Computer Test of Applicability of Graphene and Silicene in Lithium Ion Batteries
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Abstract
Lithium ion drift in flat graphene and silicene channels, including graphene–silicene channel, in the presence of a constant electric field has been studied by the molecular dynamics method. The optimal channel gap size was determined for an ion to pass through the channel fully while maintaining dynamic contact with it. Penetration of lithium ions through the porous of graphene and silicene membranes as a result of the appropriate transverse electric field's influence has been studied. The time of the ion passage through different membrane sets has been determined. In the case of graphene the ion passage of a membrane pair with divacancies is preferable, and for silicene a coupled membrane with hexavacancies is more passable, i.e. a mean time of the ion transit through it is the smallest. The stability of the membrane during the transport of lithium ion has been investigated. Hydrogenation of the flat channel edges has a positive effect only when the material for constructing the anode is graphene. The most effective method to keep a silicene structure intact is by fixing the edges, but even in this case, the initial defects in silicene cannot be prevented during the ion passage.

Introduction
Electrochemical devices for energy storage include, batteries, fuel cells, and supercapacitors. Graphene has high electric conductivity and strength, and supercapacitors based on it could find wide application in portable electronics. Porous graphene-based nanostructures with large surface areas could be used for their manufacture. However, the optimum pore size and distance between stacked graphene sheets remain undetermined. A simple static estimate of minimum distance \( h_s \) between two parallel graphene sheets that is favorable for the movement of metal ions without interference from the molecular force field was made in (1). For lithium ions (Li\(^+\)), this value was 0.50 nm.

The energy density strongly depends on the specific capacity of the electrode. Anodes based on silicon have attracted significant attention due to their high theoretical capacity (4200 mAh / g) compared with 372 mAh / g for graphite (2). The main disadvantage of using a silicon anode structures is its swelling during lithiation (3), which leads to destruction and consequent reduction in speed of movement of the charge. A possible way to address this shortcoming is the use of two-dimensional layered materials, such as graphene and silicene. Studies of the electronic structure of fully lithiated silicene have shown that there is a transformation of the band structure of a zero semiconductor in the structure of a semiconductor with the band gap of 0.37 eV. This distinguishes graphene from silicene, which after lithiation behaves like a metal (4). Once fully delithiated silicene is restored to its original condition in contrast with the crystalline Si which experiences significant structural changes. The hydrogenated silicene is more resistant to the formation of the bulk counterpart than unfunctionalized silicene (4).

Electric fields at the atomic scale are characterized by significantly higher values of strength than commonly used fields. Strength of the electric fields (10\(^3\) V/m for
graphene and $10^5$ V/m for silicene) used in this study were selected empirically. These fields cannot have a significant impact on the parameters of the electron orbits of atoms and consequently make changes to the widely used interatomic interaction potentials.

The purpose of this work is to investigate the physical properties of bilayer graphene and silicene, including porous, during their interaction with the lithium ion in a constant electric field.

**Computer Model**

Our calculations were performed using classical molecular dynamics (MD). The Tersoff potential was used as the basis of interactions in graphene and silicene (5). The Lennard–Jones potentials are used to represent Li–C, and Li–Si interactions (6-8).

Our sheets of graphene contained 406 atoms and were rectangular in shape at $3.4 \times 3$ nm (the sheet had 14 atoms along each edge). The high capacity of the electrode is achievable upon the rapid movement of electrolyte ions, so the self-diffusion coefficient of the ion would lay within the range of $10^{-10}$ to $10^{-13}$ cm$^2$/s (9). In preliminary computer experiments with a gap of 0.50–0.65 nm between the graphene sheets, we showed that this effect was achieved starting from a value of electric field intensity close to $10^3$ V/m. A constant electric field with an intensity of $10^3$ V/m accelerated ions along axis $\alpha x$ oriented along the zigzag direction of the graphene sheets. The graphene sheets were arranged in accordance with Bernal laying (ABAB…) in exactly the same manner as in bulk graphite. The gap of value $h_g$ was set between the two parallel sheets of graphene. Two series of calculations were performed that corresponded to schemes 1–2 and 1–3 (Fig. 1a). In the first series, an

![Diagram](image_url)

**Fig.1.** (a) Scheme of the atoms’ arrangement at time = 0: (1) view of the frontal plane; (2, 3) side view (on plane) of the external and internal location of an Li$^+$ ion in channel, respectively; (b) flat channel of graphene–lithium ion system configuration at moment 100 ps and = 0.60 nm. The electric field intensity is directed along axis $\alpha x$. Initially, the Li$^+$ ion is located at the front of plane outside the channel. Distances are given in nm.
ion at the initial moment in time was in front of the gap formed by graphene sheets, and in the second series - near the gap within a plane channel. Each series consisted of four calculations with a duration of 1 million time steps $\Delta t = 1 \times 10^{-16}$ s with different values of $h_g$. Values of $h_g = 0.50, 0.55, 0.60, \text{ and } 0.65$ nm were used. For both series, the initial location of the ion corresponded to a height of $h_g/2$.

Here we consider the case of the 4 × 4 silicene surface reconstruction. The unit cell of a silicene structure contains the 18 Si atoms. Six Si atoms of the unit cell are displaced by the distance perpendicular to the surface of 0.074 nm, and the other Si atoms are on the same (original) plane. Such a structure of the sheet is similar to the silicene surface observed on the Ag-(111) substrate (10). If the top sheet atoms of the dual layer of silicene protrude above the original silicene surface, such atoms in the lower sheet nominate down. Silicene sheet had a size of 4.8 × 4.1 nm. In order to study the passage of Li + ion inside the flat channel we used 7 values of distances between the sheets of silicene: 0.50, 0.55, 0.60, 0.65, 0.70, 0.75 and 0.80 nm. These distances are significantly higher than the distance of 0.2481 nm between the sheets of the two-layered silicene with AB packing derived from the calculations by the density functional theory. The study of the Li + ion permeation through the pores in Si-membranes was performed at the gap between the sheets of silicene of $h_g = 0.2481$ nm.

We investigated the simultaneous movement of 10 Li + ions through a graphene membranes. At the initial instant, the lower part of the cell was filled with ten ions by a random–number generator; each ion had an electric charge of +1.0e, where $e$ is the elementary charge. The directed ion motion (upwards) was provided by a positive electric charge of +10e of the lower cell base and a negative charge of –10e of the upper base.

The basic_cell diagram is shown in Fig. 2. One of the graphene membranes used is shown schematically, with C atoms not highlighted, at the top. The pores in the upper
membrane are shifted by a distance no larger than the graphene lattice period to avoid direct vertical propagation of the Li$^+$ ion through two membranes at once. The lower and upper membranes could be of either identical or different type. Each of basic cells was divided into three chambers with identical heights (0.6 nm): lower, intermediate (enclosed between graphene membranes), and upper. The positive charges of CH groups and negative charges of hydrogen–free C atoms at the pore edges had a fluctuating nature and were set by the random–number generator.

The temperature in the model was maintained constant by applying a Berendsen thermostat with the bonding constant $\tau = 4$ fs (11). The maintained temperature did not correspond to the specified one (300 K) because of the slow kinetic energy exchange. The ion motion in the planar channel was simulated with mobile C atoms in the graphene sheets. The simulation of lithium-ion propagation through the graphene membranes was performed with immobile C atoms.

The study of vertical (perpendicular to the plane of the membrane) passing ion Li$^+$ through silicene sheets was performed by 20 testing attempts for each set of membranes. Twenty points of the ion’s initial finding were placed almost evenly over the top sheet of silicene. Each test was carried out for the new location of the ion and had duration of 1 million time steps. During this time, most of the ions successfully overcame the double-barrier silicene membrane containing mono- or poly-vacations. On the basis of these tests we determine the average time taken by a lithium ion to overcome obstacles. Only successful tests were taken into account.

Securing the edges of silicene sheets creates conditions for preserving the morphology of porous silicene and represents the consolidation of this sample on the frame in the physical experiment. However, for the study of lithium ion movement in the gap between the silicene sheets another workable method was applied too. Hardening of the two-dimensional material was carried out by the hydrogenation of the silicene edges. Formation of the CH-group at the sheet edges was modeled according to the monatomic scheme (12). The interaction between the groups CH, CH with lithium ion and Si atoms was described by the Lennard-Jones potential.

The numerical solution of the equations of motion was performed by the Runge-Kutta method of the order 4 with the time step $\Delta t = 1 \times 10^{-16}$ s. In the calculations we used the modified code for parallel computing method of molecular dynamics LAMMPS (13). Fragments of the program were introduced to calculate kinetic and mechanical properties of the system. Calculations were performed using the hybrid computer cluster “URAN” Institute of Math and Mechanics UB RAS) with the peak capacity of 216 Tflop/s and 1864 CPU.

To calculate stresses that appear in a hexagonal mesh, the graphene or silicene sheet was divided into surface elements. The stresses $\sigma_{\alpha\beta}(l)$ that appear under the action of the forces of direction $\alpha$ ($\alpha = x, y, z$) are calculated on each element with the order number $l$, which has the orientation $u$. In these calculations, the products of the projections of the velocities of atoms and of the projections of the forces $f_{ij}$.
acting on the \( l \)th element from the other atoms with the fulfillment of corresponding conditions (14) are used as follows:

\[
\sigma_{\alpha\alpha}(l) = \left( \sum_{i} \frac{1}{\Omega} \left( mv_{\alpha}^{i} v_{\alpha}^{i} \right) \right) + \frac{1}{S_{l}} \left( \sum_{i} \left( u_{i}, \sum_{j} \sum_{u_{j}} f_{ij}^{u} \right) \right),
\]

(1)

Here, \( k \) is the number of atoms on the element \( l \), \( \Omega \) is the volume per atom, \( m \) is the mass of an atom, \( v_{\alpha}^{i} \) is the \( \alpha \) projection of the velocity of atom \( i \), and \( S_{l} \) is the area of the element \( l \). The conditions for summation over \( j \) in the last sum in expression (1) are given in the lower and upper indices of the sum, the force that appears upon the interaction of atoms \( i \) and \( j \) goes through the \( l \)th element, and \( u_{i} \) is the current coordinate of the atom \( i \). The upper index \( u \) in the last sum assigns the coordinate of the point at which the line connecting the centers of atoms \( i \) and \( j \) intersects the \( l \)th element.

**Results and Discussion**

An ion localized initially in front of the entrance to the channel passes over the length of the graphene during 100 ps when the gap is 0.60 or 0.65 nm wide. Coming out of the channel, the ion does not travel too far from it; instead, it is attracted to the lower sheet of graphene, indicating there is tangible interaction between C atoms and the ion (Fig. 1b).

The trajectories of an Li\(^{+}\) ion in front of a flat graphene channel and moving under the effect of a constant electric field with an intensity of \( 10^{3} \) V/m are shown in Fig. 3a. For the detection of transverse oscillations during the ion’s movement, the scale on the vertical axis (\( oz \)) was stretched about 4 times. The movement of the ion along the

![Fig.3. (a) trajectories of the lithium ion in a flat channel of graphene with a gap of (1) 0.50, (2) 0.55, (3) 0.60, (4) 0.65 nm, the beginning and end of the trajectory are shown as an open and solid circles, respectively; (b) distribution of stress \( \sigma_{zz}(x) \) averaged.](image)
over both sheets of graphene along axis \( ox \) (zigzag direction) coinciding with the direction of the electric field intensity at different gaps.

channel under the constant electric field was due to the presence of an energy barrier to inertial movement both at the entrance and the exit of the channel. Increasing the gap even more (to 0.60 nm) allows the ion to travel the length of the channel. Low-frequency quasi-periodic oscillations are superimposed on the translational motion of the ion. The amplitude of these oscillations is much larger than at \( h_g = 0.55 \) nm. The trajectory of the ion leaving the channel is deflected downward. Further expansion of the gap (to 0.65 nm) does not appreciably alter the path of the ion in the channel. The ion in this case performs aperiodic oscillations and flies upward upon exiting the channel.

The distribution of the greatest strains \( \sigma_{zz} \) in the graphene sheets (lower and upper combined) along axis \( ox \) (the zigzag direction) is shown in Fig.3b for four values of the intersheet gap. Increasing the gap slows the rate at which the Li\(^+\) ion enters the channel (due to weakening of the attraction of C atoms). The decelerated ion is deflected more strongly by the molecular force field. This results in more pronounced fluctuations of \( \sigma_{zz} \) at the entrance to the channel when \( h_g = 0.60 \) and 0.65 nm. For free two-layer graphene, the fluctuations of function \( \sigma_{zz}(x) \) do not exceed ±50 GPa (15-17). This range also fits the oscillations of function \( \sigma_{zz}(x) \) when an Li\(^+\) ion moves between sheets of graphene with a gap \( h_g = 0.50 \) nm. Increasing the gap leads to increased fluctuations. In the range of \( x \approx 1.1 \) nm at \( h_g = 0.55 \) nm, particularly strong fluctuations are observed due to the considerable deflection of the Li\(^+\) ion upward. The ion is decelerated near the exit of the channel, further strengthening the \( \sigma_{zz}(x) \) fluctuations. The optimum size of the gap between the planes does not prevent moderate stains from arising in the graphene sheets.

We investigated the lithium ion drift through graphene membrane pairs in the basic cell that include monovacancies, divacancies, trivacancies, and hexavacancies in various combinations. The best result of Li\(^+\) ion propagation through the membranes was achieved in version with two bivacancies. In this case, nine of ten ions reached
Fig.4. (a) Basic cell with the bivacancy membrane combination of graphene after 4 mln. timesteps; (b) The projection of the upper silicene membrane with trivacancies on a horizontal plane corresponding to the time of 100 ps.

the upper cell base after four million time steps; one ion was stopped by the lower membrane within the same time (Fig.4a). During the “charging” period, Li+ ions have the lowest mobility in the horizontal directions and the highest mobility in the vertical direction in the case of an efficient transmission membrane pair.

First let us consider the situation where the direction of the electric field vector is perpendicular to the plane of the silicene membrane. Vertically moving ion is first diffused over the surface of silicene until it finds a position to enter the flat channel. Then, describing a complex trajectory, it looks for a way out of this channel and when it finds a vacancy in the lower layer, it leaves the channel. Securing the edges of silicene sheets allows saving of all types of pores throughout the total calculation. For example, the horizontal projection of the upper sheet of two-layered silicene that has hexavacancies after 1 million timesteps reflects a noticeable distortion (Fig.4b).

Ion Li+ that starts to move in one of the 20 points evenly distributed over the surface of silicon is not always able to pass through the bilayer silicene membrane. In some cases (in particular it relates to membranes of single vacancies) ion was moving along the surface of the top sheet of silicene throughout the time and non-penetrating through it. An example of such a trajectory is shown by the curve "b" in Fig. 5a. The curve "a" shows the trajectory when Li+ ion after a short walk passes through the membrane of the bilayer silicene. The direction of the electric field intensity is shown by the arrow.

The average time $\langle t \rangle$ required by the ion Li+ to overcome each of the layers of silicene is shown in Fig. 5b. It is seen that $\langle t \rangle$ of the passage of the first (upper) layer has a substantially larger value only in the case where the silicene sheets contain monovacancies. The same trend applies to the second (bottom) layer. A distinctive

Fig.5. (a) Two trajectories of lithium ion moving under the influence of the electric field $E$; 1, 1' - ion motion start points; 2, 2' - locations of the Li+ ion through the 100 ps; points 1, 2 refer to the path "a", 1', 2' - to the "b" path. (b) The average time of a
lithium ion passage through the first and second layer of a dual layer silicene. The numbers on the x-axis denotes the defect type in the membranes: I monovacancy, II divacancies, III trivacancies, IV hexavacancies.

![Fig.6.](image)

**Fig.6.** System configurations of «silicene channel with monovacancies – ion Li⁺» corresponding to the time intervals of 100 and 30 ps for the gaps: (a) 0.75 nm, (b) 0.80 nm.

Feature of the ion passage of the second layer of silicene is that at the presence in the silicene sheets of bivacancies and trivacancies time \( \langle t \rangle \) is significantly greater than that for hexavacancies. In addition time \( \langle t \rangle \) for bivacancies is only slightly higher than that for trivacancies.

Movement of Li⁺ ion in a flat silicene channel should be regulated essentially by a larger electric field (10⁵ V/m) than the movement of the ion in the graphene channel (10³ V/m). Furthermore, for the passage of Li⁺ ions inside the flat channel under an electric field much larger gap between the sheets of silicene is required than that between graphene sheets. Even when the value \( h_g = 0.75 \) and 0.80 nm, the ion is not
Fig. 7. Lithium ion trajectories when driving through silicene channel by the field intensity $E$. The channel has gaps: (a) 0.75 nm, (b) 0.80 nm. 1 is the ion motion start point; 2 is a location of the Li$^+$ ion through 100 ps.

Fig. 8. Distribution of the average hydrogenated porous silicene stress tensor components on both sheets: (a) $\sigma_{xx}$, (b) $\sigma_{zz}$ along the axis perpendicular to the direction of the electric field vector.

always between the sheets of silicene. Thus, in the case where the channel is formed from sheets of silicene with monovacancies, ion penetrates inside it with a gap of $h_g=0.80$ nm and does not pass the channel when $h_g = 0.75$ nm. Si-system configuration with gaps of 0.75 and 0.80 nm relating to the time instants of 100 and 30 ps respectively are shown in Fig. 6. There are $xy$-projections of the lower sheets in Fig.6 too. The ion extends outwardly from the front surface of the channel (input area) in the first case and the back surface - in the second. Moreover, the ion does translationally oscillating movement along the outside of the side surface, leaving the
channel through the entrance at $h_g = 0.75$ nm (Fig. 7). At the gap $h_g = 0.80$ nm the ion at the exit, after a number of vertical vibrations, departs the channel through the rear surface.

The passage of the Li$^+$ ion along the silicene channel creates stress in the silicene sheets. To compare the effect of different types of vacancies we show the average of the layers of stress distribution in the plane of silicene in Fig. 8. Here we look at the profiles $\sigma_{\alpha\beta}$ that are deployed along silicene sheet’s width (along the $oy$ axis). We received the alternating stresses that are characterized by the values of the same order. The strongest local stresses appear in the silicene with monovacancies. As a rule, the increase in the vacancy size does not lead to increased stress surges in the silicene. The silicene with hydrogenated edges suffers significant damages during the ion drift.

**Conclusion**

Moving the lithium ions is more manageable as it moves through graphene channel than silicene analog in which the ion trajectory covers a large area of the silicene sheet. Easier input of Li$^+$ ion in a flat channel occurs in the case of silicene, but it usually gets stuck in the channel even if there are sufficiently large $h_g$ and significantly higher values of applied electric field. In other words the ion Li$^+$ «clings» to silicon sheets and brakes in the channel. Consequently, Li$^+$ ion in the silicene channel easily makes movement in the opposite direction to the applied electric field. The studied devices can find an application not only for developing graphene–silicene anodes for lithium batteries but also for some other applications.

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**References**