An ideal polymeric C\textsubscript{60} coating on a Si electrode for durable Li-ion batteries

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\textbf{ABSTRACT}

Fullerene-deposited thin films on silicon substrate, their growth conditions and feasibility for durable lithium ion batteries were examined using molecular dynamics and \textit{ab initio} calculations. An ideal polymeric fullerene film was obtained when the fullerene incident energy was 180 eV; otherwise, the films were ill-grown or amorphized at different energies. The polymeric film coating was demonstrated as a promising approach for durable batteries because it is sufficiently soft and flexible enough to continue covering the silicon anodes under a high volume change during charging and discharging cycles, which maintains a selective conducting channel for lithium ions and an electron-conducting channel. Our calculations provide insight into ideal carbon coating via loosely connected porous sp\textsuperscript{2} carbons on a silicon anode surface for durable lithium-ion batteries.

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1. Introduction

Recently, lithium ion batteries (LIBs) have attracted much attention as a promising energy storage system due to its relatively high energy density [1]. Due to broad use of mobile electronic devices and electric vehicles, including hybrid electric cars, the demand for higher capacity has grown rapidly and steadily; thus, further improved energy density in LIBs has become a major area of research for LIBs. Thus far, the most promising approach has been to replace the conventional anode material, graphite, with silicon because silicon can theoretically store about 10 times more lithium (4200 mAh/g) than graphite (372 mAh/g). However, poor durability due to a large volume change for silicon is the main obstacle. Silicon expands up to 300% during lithiation and shrinks during delithiation. Many cracks develop due to the volume change, and eventually the silicon anode is broken into pieces after a few charge and discharge cycles, which permanently degrades the performance [2,3].

Rationally designed nano-structures and carbon composites have been suggested and tested to surmount this problem [4], including porous structures [5,6], nano-particles and wires [7,8], silicon–carbon core–shell structures [7,9,10], coating on silicon anode with carbonaceous materials [11–14], silicon–graphene multi layers [15] and silicon carbide with epitaxially grown graphene [16]. Nano-structures and nano-particles have enough empty space to accommodate a volume change and are smaller than pulverized silicon anode cracks; thus, cracks are not expected to develop. Carbon composites are expected to have improved lithium capacity compared with graphite due to the silicon and are expected to be more durable than a silicon anode due to the carbon.
Three effects are expected for carbonaceous coating on silicon. First, it plays a role as a mechanical support by either enhancing the mechanical strength or buffering the mechanical stress, thereby retaining electrode structural integrity against Si volume changes during battery cycling [17–20]. Second, it separates the silicon anode from the electrolyte and prevents the solid-electrolyte interface (SEI) from directly contacting the silicon. Third, it will improve electron conductivity, which is also a drawback for silicon anodes. All of the effects will improve LIB durability and performance.

Recently, it has been reported that fullerene ($C_{60}$) coating on silicon provides a stable performance without unfavorable surface cracking over many lithiation–delithiation cycles [12,13]; the authors showed that the fullerene film is not amorphous but polymeric and anticipated that such a film could serve as a good conductor and an artificial SEI due to fullerene’s good electrochemical properties as well as mechanical support. However, to date, only a few microscopic studies on polymeric fullerene films have appeared in the literature [21–23], and to our knowledge, the role of the coating film has not been investigated at the atomic level.

In this paper, we provide the conditions for forming polymerized $C_{60}$ films and evaluate whether the film has the film using classical film was modeled using a slab in periodic predictions will improve LIB durability and performance.

We simulated the growth process for $C_{60}$ using the SIESTA [28] density functional theory (DFT) program within a generalized gradient approximation (GGA-PBE) [29]. $C_{60}$ film was modeled using a slab in periodic supercell whose size is 23.02 Å × 23.02 Å × 150 Å. Slabs in different cells were separated by about 25 Å of vacuum. All carbon atoms from the MD simulation were included, while the silicon atoms that were greater than 9 Å away from the carbon atoms were excluded. Our model slab composed of 4589 carbon, 360 silicon, and 72 hydrogen atoms. Hydrogen atoms saturate dangling bonds at the bottom silicon atoms. We used the double-zeta (DZ) pseudo atomic orbital (PAO) basis set, Troullier–Martins type of norm-conserving pseudopotentials [30], a 100 Ry energy cutoff for the real space electron density, and single $k$-point ($f$-point) for Brillouin zone sampling. Single $k$-point is enough for electronic structure calculations since simulation cell is very large. Dipole correction was applied to remove an artificial effect of built-in dipole potential in periodic slab on electronic structures [31].

2. Simulation method

We simulated the growth process for $C_{60}$ film using classical molecular dynamics (MD) simulations by shooting $C_{60}$ molecules on the Si substrate one-by-one every 50 ps at various kinetic energies. The Si substrate was modeled by a 2.3 nm × 2.3 nm × 5 nm slab ($N = 1332$ atoms), which was periodic in the lateral direction. We note that the dependence of sample size and film thickness on both the growth behavior and stress–strain curves was verified using a larger Si substrate, which was scaled up 6 times for each lateral side (approximately 14 nm × 14 nm × 5 nm; thus, $N = 48012$). The three bottom layers were fixed to maintain the silicon bulk structure, ten atomic layers from the top remained free without constraints to avoid interrupting fullerene–surface interactions during deposition, and the in-between layers are heat reservoirs to prevent temperature increases upon deposition. A thermostat was not applied to the free layers; otherwise, the structural and chemical bond changes cannot be properly described because atoms that are much faster than the thermal velocity will suddenly slow down due to the velocity re-scaling [24].

Once the fullerene films were obtained, we investigated their mechanical strength and ductility under biaxial tensile or compressive strains through elongating and shortening the lateral dimensions of the cell at the constant engineering strain rate $\varepsilon$. Thus, the box length $L(t)$ at the elapsed time $t$ will change from the initial length $L_0$ as $L(t) = L_0(1 + \varepsilon t)$. The strain rate $\varepsilon$ was $10^8$ sec$^{-1}$ (0.1 ns$^{-1}$) in all loading tests.

All MD simulations were performed using a parallel MD code, LAMMPS [25], and the modified Tersoff potential, which was re-parameterized with improved transferability by Erhart and Albe [26]. This potential provides a good description for C-C, C-Si, and Si-Si interactions in diamond, silicon, silicon carbide, and carbon allotropes such as fullerene [22]. The potential was benchmarked through calculating the lattice constant, cohesive energy and elastic modulus in certain model systems, which reproduced correct values. The benchmarking data are available in the Supplementary materials. The MD time step was 0.5 fs, and the heat reservoir portion was maintained at the constant temperature 500 K, which is comparable to previous experiments [12,13], using the Berendsen scheme [27] with a 0.1 ps relaxation time.

We calculated the electronic structures of a polymerized $C_{60}$ film using the SIESTA [28] density functional theory (DFT) program within a generalized gradient approximation (GGA-PBE) [29]. $C_{60}$ film was modeled using a slab in periodic supercell whose size is $23.02 \text{ Å} \times 23.02 \text{ Å} \times 150 \text{ Å}$. Slabs in different cells were separated by about 25 Å of vacuum. All carbon atoms from the MD simulation were included, while the silicon atoms that were greater than 9 Å away from the carbon atoms were excluded. Our model slab composed of 4589 carbon, 360 silicon, and 72 hydrogen atoms. Hydrogen atoms saturate dangling bonds at the bottom silicon atoms. We used the double-zeta (DZ) pseudo atomic orbital (PAO) basis set, Troullier–Martins type of norm-conserving pseudopotentials [30], a 100 Ry energy cutoff for the real space electron density, and single $k$-point ($f$-point) for Brillouin zone sampling. Single $k$-point is enough for electronic structure calculations since simulation cell is very large. Dipole correction was applied to remove an artificial effect of built-in dipole potential in periodic slab on electronic structures [31].

3. Results and discussion

Polymerized fullerene film was grown when the incident energy for the $C_{60}$ molecule was 180 eV, while the film did not grow well at a lower energy, and amorphous carbon (a-C) film grew at higher energies (Fig. 1). When the incident energy was 60 eV, the fullerene molecules passivated on the silicon surface at an early stage; soon thereafter, almost all of the incident molecules elastically bounced back into the vacuum. The fullerene structures were completely broken at high energy incident conditions (300 and 600 eV), thus leading to growth of a-C film. Polymerized film can grow only under moderate incident energy because polymerization begins to flourish, wherein collision impact distorts only local portions of the fullerenes and combines the fullerenes as polymers. The fullerene-fullerene reaction depends on the energies, which was supported by previous quantum molecular dynamics, wherein the dominant reaction changed from fusion (polymerization) to fragmentation as the impact energy increased, and the onset energies (or transition barrier) were estimated at 80 and 200 eV, respectively [32,33]. Note that the majority of molecules elastically bounced back
even at 180 eV; only 76 of 1700 incident molecules remained in the film. As the radial distribution function (RDF) plots in Fig. 2 show, all of the RDF peaks for the pristine fullerene molecule remain up to 180 eV, which demonstrates that \( \text{C}_60 \) is the building block: fullerene molecules are piecewise connected mostly by carbon atoms of which coordination number (CN) are 3 and 4 (as also shown in Fig. 3). For 300 and 600 eV, the second and third nearest neighbor sequences merged, and the longer-distance peaks vanished. This energy dependence of film structure is consistent with experimental findings by Huck et al., wherein the Raman signals for \( \text{C}_60 \) survived up to 200 eV of incident energy, while amorphous signals were observed at higher energies [34].

The density, residual stress and population of \( \text{sp}^3 \) bonds were greater for higher incident energies; fullerene molecules intensely impact the substrate at the high incident energy. The values listed in Table 1 were extracted from a stable region inside each film. The density was low at 1.6 g/cm\(^3\) as long as the fullerene structure was preserved; then, it suddenly jumped when it broke because the large void inside and in between the fullerenes collapsed. All films were under compressive stress because the incident molecules force the films down. The RDF peaks correspond to the first nearest neighbor and reflect the bond population: the unchanged peak position indicates that the \( \text{sp}^2 \) bonds are dominant, and an asymmetrically broadened shape for the high energy indicates an increasing \( \text{sp}^3 \), while the \( \text{sp} \) is not increased as much as the \( \text{sp}^3 \) bonds.

If polymerized films are soft and flexible in comparison with bare substrate, those coatings could slightly decrease the mechanical strength of whole slab (in terms of Young’s modulus), while amorphized films are stiff and tough such that the slab strength could be increased. This is predicted by a simple “rule of mixture” approach. Amorphous films are the most stiff, which is indicated by Young’s modulus \( Y \), polymeric film is the most soft, and coated Si substrates are

**Fig. 1** – Cross-sectional perspectives for films after depositing 1700 fullerenes on the Si substrate at different incident energies. The atoms’ color (blue-to-red) reflects their deposition sequence. (A colour version of this figure can be viewed online.)

![Fig. 1](image1)

**Fig. 2** – Radial distribution functions \( g(r) \) for fullerene-deposited films generated at different energies. The arrows indicate the peak positions of the pristine fullerene. (A colour version of this figure can be viewed online.)

![Fig. 2](image2)

**Fig. 3** – Graphical representation of the polymerized fullerene film grown at \( E = 180 \) eV. Each \( \text{C}_60 \) molecule was colored differently, but same color was used when they are connected by carbon atoms of which CN are 3. Black balls are carbon atoms with 2 and 4 of CN. (A colour version of this figure can be viewed online.)

![Fig. 3](image3)
intermediate (Table 2). The Young’s modulus of C_{60}/Si or a-C/ Si slabs is estimated by the arithmetic average $K_{a} + K_{u}$, where $K_{a}$ and $\varphi_{u}$ are the elastic modulus and volume fraction of the i-phase (polymerized C_{60} or a-C film), respectively. The values are 90 GPa for polymerized fullerene-coated Si film and 334 GPa for an a-C coated film, which are consistent with our MD results in Table 2. Based on this $Y$ value, a polymerized fullerene is in the range of a typical glass (50–90 GPa) and is soft compared with Si but stiff compared with rubber (typically hundreds of MPa) [35].

The biaxial tensile behaviors of uncoated, bare Si films and films with fullerene coatings at different energies are shown in Fig. 4. For bare Si films, the stress increases with increasing strain, showing its stiffness ($Y = 159$ GPa), while permanent deformation occurs beyond the yield point $\varepsilon = 0.23$. In contrast, the Si films coated with polymerized fullerene are softer and less stiff ($Y = 103$ GPa for $E = 180$ eV). The polymerized fullerene film without the Si substrate is significantly softer and flexible with the lowest value $Y = 55$ GPa. Such polymeric mechanical behavior is attributed to peculiar bonding characteristics of the polymerized fullerene, where only "glue" atoms are associated with linking neighbor fullerenes, in sharp contrast to the homogeneous bonding nature of amorphous films (Fig. 3). The stress–strain curve was also verified using a larger sample size, but it does not show different tendencies.

The polymerized film successfully continues to cover the silicon substrate even when the silicon substrate is broken under huge tensile and compressive strains. Fig. 5 shows cross-sections of the polymerized fullerene-coated Si films, which is $14 \text{ nm} \times 14 \text{ nm}$ for xy dimensions and grown at 180 eV immediately after yield under biaxial compressive (Fig. 5b) and tensile loading (Fig. 5c). A dislocation band under compressive loading and a necking of silicon under tensile loading were initially generated at the interface and propagated to the bottom due to weak bonding at the interface (see the MD movie in the Supplementary materials). Although it was slightly ruptured at the 0.38 strain, the polymerized film was successfully stretched to 0.5 without mechanical failure, which is larger than $\sqrt[3]{3} - 1 = 0.44$, the corresponding length change for 300% volume expansion of fully lithiated silicon. These data imply that polymerized film is sufficiently flexible to adapt to silicon anode volume changes.

Soft but tough features are desirable in an ideal coating because a large volume change is inevitable for a high energy capacity; high lithium storage capacity, large volume expansion are two sides of the same coin. A desirable feature for the coating film is not hardness, which confines the silicon, but softness and flexibility to adapt to volume changes as well as toughness for the film to continue covering the silicon. Cracking alone would not significantly degrade the battery performance because anodes that consist of small silicon particles operate well [4]; however, detaching the silicon pieces from the current collector would significantly degrade the battery. A desirable coating responds flexibly and continues to wrap the silicon, regardless of being broken into pieces, and preserves good contact with the current collector.

We found an exclusive conducting channel for Li ions in the polymerized C_{60}, which was grown with 180 eV of kinetic energy, as Fig. 6 shows. The ion conducting channel in this article is the void that extends from the top of the C_{60} film (i.e., the electrolyte) to the Si substrate without disconnection. The channel is defined by a cutoff radius $R$ such that all points in the channel are farther than $R$ from all atoms, which is conceptually similar to a Van der Waals surface. However, isolated voids, such as voids inside the C_{60} molecules, are...
excluded because lithium ions rarely enter such voids. Fig. 6b shows the ion channel for $R = 2.2$ Å, which is the Li–graphene distance [36], and a portion of this ion channel in intersection parallel to the substrate. The red arrow in Fig. 6b points to the narrowest position of the channel. The sizes of the channel at the narrowest position for a given $R$ are plotted in Fig. 6a. The channel in the polymerized film opens up to $R = 2.6$ Å, wherein a Li ion can transfer through the film while it is closed at $R = 1.6$ Å in an amorphous carbon film. However, even the largest channel size in the polymerized film is too small for electrolyte transfer. The polymerized film can sift out the electrolyte molecules and exclusively transfer the Li ions, similar to a “nano-sieve”; thus, it can prevent SEI formation on silicon substrate.

Fig. 5 – Cross-sectional views before loading (a) and immediately after the first yield through biaxial compressive loading (b; strain $\varepsilon = 0.12$) and tensile loading (c; $\varepsilon = 0.19$). The atoms color is encoded using a coordination number: burly wood for 2; forest green for 3; gray for 4; and red for 5. (A colour version of this figure can be viewed online.)

Fig. 6 – Ion-conducting channel. (a) The minimum ion channel size as the cutoff radius $R$ changes. (b) Ion-conducting channel (yellow) for $R = 2.2$ Å (left) and its relative area in the surface normal direction. The red arrow points the narrowest position of the channel, the value for which is plotted in (a). (A colour version of this figure can be viewed online.)
Because the sp² carbon network survives, the polymerized film can deliver electrons between silicon and the current collector, and it supplements the poor electric conductivity of silicon. As electrons travel easily in extended electronic states, we quantified the level of localization for electronic states to verify good conductivity using delocality. Delocality ($V_L$) is defined using the formula below:

$$
\frac{\int_{E_F}^{E_F+\Delta E} \rho(r) \, dr}{\int_{E_F}^{E_F+\Delta E} \rho(r) \, dr} = V_L
$$

where $\psi_i$ is a single-electron wave function with the eigen-energy $E_i$; thus, $D_L(r)$ is the local density of states (LDOS), and $D_L(r; -\infty, \infty)$ is the electron density. Delocality ($V_L$) is the characteristic volume at which $D_L(r)$ is localized. For example, $V_L = V$ when $D_L(r)$ is constant and non-zero only in volume $V$:

$$
D_L(r) = \begin{cases} 
D_L^0, & \text{if } r \in V \\
0, & \text{if } r \not\in V 
\end{cases}
$$

$V_L$ well quantifies the degree of localization for the positive-definite function $D_L(r)$ because a more localized $D_L(r)$ yields a smaller $V_L$. We calculated $D_L(r)$ from DFT calculations as explained in the Simulation Method section. The $V_L$ for the (pseudized) valence electron density of a single C₆₀ molecule is 217.0 Å³.

As it is shown in Fig. 7, the LDOS extends to the entire C₆₀ film and is highly delocalized; delocality is approximately 60% of the upper limit (Fig. 7c) in which every carbon atoms equally contribute to $D_L(r)$. We find that LDOS with 0.1 eV interval in the range of $[E_F - 1 \text{ eV}, E_F + 1 \text{ eV}]$ are extended to the entire film, as very similar to (a) and (b) of Fig. 7, and enough number of states are in that energy range (1564 states in $23 \times 23 \times 120 \text{ Å}^3$ including spin, Fig. 7d). We did not check how widely individual eigen states are extended. However, even if each eigen state is not extended widely, electrons can flow by hopping between states localized at different position. Thus electrons can flow very easily through the polymerized film, and electric conductivity of anodes will be improved.

4. Conclusions

The growth of polymeric fullerene film through a deposition process and its features for an ideal coating on a silicon substrate were investigated using molecular dynamics and
density functional theory calculations. Polymeric fullerene film is obtained through impacts of fullerenes with incident energy of 180 eV. This fullerene film exhibits sufficiently soft and flexible as to accommodate large silicon anode volume changes during charging and discharging cycles while maintaining its wrapping. The polymeric film includes a selective conducting channel for lithium ions. This film is ideal for a durable silicon anode in rechargeable batteries due to high flexibility and the lithium conduction channel. Moreover, the film coating can aid in electron conduction between the silicon anode and current collector as well as compensate for the poor electric conductivity of the silicon anodes. Such an ideal film was only grown with the moderate fullerene incident energy. Our computational work exemplifies the features of ideal coating for durable silicon anodes, which would provide insight into rational design of durable lithium ion batteries for which loosely connected porous sp³ carbon film could be a promising coating for silicon anodes.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.carbon.2014.06.049.

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