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Two-Layer Silicene on the SiC Substrate: Lithiation Investigation in the Molecular Dynamics Experiment

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The functioning of the lithium-ion battery anode composed of silicene/SiC composite is studied by molecular dynamics. In this composite, silicene has multiple vacancy defects. Approximately the same degree of lithium filling in such an anode is considered for both horizontal and vertical intercalations. During the horizontal intercalation lithium atoms not only fill the channel and deposit on its walls, but also penetrate into the substrate. In both cases, the self-diffusion coefficients of lithium

atoms have similar values. However, the process of filling the system with lithium occurs with a smoother total energy change when the intercalation is performed vertically. A detailed study of the lithium atoms packing via the construction of Voronoi polyhedra for each of the systems under consideration shows the better uniformity of the Li atoms distribution over the volume of the system during the vertical intercalation.

Introduction

Thin-film lithium-ion batteries (LIB) are promising autonomous power sources that demonstrate high energy density. The used graphite anodes have a maximum charge capacity of 372 mAh/g. Alternative silicon-based materials are more suitable for use as LIB anodes due to their superior theoretical specific capacity (up to 4200 mAh/g).^[1,2] For example, following the DFT calculations, the ideal theoretical specific capacity of a single-layer silicene anode is estimated as 954 mAh/g.^[3] For a two-layer silicene anode, it has a value of 1384 mAh/g.^[4] Silicene is believed to be more stable when it contains up to several layers. So, it should be expected that the many-layered silicene structure would provide the higher specific capacity. In addition, silicon-based materials are quite widespread in present microelectronics. This facilitates the use of silicon-containing materials both as anodes for miniature LIBs and for microelectromechanical systems.^[5]

The main problem of silicon anodes is a significant change in their volume during the charge/discharge cycles of electrochemical battery. Thin layered materials such as silicene may be an alternative in this case. Silicene is represented as a two-dimensional object with Si atoms located at the nodes of its six-membered ring structures. Silicene is obtained on various metallic^[6,7] and non-metallic^[8,9] substrates, together with which it forms thin composite materials. It was experimentally shown that if a thin SiC film is incorporated into the composite, then it is possible to control the volume change, and thus improve the LIB capacitance characteristics for a longer period.^[10] The ideal predicted specific capacity of SiC during lithiation is 1430 mAh/g.

Theoretical estimates have demonstrated that the capacity of the silicone anode with SiC as a component can be maintained at a value of 1200 mAh/g for 200 charge/discharge cycles.^[12,13] The battery capacity is effectively modulated by varying the geometric characteristics of a unit cell built on the basis of silicene and its substrate.

Attention of researchers to the use of SiC in this area has recently increased. However, the electrochemical mechanism of the interaction between SiC and Li in the composite anode remains poorly understood. Most often, SiC is used in LIB in a nanostructured form (nanoparticles and nanowires).^[14] It has been experimentally shown that thin nanocrystalline SiC films are stable after 60 cycles of intercalation/deintercalation with a charge capacity of 309 mAh/g, which decreases with the increasing film thickness.^[12]

Two-dimensional SiC has already proved to be a suitable supplementary material for such 2D systems as graphene, stanene, and phosphorene.^[15] It is able to maintain high mechanical strength and has a wide band gap of ~2.52 eV in its pure form.^[16] In addition, SiC exhibits such extraordinary properties as high thermal conductivity (~313 Wm⁻¹ K⁻¹),^[17] significant in-plane rigidity,^[18] high exciton binding energy (~2.0 eV).^[19] It seems promising to use silicene on the SiC substrate as the LIB anode material. The reason for that is an insignificant discrepancy between the lattice parameters of silicene and SiC (~2%), high binding energy, significant mechanical stability, and the ability of silicene to restore its shape after the charge/discharge cycles.

Multifunctional devices of a new generation can be constructed on the base of layered materials with the extraordinary properties. These properties can significantly exceed those of individual components thanks to the correct combination of materials and their stack in layered structures.^[20,21] Computer simulation methods can be of great assistance in the search for such materials.

Molecular dynamics experiments have shown that silicene (when it is located on different metal substrates (Ag, Ni, Cu) as well as on graphene) can remain stable after a single lithiation/

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delithiation cycle.^[22–26] Silicene is not destructed and returns to its original volume. In this case, defect-free silicene can have more significant stresses and a lower capacitance than silicene modified with vacancy defects.^[27] Silicene doped with phosphorus (as a result of transmutation) shows extraordinary stability and the improved charge characteristics during the lithiation when it is located on the copper-doped nickel substrate^[28,29] as well as on the nitrogen-doped graphite one.^[30] The structure^[31] and growth of graphene^[32] on the SiC substrate is studied in the MD model. The capacitive characteristics of the silicene anode^[33] located on the metal (Al, Ag, Au)^[34] and carbon^[35] substrates of various thickness are estimated using *ab initio* calculations.

In this study, we consider the configuration of the LIB anode composed of a silicene/SiC composite material, i.e., two-layer silicene on the thin SiC film substrate. The aim of this work is to study the process of Li intercalation in such an anode with its vertical and horizontal filling. As a result of this study, the conclusion will be made about the possibility of using the silicene/SiC composite structure as an LIB anode.

Computational Details

Molecular dynamic (MD) simulations have been carried out using the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS)^[36] to estimate the possibility of using two-layer silicene on the SiC substrate as a unit cell for a new generation LIB.

The rectangular silicene sheets (the unit cell was designed as a flower structure^[30]) were stacked on top of each other using Bernal stacking (ABAB...) in such a way that a channel was formed. Defects of the vacancy type: bi-, tri-, and hexavacancies were created in each of the sheets by removing 2, 3, or 6 Si atoms. In each case, 9 polyvacancies were created in the silicene sheet. These defects were almost evenly distributed over the area of the silicene sheet. The defect-free sheet contained 528 Si atoms. The number of Si atoms in the sheet with defects of different sizes was 510, 501, and 474, respectively.

The initial value of the channel gap (the distance between the silicene sheets) was $h_g = 0.75$ nm. However, over time, the average h_g value could change due to the deformation of the silicene sheets. MD calculations^[22,26,27] showed that such initial gap ensures the entry of lithium ions into the channel. Lithium ions can overcome the entry barrier, move in the channel space, and fix or leave the channel, depending on the magnitude and direction of the strength of the applied external field.^[24]

The system was stabilized by fixing the edge Si atoms of the silicene sheets. The external electric field E was 10^4 V/m and operated along the Oz axis in the case of vertical filling of the channel with lithium ions and along the Ox axis when Li^+ ions entered the channel horizontally. To organize the effect of the field on the ions, the corresponding component of the force was added at each time step to push the ions in the required direction. We selected the field value empirically in the MD calculations when lithium intercalation in the silicene channels on metallic^[22–25] and nonmetallic^[27,30,37] substrates was simulated. The used value of the electric field ensured the entry of the lithium ion into the channel, its movement along the channel, and fixation in the channel during 1 million time steps, i.e., 100 ps. A time step was $\Delta t = 10^{-16}$ s. The simulated system was equilibrated during the first 50 ps. Then the lithization process was simulated in the NVT ensemble. A Nose-

Hoover thermostat and free boundary conditions were used. The simulation was performed at a constant temperature of 300 K.

The substrate for the silicene channel was the α -SiC modification, which is the most widespread silicon carbide polymorph. The α -SiC modification has a hexagonal crystal structure with the lattice constants of $a = 0.3075$ nm and $c = 1.0053$ nm. The number of substrate atoms was constant during all calculations and amounted to 6000 particles. The total number of particles in systems when the silicene sheets were modified with bi-, tri-, and hexavacancies was 7171, 7153, 7094, respectively. The substrate atoms performed the thermal motion (they were not fixed). Quantum-mechanical calculations,^[38] as well as MD studies,^[30,37] showed that the most probable distance r between the substrate and the silicene channel was 0.27 nm.

To describe the interactions between Si atoms of the silicene sheets and Si and C atoms in the SiC substrate, we used the well-tested Tersoff potential.^[39,40] It has successfully proven itself in modeling of two-dimensional systems.^[22–27] The interactions between Si atoms of different silicene sheets, as well as between Si atoms of silicene and substrate atoms (C or Si) were described using the Morse potential with parameters reported in.^[41] The Lennard-Jones potential was applied to describe the interactions between Li–Li, Li–Si, Li–C and parameters provided in.^[42]

A schematic representation of the initial configuration of the system indicating the dimensional characteristics, as well as the details of the computational experiment are shown in Figure 1. In the insert to Figure 1 at the bottom, a fragment of the upper layer of the SiC substrate in the enlarged scale (representing a unit cell) is shown. Here, the Si and C atoms are located in different planes. The substrate faces the silicene sheets with a face formed by hexagons with C atoms in the nodes.

In the case of vertical lithiation of the silicene channel (Figure 1a), lithium ions were initially located on the xy plane at a distance of 0.6 nm from the upper wall (silicene sheet) of the channel. Under the action of the external electric field, acting along the Oz axis, Li^+ , one after another with a time interval of 10 ps, directed to the silicene channel. Since the walls of the channel were modified with vacancies of different sizes, the Li^+ ion had several possibilities: to fix on the top silicene sheet, to penetrate into the channel through the vacancies and to localize in it, and to move further through the vacancy defects of the bottom sheet and to stop in the space between the silicene and substrate.

For horizontal lithiation of the silicene channel with the similar system sizes (Figure 1b), Li^+ ions were also launched in turn (every 10 ps) from the zy plane fixed at a distance of 0.3 nm in front of the entrance to the silicene channel. In all cases, the initial coordinates of lithium ions were set randomly. It should be emphasized that for any of the methods of intercalation used, only one charged particle existed in the system at any time. The ion lifetime was always 10 ps (this is the set controlled parameter of the model, that is suitable for the considered applied external electric field, $E = 10^4$ V/m). It is believed that this time is quite sufficient for the Li^+ ion to acquire an electron from silicene or the SiC substrate and turn into a neutral atom. The reduction of lithium ions when they enter a silicon surrounding was experimentally confirmed.^[43] According to the terahertz radiation theory, the transformation of an ion into a neutral atom in a medium with a negative electric potential requires a time of about 1 ps.^[44]

To calculate the self-diffusion D coefficient of atoms, the following ratio was used

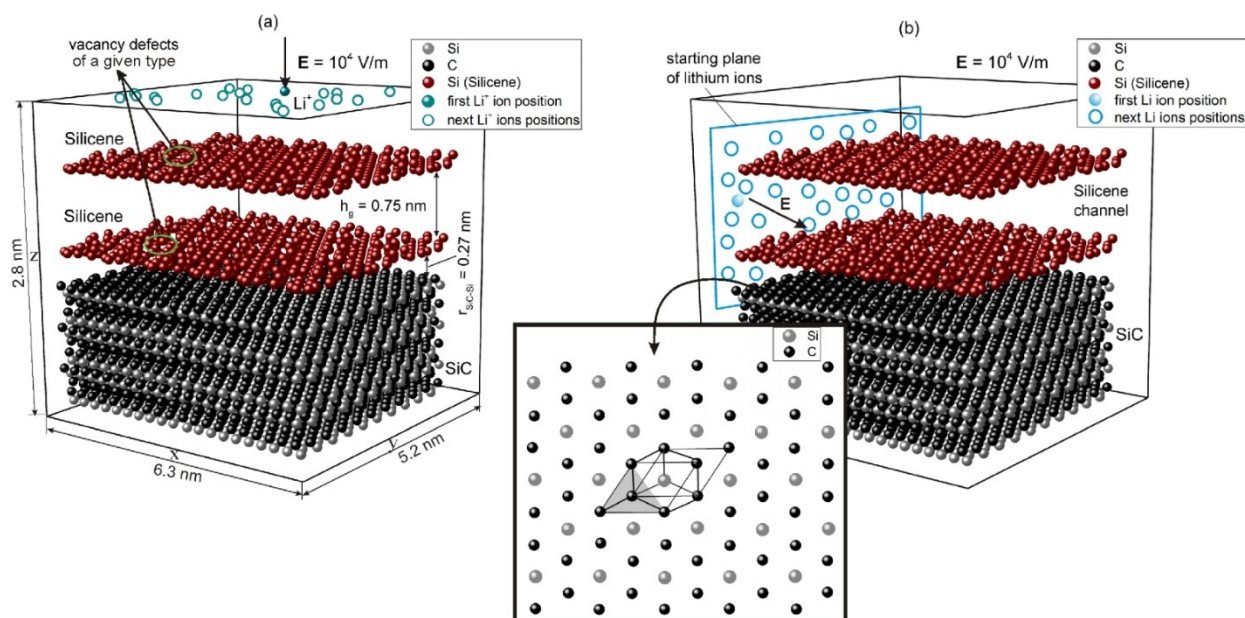


Figure 1. Schematic representation of the initial configurations (time moment $t=0$ ps) of the simulated systems in the case of (a) vertical and (b) horizontal filling of the silicene channel with lithium ions; the silicene sheets have vacancies of given sizes; the ions initial sites (open circles) belongs to (a) xy and (b) yz surfaces; the insert shows a part of the substrate upper layer and a unit cell.

$$D = \lim_{t \rightarrow \infty} \frac{1}{2\Gamma t} \langle [\Delta \mathbf{r}(t)]^2 \rangle_{t_0} \quad (1)$$

where $\Gamma=3$ is the dimension of space, $\langle [\Delta \mathbf{r}(t)]^2 \rangle_{t_0} = \langle \frac{1}{N} \sum_j^N \Delta \mathbf{r}_j \rangle_{t_0}$ is the mean square displacement of all Li atoms obtained using various initial t_0 times.

Comparison of the results obtained for different methods of lithiation of the silicene system allows us to determine the degree of influence of the orientation of filling the silicene channel with charged particles, as well as to investigate the stability of the system, and to determine its integrity and charge capacity.

The computer simulation is barely the only method that allows studying in detail the packing of lithium atoms obtained as a result of anodic intercalation. The packing of Li atoms determines the capacity of the electrode and, ultimately, the capacity and efficiency of the entire battery. We will carry out this study using the method of statistical geometry based on the construction of Voronoi polyhedra (VP).^[45,46] The Voronoi polyhedron contains a region of space, all points of which are closer to a given center than to any other center of the system. Except for the extraordinary cases (for example, when all centers distributed over space lie in one half-space relative to a given center, or all centers are located on one straight line, or fill one plane), it is possible to construct a three-dimensional protuberant Voronoi polyhedron. The elements of polyhedra are faces, edges, and ϕ -angles of the mutual arrangement of neighbors with a vertex at the chosen center, which is also the center of the polyhedron. We will characterize the packings of lithium atoms in the system by statistical topological data (the distribution of polyhedra over the number of faces and the distribution of faces by the number of sides) as well as the metric characteristic and the distribution of ϕ -angles.

Results and Discussion

Configurations of the “two-layer silicene on the SiC substrate” systems with vertical (Figure 2a) and horizontal (Figure 2b) filling of the channel with lithium is shown in Figure 2. Both configurations correspond to the final calculation time of 1.51 ns. In each case, 151 Li^+ ions were used to fill the channel. The criterion for stopping the Li^+ ions launching procedure was the impossibility for new ions to enter the channel.

As can be seen from Figure 2a, in the case of vertical filling of the channel, six Li^+ ions located above the channel do not enter it and do not “stick” to the top sheet of silicene. Using this method of filling the channel, 96 lithium atoms are attached to the upper silicene sheet by the time point of 1.51 ns, while 41 Li atoms are located inside the channel and between the bottom sheet and the substrate surface. Note that only 9% (of the total amount) of lithium atoms are located inside the channel.

When lithium ions penetrate into the silicene channel horizontally, 65 Li atoms are deposited on top of the channel (on the upper sheet), and 73 Li atoms are found inside the channel and under the bottom silicene sheet. In this case, only 2% of the total amount of the embedded lithium is located inside the channel. In addition, in this case, 13 lithium atoms were able to penetrate inside the SiC substrate. In both cases, i.e., for both vertical and horizontal intercalations of lithium, their presence above the centers of the six-membered Si rings is the most probable localization of Li atoms in the area of silicene sheets. We observed the similar effect in the behavior of lithium atoms in our previous calculations,^[23–30] when the silicene channel located on different metal substrates (Ag, Ni, Al, Cu) was horizontally filled with lithium.

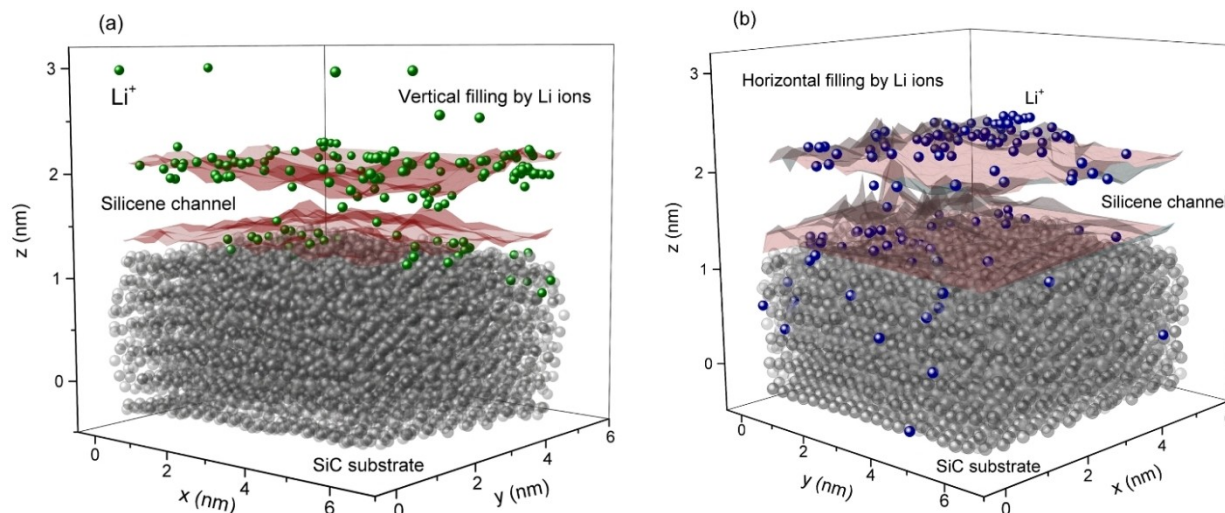


Figure 2. Configurations of intercalated systems after launching 151 Li^+ ions to inject them into the silicene channel located on the SiC substrate; the intercalation is performed: (a) vertically and (b) horizontally; silicene sheets are modified with bivacancies; for convenience of visualization, the silicene sheets are represented as surfaces and the SiC substrate is shown as a shadowed object.

Quantum-mechanical calculations show that for the single-layer free-standing silicene, the preferred location of the lithium adatom is above the center of the six-membered Si ring (hollow site) with the binding energy of $E_b = 2.23$ eV.^[47] In the case of two-layer silicene without a substrate, lithium adatoms are located on the outside of the channel formed by silicene. If they are inside the channel, they are located closer to the top sheet. At the same time, they are still bound to the six nearest Si atoms. However, the location of lithium in the space between two layers of silicene is less preferable, as well as placement of Li directly above the Si atom. The binding energy of the lithium atom (located above the center of the six-membered Si ring) is $E_b = 1.96$ eV, and for inside is $E_b = 1.48$ eV. In the fully lithiated $\text{Li}_{0.43}\text{Si}_{0.57}$ structure,^[47] all hollow sites are occupied ($E_b = 2.08$ eV). A further increase in the amount of lithium in the system in the ratio of one Li to one Si leads to a weakening of the Si–Li bonds and, as a result, to a decrease in the binding energy to $E_b = 1.03$ eV.^[3]

When the channel is vertically filled, the lithium ion initially reaches the top silicene sheet. Then it moves along the silicene surface horizontally. As a rule, it takes up to several ps to fix ion on the outside of the top Si sheet, i.e., to find a preferred location for ion. The ion can also reach the vacancy and penetrate deep into the channel through it. Moving inside the channel and passing through one of the vacancies of the bottom sheet, the ion can localize on the outer side of the Si sheet, i.e., outside the silicene channel.

In the case of horizontal lithiation, the Li^+ ion, having overcome the barrier to the entrance to the channel (~ 0.6 eV^[48]), may not be able to move deep into it due to the deformation of the channel walls. It is also possible for an ion to get into the area of action of the force field of Si atoms of any of the silicene sheets. Then the ion, moving along the sheet, fixes on it or penetrates into the space between the silicene sheet and the substrate. The existing energy barriers for entry

into the channel, for diffusion along the silicene sheet, and for penetration through the vacancy lead to the fact that, first, the top sheet of the channel is “occupied” by the Li^+ ions, and then the bottom one.

We next shift our attention to the motion of a Li^+ ion along silicene. Examples of pathways of lithium ions at different times in the case of vertical (Figure 3a, c) and horizontal (Figure 3b, d) filling of the silicene channel are considered in detail in Figure 3. The shown zx projections of the silicene sheets forming the silicene channel with trivacancies (the substrate is not shown in this figure) make it possible to estimate the degree of the sheet deformation. It can be seen that with the vertical filling, the channel walls are not subjected to significant deformations (Figure 3a, c). At the same time, by the moment of $t = 1.51$ ns, with the horizontal filling the channel, both silicene sheets turn out to be significantly distorted (Figure 3d). When trivacancies are in the silicene sheets, some of the Si atoms begin to separate from the channel walls while lithiation. That does not occur when bivacancies are in the silicene sheets.

Quantum-mechanical calculations show the absence of structural damage to a free-standing defect-free silicene sheet during the moderate lithiation.^[47] However, in the present calculations, when the silicene channel with defective walls is located on the SiC substrate, there is a tendency for the destruction of the silicene sheets in the final stage of their lithiation. In addition, due to the weak adhesion of silicene to the substrate, narrowing of the channel is already observed by the time of ~ 0.5 ns due to the deformation of the silicene sheets. In this case, lithium ions motion through the channel becomes difficult. It is energetically more favorable for Li^+ ions attracted to silicene to move along one of the sheets and to attach to it. The area inside the channel in this case turned out to be poorly filled with lithium.

Ab initio calculations^[47] show that the lithium ion moves over the sheet surface between neighboring hollow positions,

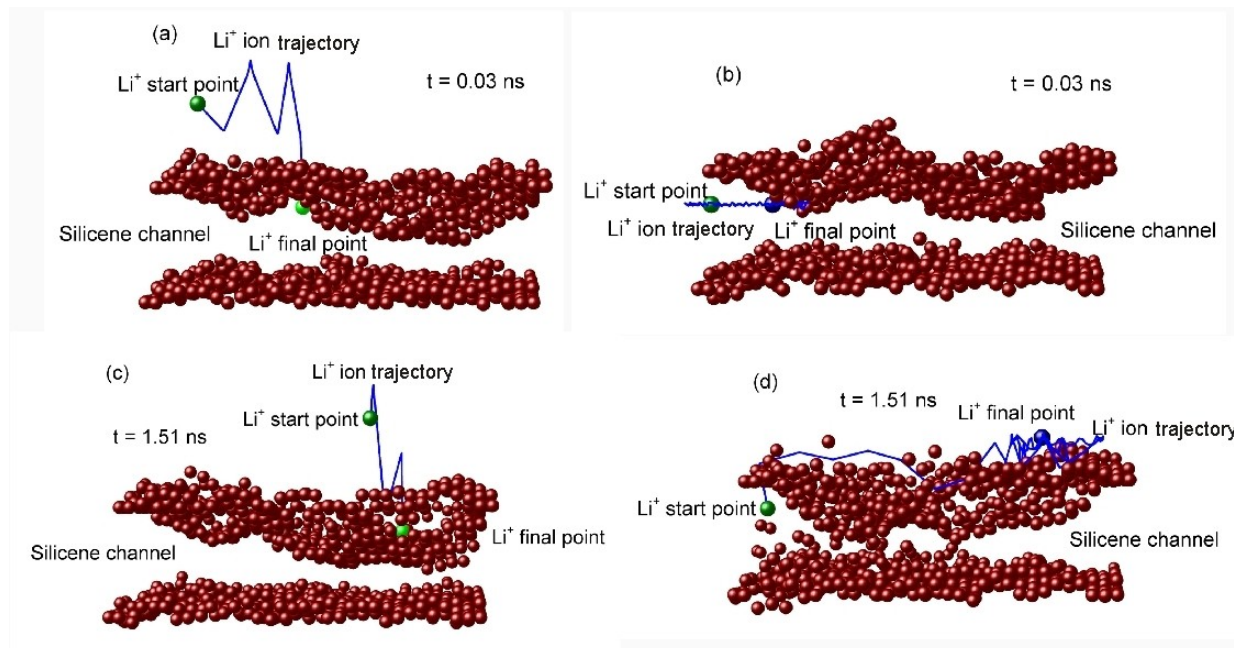


Figure 3. *zx*-projections of the silicene channel and Li^+ ion trajectory corresponding to the time moments of (a, b) 0.03 ps and (c, d) 1.51 ns, when Li^+ ions were incorporated vertically (a, c) and horizontally (b, d); the silicene sheets are modified with trivacancies; the SiC substrate is not shown in the figure.

passing through the bond between Si atoms and overcoming an energy barrier of 0.23 eV. In the case of two-layer silicene, at a low lithium concentration, the ion moves between the Si layers from the hollow position in one sheet to the hollow site of the second sheet by passing through one Si cell and entering another cell, overcoming the joint effect of 12 Si atoms that creates a barrier of 0.56 eV. At a high lithium concentration (when the most of hollow positions of one sheet are already filled), the Li^+ ion diffuses between the two hollow positions of neighboring sheets by jumping over the Si atom. The energy barrier in this case is 0.25 eV. We observed ion motions similar to those described above for both vertical and horizontal intercalations.

The behavior of the E_{tot} total energy of the silicene/SiC + Li system depending on the number of the embedded lithium ions confirms an increase in the instability of the system under investigation as the channel has been filled with lithium (Figure 4). Due to the rapid change in energy at the beginning of intercalation, on the left side of the *Ox* axis, the values of the number of lithium atoms in the system are shown with increment 1, and on the right side, with increment 10.

In the initial period up to $N_{\text{Li}}=5$ or 6, the $E_{\text{tot}}(N_{\text{Li}})$ function decreases, thereby showing the tendency of the system to equilibrium. When the channel is filled vertically, the system in which silicene is modified with bivacancies has the minimum energy (−5.349 eV) at the ratio of the number of lithium atoms N_{Li} to silicon ones N_{Si} equals to 0.010. In the case of horizontal movement of ions entering the channel, a system where silicene contains hexavacancies has the minimum energy (−5.309 eV) with $N_{\text{Li}}/N_{\text{Si}}=0.007$. Up to the time moment of 0.1 ns (i.e., when the number of Li atoms in the channel does

not exceed 10), the E_{tot} energy changes by no more than 0.5% for both ways of filling the channel. Further, as the $N_{\text{Li}}/N_{\text{Si}}$ ratio increases, the total energy of the system starts to rise: smoothly when lithium is added vertically and abruptly when lithium fills the channel in the horizontal direction.

In the case of vertical filling the channel with lithium, regardless of the size of vacancy defects, the $E_{\text{tot}}(N_{\text{Li}})$ function is much smoother than in the case of horizontal filling. In the presence of bivacancies in the channel walls, the E_{tot} energy, as a rule, takes the lower values than in the presence of other vacancy types. This is natural, because the silicene sheets in this case have less deformation. However, the E_{tot} energy for a system in which the channel walls have hexavacancies turns out to be almost everywhere lower than the analogous characteristic for the system with silicene containing trivacancies. A large deformation of silicene with trivacancies can be associated with a jagged relief of the defects boundary, while the shape of hexavacancies is a protuberant polyhedron. In addition, the passage of Li^+ ions through hexavacancies deforms the silicene sheet to a lesser extent than their penetration through trivacancies.

When $N_{\text{Li}} > 10$, the E_{tot} energy fluctuations are always more significant for the horizontal intercalation than for the vertical channel filling. However, in the presence of hexavacancies in silicene, these fluctuations are still lower than in the cases where bi- and trivacancies are found in the walls of a horizontally filled channel.

A comparison of the behavior of the self-diffusion coefficient (calculated according to equation (1)) of lithium atoms hitting the walls of the silicene channel with various defects in the cases of vertical and horizontal intercalations is shown in

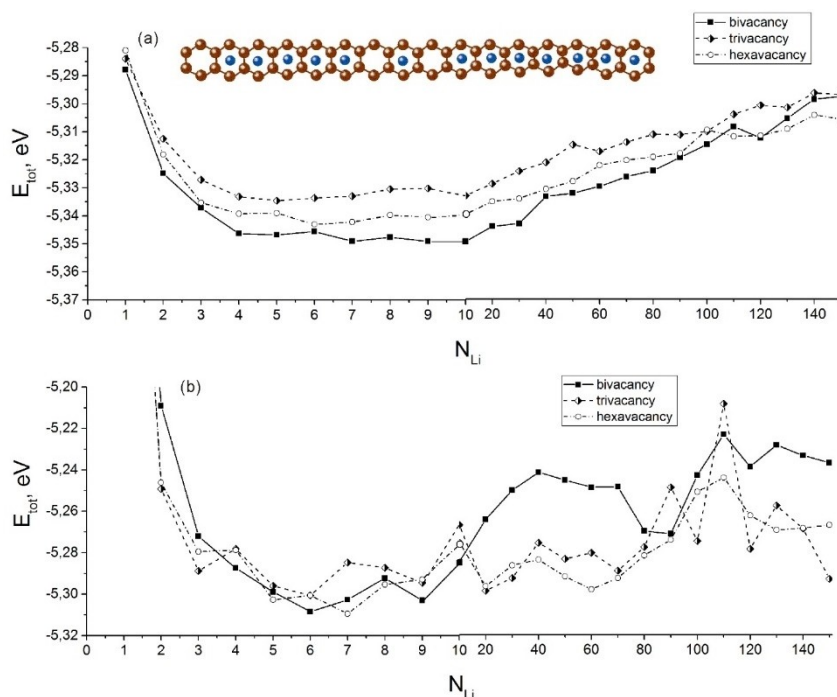


Figure 4. Total energy of the silicene/SiC + Li system, depending on the amount of intercalated Li^+ ions at: (a) vertical and (b) horizontal filling; the insert in the (a) figure shows a fragment of the silicene sheet and the preferred location of lithium ions (hollow sites in Si-rings) in silicene.

Figure 5. The D_{Li} values for the vertical filling of the channel are indicated by dots connected by broken lines; and for the horizontal filling, they are indicated by semitransparent histograms. Sharp peaks in the $D_{\text{Li}}(N_{\text{Li}})$ dependence indicate the possibility of significant displacements of lithium atoms in the vicinity of the channel walls. It can be seen that only in the cases of vertical deposition of lithium at $N_{\text{Li}} > 95$ there is a significant decrease in the intensity of fluctuations in the D_{Li} values up to their disappearance. To a greater extent, this effect is manifested for the channel walls with large defects; i.e., with tri- and hexavacancies. The reason for the decrease in fluctuations may be due to the fact that lithium atoms stop moving over long distances and only oscillate around their stable positions. On the contrary, when the intercalation is carried out horizontally, the D_{Li} fluctuations do not disappear and even increase at $N_{\text{Li}} > 95$ in the presence of hexavacancies in the channel walls.

The average values of the lithium self-diffusion coefficients D_{Li} depending on the vacancy size in the channel walls and the direction of lithium ion launch are given in Table 1. In the silicene channel with walls made of perfect silicene, the estimated value of the self-diffusion coefficient of lithium atoms during lithiation is $1.2 \cdot 10^{-5} \text{ cm}^2/\text{s}$.^[30] According to DFT calculations,^[3] the self-diffusion coefficient of the Li atom as it moves over a free-standing silicene sheet is $5.0 \cdot 10^{-5} \text{ cm}^2/\text{s}$. Taking in to account these data and the values presented in Table 1, we can conclude that the degree of mobility of lithium atoms during lithiation can be affected by the substrate, the number of the silicene sheets, as well as the size and number of defects contained in the silicene sheets.

Table 1. Average values of the lithium self-diffusion coefficients.

Vertical lithiation		Horizontal lithiation	
Vacancy type in silicene	D_{Li} $10^{-5} \text{ cm}^2/\text{s}$	Vacancy type in silicene	D_{Li} $10^{-5} \text{ cm}^2/\text{s}$
bivacancy	3.16	bivacancy	4.06
trivacancy	2.88	trivacancy	3.72
hexavacancy	3.05	hexavacancy	4.8

In addition, according to the data of Table 1, the method of the anode filling with lithium also affects the value of the self-diffusion coefficient of lithium atoms. In particular, the D_{Li} value for the horizontal lithium intercalation is higher than that for the vertical filling of the electrode with lithium for any of the considered types of defects in the walls of the silicene channel. On average, the difference between the D_{Li} values associated with different directions of launching Li^+ ions into the channel is $\sim 38\%$.

Table 1 shows that the diffusion self-coefficients of lithium atoms do not differ much in the presence of different types of vacancies in the walls of the silicene channel. As in the case of silicene on the graphite substrate,^[49] the binding energy of the lithium atom with silicene decreases with an increase in the size of vacancy defects in silicene. However, this decrease is not significant (it is only about 0.1 eV). According to Table 1, the change in the self-diffusion coefficient of lithium atoms is not as unambiguous as the change in binding energy. This is due to the fact that the binding energy is not the only limiting factor in the diffusion of lithium atoms. The shape of vacancy defects, which largely determines their stability is of no less importance.

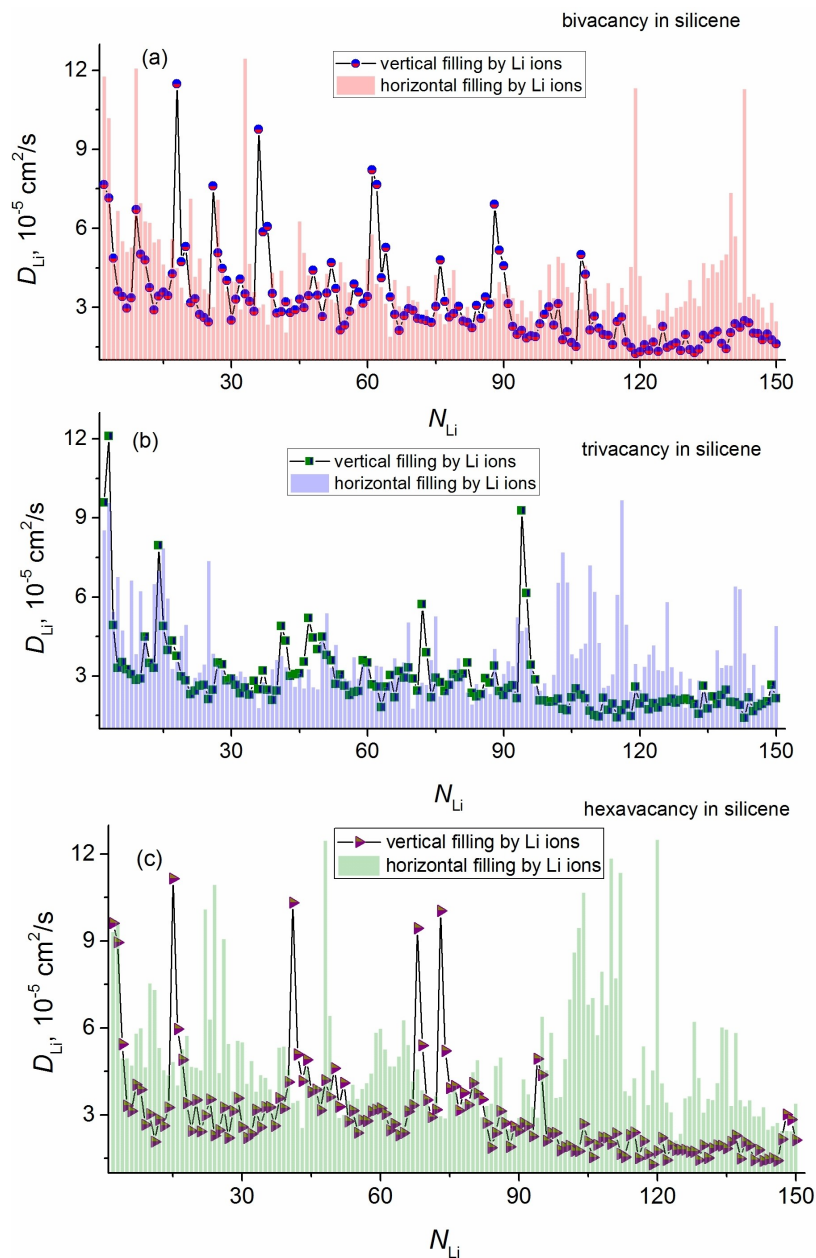


Figure 5. Self-diffusion coefficients of lithium atoms in the “defective silicene channel located on the SiC substrate” systems with various defects in the channel walls during vertical (lines and dots) and horizontal (histograms) lithium intercalations.

In the present work, in each case of filling the system with lithium, the silicene channel contained defects of the same type. Therefore, we could not observe the transition of the lithium atom within one silicene sheet with different vacancies or to another sheet with different vacancies.

The calculated self-diffusion coefficients of carbon and silicon atoms in the substrate are $D_C = 0.31 \cdot 10^{-5} \text{ cm}^2/\text{s}$ and $D_{Si} = 0.29 \cdot 10^{-5} \text{ cm}^2/\text{s}$.

Lithium packings in the silicene/SiC systems are obtained as a result of both horizontal and vertical intercalations. After the systems under consideration are completely filled with lithium, another molecular dynamics calculation is executed for each of

the systems with a duration of 1 million time steps (100 ps), during which no lithium is added to the system. During this calculation, the structural relaxation of the system is completed. The invariance of the statistical distributions for the elements of the Voronoi polyhedra calculated by us proves the presence of relaxation.

Figure 6 shows the distribution of VP over the number of faces (n -distribution) for three investigated systems (in the presence of bi-, tri- and hexavacancies in silicene) in the cases of their horizontal and vertical filling with lithium. As can be seen from this figure, the shape of the n -distributions is affected both by the type of defects in two-layer silicene and by the

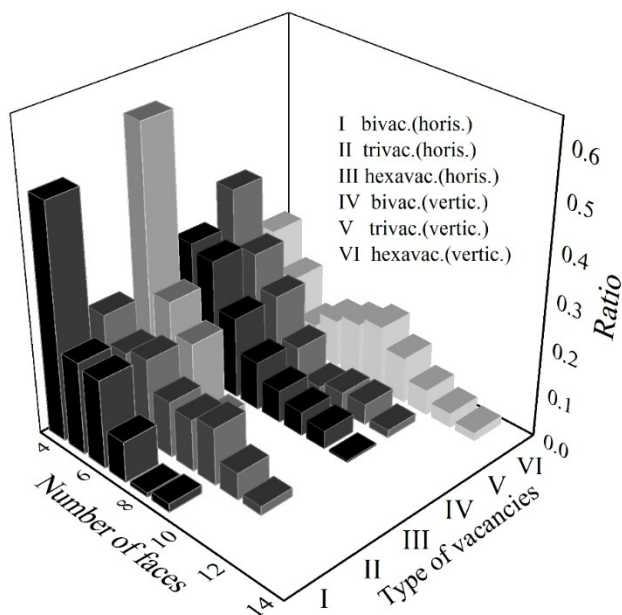


Figure 6. Distribution of Voronoi polyhedra according to the number of faces constructed for lithium packings in the silicene/SiC systems with horizontal and vertical intercalation; the two-layer silicene contained bi-, tri-, and hexavacancy defects.

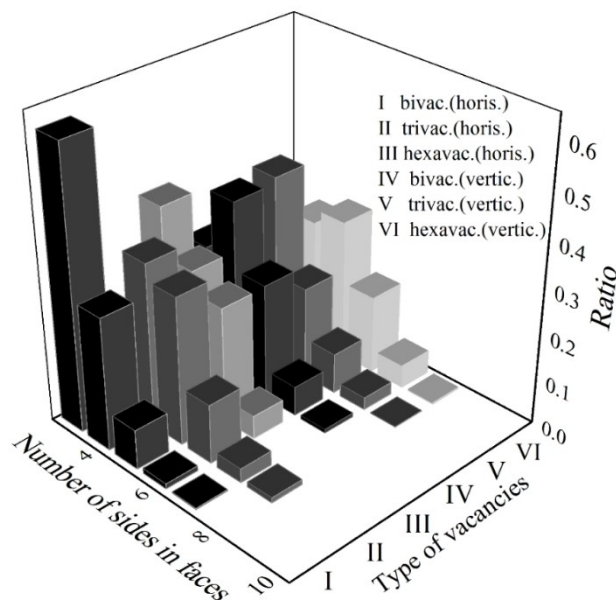


Figure 7. Distribution of faces of Voronoi polyhedra according to the number of sides; the study is carried out for lithium packings in the silicene/SiC systems with horizontal and vertical intercalation; the defects in bilayer silicene are bi-, tri-, and hexavacancies.

method of filling the silicene channels with lithium. It is noteworthy that in any of the considered cases, the maxima of the n -distributions fall on the value $n = 4$.

As a rule, with the vertical filling, the n -distributions turn out to be more “blurred” than with the horizontal filling. They are similar only if trivacancies are present in silicene. The “blurring” of the n -distribution is a characteristic of liquid and disordered media. Thus, in the case of vertical filling in the systems under investigation, more disordered packings of lithium atoms are observed. “Blurring” is minimal when hexavacancies are the defects in silicene, and the system is horizontally filled with lithium. On the contrary, when such system is vertically filled, the “blurring” is maximum.

Approximately the same situation with “blurring” is observed for the distribution of polyhedra faces over the number of sides (m -distributions), although it is much less pronounced than for n -distributions (Figure 7). In the case of horizontal filling of the system with lithium, the maximum of the m -distribution occurs at $m = 3$ or $m = 4$ (for trivacancies), and in the case of vertical filling, at $m = 4$ or $m = 5$ (for hexavacancies). To a certain extent, the m number represents the rotational symmetry in the packing of atoms.^[50] The value $m = 4$ is often found in regular packings, while $m = 5$ is typical for liquid and disordered systems.^[51] However, in this case, such interpretation may be incorrect due to the contribution of small geometric elements caused small-scale thermal fluctuations.

The angular distribution of the nearest geometric neighbors (ϕ -distribution) is a fairly precise structural identifier, allowing one to distinguish between cubic crystal structures, as well as between ordered and disordered structures.^[52] Presented in Figure 8 ϕ -distributions show that the packings of intercalated

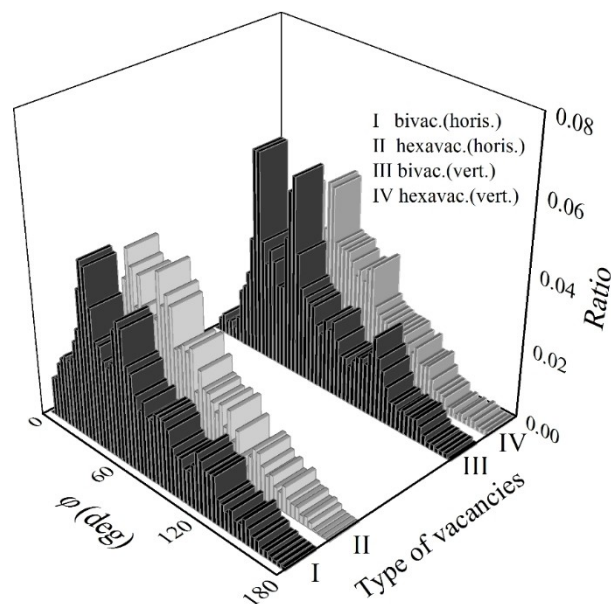


Figure 8. Angular distribution of the nearest geometric neighbors for lithium packings in silicene/SiC systems with horizontal and vertical intercalation; the data are presented for cases, where two-layer silicene contained bi- and hexavacancies.

lithium in the studied systems are mainly disordered. However, traces of regularity are still present in the lithium packing. This is especially true for packings obtained by the vertical intercalation. The significant and sufficiently resolved peaks are observed here at ϕ -angles equal to 36° and $63\text{--}66^\circ$. Some ϕ -spectra show weak peaks at other angles as well. All these are

the evidence of the local ordering of the Li atoms. In Figure 8 we show ϕ -distributions for lithium packings only in systems where silicene contains bi- and hexavacancies. Because, the corresponding ϕ -spectra for systems with trivacancies in silicene turn out to be similar in many respects to the spectra shown in Figure 8.

Conclusions

The lithiation process of a combined silicene/SiC anode is studied by the method of molecular dynamics simulation using both the vertical deposition of lithium ions and the horizontal filling of the system with lithium. The silicene sheets forming the channel are modified with vacancy defects of various sizes: bi-, tri-, and hexavacancies. In all cases, the lithium atoms arriving to the anode are predominantly located near the silicene sheets, being localized above the centers of the six-membered Si rings (hollow sites). The space between the sheets (the inner part of the channel) remained weakly filled with lithium. A part of the ions penetrated into the area bound by the SiC substrate and the bottom silicene sheet. In the case of horizontal filling of the channel, a small amount of lithium penetrated into the substrate.

The vertical intercalation of lithium did not lead to any significant destruction of the silicene sheets, although they were somewhat distorted. On the contrary, lithium ions entering the channel horizontally distorted the channel profile much more strongly. At the same time, the top silicene sheet was found to have a tendency to separate some Si atoms, while, in the bottom silicene sheet, all Si atoms remained bound until the end of the lithiation process.

During the initial stage of lithiation (until $N_{\text{Li}} \leq 10$), the E_{tot} total energy of the system for both ways of filling the channel with lithium is a decreasing function of lithium in the system. A further increase in the number of lithium atoms leads to an increase in E_{tot} . The increasing is smooth during the vertical lithiation, and $E_{\text{tot}}(N_{\text{Li}})$ becomes a strongly fluctuating function during the horizontal intercalation. Significant fluctuations in E_{tot} indicate rapid and strong changes in the channel passability.

The executed MD calculations show the stabilizing function of the SiC substrate for a two-dimensional silicon material. The existing similarity between the lattices of silicene and SiC substrate contributed to a small deformation of the bottom sheets of the silicene channel in both methods of the system lithiation. In both cases, the lower silicene sheet approached the SiC substrate during the lithium intercalation. Thus, if the initial distance between them was 0.27 nm, then by the end of filling the system with lithium, it decreased up to 0.22 nm. In this case, the interaction energy between silicene and silicon carbide decreased from -0.332 eV/atom to -0.764 eV/atom. The C atoms in the substrate are slightly more mobile than the Si ones. The C atoms self-diffusion coefficients are on average 6% higher than that of Si ones. The substrate was slightly deformed and saved its integrity during the entire calculation length (1.51 ns).

When the silicene channel is filled vertically, the fluctuations of the self-diffusion coefficient D_{Li} decrease as the number of lithium atoms in the system increases. This indicates that lithium atoms gradually find their most stable positions above the centers of Si-rings and stop migrating. Ultimately, almost all locations above the centers of Si-rings are filled with lithium atoms. When lithium ions are horizontally launched into the channel, the $D_{\text{Li}}(N_{\text{Li}})$ dependence demonstrates rather significant fluctuations, which can even increase as N_{Li} rises in the system. The obtained self-diffusion coefficients of lithium atoms in the systems under consideration are in the range of $2.88\text{--}4.8 \cdot 10^{-5}$ cm²/s.

A detailed analysis of lithium packings in the silicene/SiC systems showed that the arrangement of Li atoms in the intercalated system depends not only on the nature of the defects presented in the walls of the silicene channel, but also on the method of its filling. The vertical lithium charging of the investigated system leads to a more uniform distribution of Li atoms over its volume. Such charging is carried out in a gentler mode than the horizontal intercalation, in which Li atoms penetrate not only into the space occupied by the channel (including its outer surface) but also into the SiC substrate. However, it is likely that this negative effect can be corrected using a metal substrate instead of SiC one, the adhesion of which to silicene is much stronger.

The decrease in the electrical conductivity of the silicene/SiC system is associated with a slight increase in the band gap of silicene due to interaction with the SiC substrate.^[53] However, when the silicene channel on the SiC substrate is filled with lithium, the electrical conductivity of the system increases,^[33] a semiconductor-conductor junction appears. Therefore, low electrical conductivity will reduce the performance of the battery only at the initial stage of the anode charge. Theoretical specific capacities estimated for the studied silicene/SiC systems are 1527.2, 1507.7, 1497.9, and 1468.1 mAh/g in the absence of defects in silicene, as well as in the presence of bi-, tri-, and hexavacancies, respectively.^[33,35]

The prevalence of silicon in nature, the high capacity of silicene with respect to adsorption of lithium, the flexibility of the monatomic thickness silicene layers, and the low energy barrier for lithium diffusion in silicene—all these factors insist on the development of LIBs based on the silicene/SiC composite material with a defects size in silicene not exceeding the bivacancy. Anodes constructed from such a material will have a high energy density and a longer life cycle.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Data available on request due to big size of origin files.

Keywords: diffusion coefficient · lithiation · silicon carbide substrate · system total energy · two-layer silicene

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