension).

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As summarized in Table 2, our results from Bader charge analysis suggest the charge transfer from Li to both Si and C

Table 2. Calculated Bader Charges for C (in Graphene), Li, and Si Atoms in Selected Li1.0Si-Gr Systems

<table>
<thead>
<tr>
<th>x</th>
<th>C</th>
<th>Li</th>
<th>Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.00</td>
<td>-0.07±0.01</td>
<td>+0.85±0.00</td>
<td>-1.49~−0.22</td>
</tr>
<tr>
<td>1.67</td>
<td>-0.08±0.01</td>
<td>+0.83±0.00</td>
<td>-2.30~−0.59</td>
</tr>
<tr>
<td>3.57</td>
<td>-0.13±0.00</td>
<td>+0.80±0.01</td>
<td>-3.32~−1.58</td>
</tr>
</tbody>
</table>

(in graphene), which is not surprising considering their relative electronegativity values ($\chi_{Li} = 0.98$, $\chi_{Si} = 1.90$, and $\chi_{C} = 2.55$).

The C atoms are more negatively charged with increasing Li content ($x$), while the Li charge state remains nearly constant, and the Si charge state varies significantly depending on the Si–Si connectivity.\(^{59}\) As such, it is apparent that the alternative layering of Li and Si is due to the electrostatic interaction between them; that is, the excess negative charges on graphene create an electric field, which attracts Li\(^{+}\) co-ions to screen the field, as illustrated in Figure 3.

With increasing Li content, we see a rise in excess negative charges on graphene, which in turn causes more Li cations accumulating at the interface. Also note here, Li atoms are randomly dispersed across the graphene surface rather than each locating on top of the C hexagonal (as seen in the case of single Li adsorption on graphene\(^ {57,60} \)). This difference together with the aforementioned larger Li-Gr distance of $\sim$2.3 Å (as compared to 1.73 Å for single Li adsorption on graphene) suggest that the interaction of Li with graphene in Li1.0Si-Gr systems is somewhat weaker than that in the Li-Gr case; this can be attributed to the additional interaction between the Li and Si layers.

For a better understanding of the interfacial interaction, we conducted more detailed analysis of atomic arrangement, charge transfer, and charge distribution in the Li1.0Si-Gr system. Figure 4a presents the number density, $\langle \rho_0 \rangle$, profiles of Li and Si along the direction normal to the graphene surface, which clearly demonstrates their alternative layering near graphene.

All the results are averaged (denoted by angular bracket) based on three different samples. As shown in the inset of Figure 4, the corresponding charge redistribution is quantified by the charge-density difference $\langle \Delta \rho \rangle$, which is obtained by subtracting the charge densities of isolated Li, Si, and graphene from that of Li1.0Si-G (i.e., $\Delta \rho = \rho_{Li1.0Si-Gr} - \rho_{Li} - \rho_{Si} - \rho_{Gr}$). The $\Delta \rho$ plot illustrates the excess electron accumulation on graphene with an appreciable polarization toward Li cations, which suggests a dominant ionic bonding character. Perturbed by the electrostatic interaction with Li ions, significant charge redistribution also occurs within the graphene layer, leading to electron puddles (with some electron depletion in the C–C bonds) in the vicinity of Li atoms. Similarly, the excess electron charge on Si also exhibits noticeable polarization toward Li (along with slight charge depletion in the Si–Si bonds), indicating that the Li–Si bonding is predominantly ionic.

The charge density difference averaged over the $x$–$y$ plane, $\langle \Delta \rho \rangle$, as a function of $z$ is shown in Figure 4b with the position of the graphene sheet set at $z = 0$ Å. The $\langle \Delta \rho \rangle$ profile fluctuates extensively near graphene and gradually damps till nearly flat in the bulk region. The positive $\langle \Delta \rho \rangle$ humps around 0.6 Å and 3.0 Å correspond to electron gain in the graphene and Si layers, respectively; notice that both humps deviate slightly from their corresponding atomic positions ($\langle \rho_0 \rangle$ peak positions) with a shift toward the Li layer, as indicative of the appreciable polarization due to the electrostatic interaction with the Li layer.

As demonstrated earlier, the excess electrons on graphene create an electric field ($E_{ES}$) that causes the redistribution of Li and Si ions, which in turn gives rise to a charge imbalance at the Li1.0Si/Gr interface. The resulting electric-potential $\langle \phi \rangle$ profile along the direction normal to the graphene surface is obtained by solving Poisson’s equation:

$$V^2 \phi(z) = \langle \Delta \rho(z) \rangle / \varepsilon_0$$

with \(-V\phi_{ES} = E_{ES}\)

where $z$ is the distance from the graphene plane, $\langle \Delta \rho \rangle$ is the $x$–$y$ planar averaged charge-density difference, and $\varepsilon_0$ is the vacuum permittivity. By integrating eq 1, we can evaluate the potential variation near the Li1.0Si/Gr interface:

\begin{align*}
\phi(z) &= \phi(z_0) + \int_{z_0}^{z} \left( \langle \Delta \rho(z) \rangle / \varepsilon_0 \right) \, dz + \int_{z_0}^{z} \varepsilon_0 \frac{\partial \phi}{\partial z} \, dz \\
&= \phi(z_0) + \int_{z_0}^{z} \left( \langle \Delta \rho(z) \rangle / \varepsilon_0 \right) \, dz + \varepsilon_0 \int_{z_0}^{z} \frac{\partial \phi}{\partial z} \, dz
\end{align*}
\[ \phi(z) = -\frac{1}{e_0} \int_0^z (z - z') (\Delta \rho(z')) \, dz' \]  

(2)

Figure 4c shows a calculated potential profile (with a bin size of 0.1 Å) near the graphene plane with respect to the bulk potential (which is set equal to 0 V). The result shows that the potential drops rapidly across the first Li layer, indicating that the accumulated Li counterions effectively screen \( E_{ES} \).

**3.2. Interface Effect on Li Diffusion.** To examine how the presence of graphene affects Li diffusion, we calculated the diffusivity of Li near graphene, in comparison to the corresponding a-Li<sub>1.0</sub>Si bulk alloy. Figure 5 shows the total and decomposed mean squared displacement (MSD) profiles in \( x, y \), and \( z \)-directions for Li atoms near graphene (in a-Li<sub>1.0</sub>Si-Gr) at 800 K. For comparison, the MSD profiles for Li atoms in bulk a-Li<sub>1.0</sub>Si are also presented in the inset.

At 800 K, the AIMD duration of 18 ps (ps) appears to be sufficient as the MSDs of Li atoms in both a-Li<sub>1.0</sub>Si-Gr and a-Li<sub>1.0</sub>Si were well converged after 9 and 12 ps, respectively. For Li atoms in a-Li<sub>1.0</sub>Si, the decomposed MSD profiles are compatible in all three directions, indicating that the movements of Li atoms are isotropic as expected. Contrarily, Li atoms near graphene (in the a-Li<sub>1.0</sub>Si-Gr system) exhibit very different mean square displacement behavior; the MSDs in \( x \) - and \( y \)-directions increase progressively at compatible rates while the MSD value in the \( z \)-direction is negligible. This finding provides a clear picture that Li diffusion near graphene is two-dimensional parallel to the graphene sheet. Once MSD profiles are well converged, corresponding Li diffusion coefficients can be obtained using the Einstein relation, \( D = \langle \text{MSD} \rangle / (nt) \) with \( n = 6 \) (4) for three (two) dimensional diffusion; the angular bracket denotes an ensemble average over the AIMD interval. Disregarding the first few picoseconds, as illustrated in Figure 5, a linear fit over the time interval yields \( D_{Li} = (4.74 \pm 0.60) \times 10^{-5} \text{ cm}^2/\text{s} \) near graphene in the bcc-Li<sub>1.0</sub>Si-Gr system, which is about five times greater than \( D_{Li} = (1.02 \pm 0.40) \times 10^{-5} \text{ cm}^2/\text{s} \) in the counter alloy bulk alloy at 800 K. Our results suggest that \( D_{Li} \) can be substantially enhanced in Si–C nanocomposites due to facile diffusion along the Si/C interface, which is consistent with previous experimental observations that show significantly increased lithiation rates in Si–C composite systems.\(^\text{7,53} \)

**3.3. Energetics and Structural Evolution of Lithiated Si-Gr Systems.** We calculated the relative formation energies of the Li-Si-Gr systems as a function of Li content (0 \( \leq x \leq \) 4.33), with respect to crystalline Si (c-Si), body-centered cubic Li (bcc-Li), and free-standing graphene (Gr). Here, the formation energy per Si atom \( (E_f) \) is given by

\[ E_f = (E_{Li_{1-x}Si} - E_{Gr}) / N_{Si} - (xE_{Li} + E_{Si}) \]  

(3)

where \( E_{Li_{1-x}Si} \) and \( E_{Gr} \) are the total energies of the Li<sub>1-x</sub>Si-Gr system and free-standing graphene, respectively, \( N_{Si} \) is the number of Si atoms, \( x \) is the Li content per Si, and \( E_{Li} \) and \( E_{Si} \) are the per-atom energies of bcc-Li and c-Si, respectively.

As shown in Figure 6a, the calculated \( E_f \) decreases monotonically with increasing \( x \) and approaches a minimum value around \( x = 4 \). During early stages of lithiation, Li atoms are preferably accommodated near graphene, and as \( x \) continues to increase more Li atoms are further dispersed into the Si bulk region forming well mixed Li–Si alloys. Reaching the minimum-energy “plateau” around \( x = 4 \) implies that the Li<sub>1-x</sub>Si/Gr system is fully lithiated. The predicted capacity is close to that of pure Si, which is consistent with previous experiments that demonstrate a high Li storage capacity of 3890 mAh/g in Si/C films (≈Li<sub>1-x</sub>Si/C).\(^\text{24} \) Our results suggest the presence of graphene has a negligible impact on Li incorporation in the Si matrix, which is not surprising considering the extent of Li<sub>1-x</sub>Si/Gr interface effect is predicted to be very shallow.

Based on the calculated \( E_f \) profile, the voltage-composition (\( V-x \)) curve for lithiated Si-Gr in comparison to that of pure Si.

Taking the negative of the derivative of the third order polynomial fittings according to eq S, the \( V-x \) curve of lithiated Si-Gr with comparison to that of bulk Si is shown in Figure 6b. The curves turn out to overlap each other almost in the entire composition range, showing the Si-Gr lithiation voltage profile is nearly the same as the case of pure Si. Such a similarity is reasonable, because given the C:Si atomic ratio in the Li<sub>1-x</sub>Si-Gr system considered, the majority of Li atoms are incorporated in the Si matrix rather than at the Li<sub>1-x</sub>Si/Gr interface, and thus the voltage profile is dominated by Si lithiation.

Next, the structural evolution of selected Li<sub>x</sub>Si-Gr systems (\( x = 1.00, 1.67, \) and 3.57) was analyzed in terms of Si coordination.
4. CONCLUSIONS

DFT calculations were performed to examine the atomic arrangement, bonding mechanism, Li diffusion, and lithiation energetics in the Li-Si-Gr systems ($x = 0$ to 4.33). Our simulations predict a unique alternative Li$_x$Si network structure near graphene, due to the electrostatic interactions between positively charged Li and negatively charged Si and graphene. Such layering is found to extend about 2–3 atomic layers, beyond which uniform mixing is restored as in bulk a-Li$_x$Si alloys. The average Li-Gr distance in selected Li$_x$Si-Gr systems ($x = 1.00$, $1.67$, and $3.57$) is around 2.3 Å, which is larger than 1.73 Å as estimated for single Li adsorption on free-standing graphene; this may suggest the interaction of Li with graphene in the Li-Si-Gr system is relatively weaker than that in the Li-Gr case, due to the additional interaction with Si. We also examined the effect of graphene on Li diffusion via AIMD simulations; for Li$_{1.0}$Si-Gr at 800 K, the Li diffusivity near graphene is predicted to be approximately five times larger than that in the bulk a-Li$_{1.0}$Si alloy. We expect that such a significant enhancement in Li mobility could contribute toward high performance anodes with fast charge/discharge rates. Moreover, our calculations demonstrate that during lithiation Li atoms are mainly incorporated in the Si matrix rather than at the Li$_x$Si/Gr interface. As such, the predicted voltage profile and theoretical capacity exhibit close resemblance to the case of pure Si. The present work will assist in understanding the lithiation properties and performance of Si-C nanocomposites, and may provide a framework for the comparative study of various lithiated composite systems.

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Notes

The authors declare no competing financial interest.

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REFERENCES