

Yu.O. Prikhozha, R.M. Balabai

Intercalation of Li Atoms in a SnS₂ Anode of Battery: *ab initio* Calculation

Kryvyi Rih State Pedagogical University, Kryvyi Rih, Ukraine, 50086, prihozhaya.yuliya93@gmail.com

Applying the methods of the functional of electron density and *ab initio* pseudopotential, we carried out computational experiments, we have obtained the spatial distributions of the density of valence electron, the energy reliefs of migration of Li atoms in the SnS₂ interlayer under various degrees of filling of the interlayers spatial of metal atoms. It was established that the motion of Li atoms was accompanied by the overcoming of energy barriers. Barriers depended on the degree of filling of the SnS₂ layer with metal atoms. The optimum filling of the SnS₂ layer with the Li atoms in 75 % was recorded at which the motion of Li atoms was accompanied by the least energy costs.

Keywords: anode of battery, Li atoms, SnS₂ films, electron density functional, *ab initio* pseudopotential, energy reliefs of migration.

Work arrived to the editor 11.06.2019.; accepted for printing 15.06.2019.

Introduction and Statement of the Problem

Energy storage is arguably the most crucial component in the development of sustainable energy resources, grid storage, electric vehicles, as well as consumer electronics. There are many energy different storage technologies for these different systems, for example, molten salts and phase change materials for solar thermal systems, gas turbines for grid storage, and different battery technologies for electric vehicles and consumer electronics [1-4]. Lithium-ion batteries are among the most promising power supplies for various electronic devices and electric vehicles in the modern world [5]. High energy density of the lithium-ion batteries is well achieved by improving the intrinsic properties of the materials, but the anode design influences the overall performance of a battery system in a drastic way [6].

Usually carbon anodes have some disadvantages associated with low specific power, and so on. In order to eliminate such shortcomings, there is a need for new materials for lithium-ion battery anodes. Such materials should have high specific power, stable behavior when used and economically viable. Materials based on tin (Sn), especially tin disulphides (SnS₂) are successfully used as an anode material for lithium-ion batteries [7-10], which has a layered structure consisting of Sn-S-Sn atoms layers connected with each other by Van der

Walsh interactions [11]. Such a layered structure SnS₂ contains sufficiently large volumes for the motion of intercalated Li and Na atoms [12-14]. Therefore, the optimization of anode architecture of the composite materials is crucial to reach high performances. The purpose of this work is *ab initio* calculation of the energy reliefs of migration of Li atoms in the SnS₂ anode under various degrees of filling of the interlayers spatial of metal atoms.

I. Methods and Models of Calculation

The calculated results were obtained using the author's program code [15]. The basic states of the electron-nucleus systems were detected by means of the self-consistent solution of the Kohn-Sham equations. Electronic variables were determined only with the atomic cores fixed. Following Kohn-Sham [16, 17], electronic density was written down in terms of occupied orthonormal one-particle wave functions:

$$n(\vec{r}) = \sum_i |\Psi_i(\vec{r})|^2, \quad (1)$$

The point on the potential energy surface in the Born-Oppenheimer approximation was determined as a minimum energy functional with regard to the wave functions:

$$E[\{\Psi_i\}, \{R_j\}, \{a_\nu\}] = \sum_i \int_{\Omega} d^3r \Psi_i^*(r) \left[-\frac{\hbar^2}{2m} \nabla^2 \right] \Psi_i(r) + U[\{n(r)\}, \{R_j\}, \{a_\nu\}] \quad (2)$$

where R_j are coordinates of atomic cores and a_ν are any external influences on the system.

In the generally accepted formulation, minimization of the energy functional (2) with respect to one-particle orbitals with additional orthonormal constraint on the one-particle orbitals with additional orthonormal constraint on the one-particle orbitals results in Kohn-Sham one-particle equations [18]:

$$\left\{ -\frac{\hbar^2}{2m} \nabla^2 + \frac{\partial U}{\partial n(r)} \right\} \Psi_i(r) = \varepsilon_i \Psi_i(r), \quad (3)$$

In the solution of those equations, the Becelet-Hemen-Schloter pseudopotential formalism [19-20] was used, according to which a solid is considered as a sat of valence electrons and the ion cores. In the pseudopotential approximation, the operator of the pseudopotential V_{PS} , which describes the interaction of valence electrons with the core, is small, and the corresponding pseudo-wavefunction is smooth. Pseudopotential is required to correctly represent the long range interactions of the core and to pseudo-wavefunction solutions that approach the full wavefunction outside a core radius r_c . In addition, it is desired for a pseudopotential to be transferable, which means that one and the same pseudopotential can be used in calculations of different chemical environment resulting in calculations with comparable accuracy. For example, Bachelet et. al pro- posed an analytic fit to the pseudopotential. This ab initio pseudopotential is used by us.

The full crystalline potential is constructed as the sum of ion pseudopotentials that are not overlapping and

associated with ions (nucleus + core electrons), located at the \vec{R}_S positions that are periodically repeated for crystals:

$$\Psi_j(\vec{k}, \vec{r}) = \frac{1}{\sqrt{N_0 \sqrt{\Omega}}} \sum_{\vec{G}} b_j(\vec{k} + \vec{G}) \exp(i(\vec{k} + \vec{G})\vec{r}), \quad (4)$$

For nonperiodic systems, such as a thin film or a cluster, the problem of lack of periodicity is circumvented by using of the supercell methods [21]. Namely, the cluster is periodically repeated but the distance between each cluster and its periodic images is so large that their interaction is negligible. The ubiquitous periodicity of the crystal (or artificial) lattice produces a periodic potential and thus imposes the same periodicity on the density (implying Bloch`s theorem). The Kohn-Sham potential of a periodic system exhibits the same periodicity as the direct lattice and the Kohn-Sham orbitals can be written in Bloch form:

$$V_{\text{KPHCT}}(\vec{r}) \rightarrow V_{PS}(\vec{r}) = \sum_{\vec{p}} \sum_S \widehat{V}_S^{PS}(\vec{r} - \vec{p} - \vec{R}_S) \quad (5)$$

where \vec{k} is a vector in the first Brillouin zone. The function $u_i(\vec{r}, \vec{k})$ have the periodicity of the direct lattice. The index i runs over all states. The periodic function $u_i(\vec{r}, \vec{k})$ are expanded in the plane wave basis. This heavily suggests using plane waves as the genetic basis set in order to expand the periodic part of the orbitals. Since plane waves form a complete and orthonormal set of functions, they can be used to expand orbitals according to

$$\Psi_j(\vec{k}, \vec{r}) = \frac{1}{\sqrt{N_0 \sqrt{\Omega}}} \sum_{\vec{G}} b_j(\vec{k} + \vec{G}) \exp(i(\vec{k} + \vec{G})\vec{r}) \quad (6)$$

where \vec{G} is the vector in the reciprocal space, Ω is the volume of the elementary cells, which consist of a periodic crystal or an artificial superlattice when reproducing nonperiodic objects.

Equation (3) after the Fourier transform to the reciprocal space has the form:

$$\sum_{\vec{G}} \left[\left\{ \frac{\hbar^2}{2m} (\vec{k} + \vec{G})^2 - \varepsilon_j \right\} \delta_{\vec{G}, \vec{G}'} + V_{KS}(\vec{k} + \vec{G}, \vec{k} + \vec{G}') \right] b_j(\vec{k} + \vec{G}) = 0 \quad (7)$$

where V_{KS} is the Kohn-Sham potential:

$$V_{KS}(\vec{k} + \vec{G}, \vec{k} + \vec{G}') = V_{ps}(\vec{k} + \vec{G}, \vec{k} + \vec{G}') + V_H(\vec{G}' - \vec{G}) + V_{XC}(\vec{G}' - \vec{G}) \quad (8)$$

where V_{KS} is the exchange and correlation potential. To calculate it, we used Ceperluy-Alder`s approximation that has been parameterized by Perdew and Zunger.

In the general case, the expressions describing the potentials of interactions are complex. The use of the atomic bases containing the inversion operation in the point symmetry leads to the fact that the Fourier components in the expansion of all expressions are real [22].

The main value in the formalism of the functional of the electron density is the charge density. It is estimated from self-consistent solution of (7), which should be performed at all points of the nonreduced section of the Brillouin zone:

$$\rho(G) = \frac{2}{N_T} \sum_k \sum_j \sum_{\alpha \in T} \sum_{\vec{G}} b_j^*(k + G + \alpha G) b_j(k + G) \quad (9)$$

where the index j runs over all occupied states, k is a vector in the first Brillouin zone, N_T is the number of the

operators α in the point group T of the atomic basis, and the factor 2 takes into account the spin degeneracy.

Estimated effort can be reduced if there is the integral over the Brillouin zone to approximate by summing over special points of the Brillouin zone. It is possible to replace (with satisfactory precision) the summation by the finite number of special points [23] to one point in the Brillouin zone. It is possible to restrict only the Γ -point in the Brillouin zone, especially as it relates to the artificial periodic systems [24].

The total energy per elementary cell has the form:

$$\begin{aligned} \frac{E_{total}}{\Omega} = & \sum_{\vec{k}, \vec{G}, i} |b_i(\vec{k} + \vec{G})|^2 \frac{\hbar^2}{2m} (\vec{k} + \vec{G})^2 + \frac{1}{2} 4\pi e^2 \sum_{\vec{G}} \frac{|\rho(\vec{G})|^2}{G^2} + \sum_G \varepsilon_{xc}(\vec{G}) \rho^*(\vec{G}) \\ & + \sum_{\vec{k}, \vec{G}, \vec{G}', i, l, s} S_s(\vec{G} - \vec{G}') \Delta V_{l, s}^{NL}(\vec{k} + \vec{G}, \vec{k} + \vec{G}') b_i(\vec{k} + \vec{G}) b_i^*(\vec{k} + \vec{G}') \\ & + \sum_{\vec{G}, s} S_s(\vec{G}) V_s^L(\vec{G}) \rho^*(\vec{G}) + \left\{ \sum_s \alpha_s \right\} \left[\Omega^{-1} \sum_s Z_s \right] + \Omega^{-1} \gamma_{Ewald} \end{aligned} \quad (10)$$

where \vec{k} is of the first Brillouin zone, \vec{G} is the vector of the reciprocal lattice, $\Psi_i(\vec{k} + \vec{G})$ is the coefficient of the expansion of the wave function, i denotes occupied states for a certain \vec{k} , $\rho(\vec{G})$ is the coefficient of decay of the density of valence electrons, s number atoms in an elementary cell, $S_s(\vec{G})$ is a structural factor, V_s^L is a local (l -independent) spherically symmetric pseudopotential, l denotes the quantum orbital number, $\Delta V_{l, \vec{k}}^{NL}$ is a nonlocal (l -dependent) additive to V_s^L , Z_s is an ion charge, γ_{Ewald} is the Madelung energy of points ions.

The cut off energy for decomposition (6) was chosen so that that there were 20-30 plane waves per atom of atomic base.

To reproduce the material of the battery anode for the accumulation of Li atoms in the form of two endless monolayers SnS_2 the orthorhombic type artificial superlattice was created ($a \neq b \neq c, \alpha = \beta = \gamma = 90^\circ$). The research object determined parameters of the superlattice and the atomic base. For simulation of the film structure, the lattice parameter cell in the direction

of the a, b , crystallographic axis were modeled the infinite SnS_2 film, in a plane perpendicular to the surface the c crystallographic axis was chosen so that the translationally located films would not influence one another. The atomic basis of a primitive cell consisted of 8 S atoms and 16 Sn atoms. In the interlayer SnS_2 space could range from 0 to 16 Li atoms per cell. Li atoms were placed according their location in solid state at low temperatures.

II. Results and Discussion

The spatial distributions of the density of valence electrons, the energy barriers of migration of Li atoms in the SnS_2 layer are calculated. Such a transfer was estimated at various degrees of filling of the layer with metal atoms.

Algorithm for calculating the energy barriers of migration of Li atoms was such that for each atomic configuration that corresponded to the elementary step of

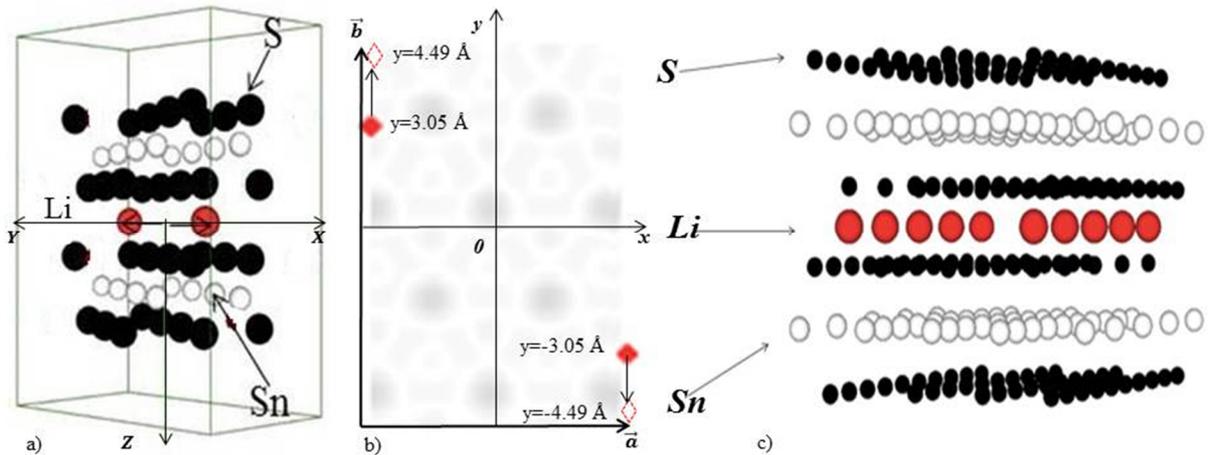


Fig. 1. The direction of migration of Li atoms from each other into the interlayer of SnS_2 layer within the cell, view of a primitive cell with an atomic basis (a); the cross section of the cell at the $\frac{c}{2}$ level with indication of the locus of migration of Li atoms in the SnS_2 interlayer (b); the fragment of an infinite SnS_2 film with intercalated in its interlayer space of Li atoms (c).

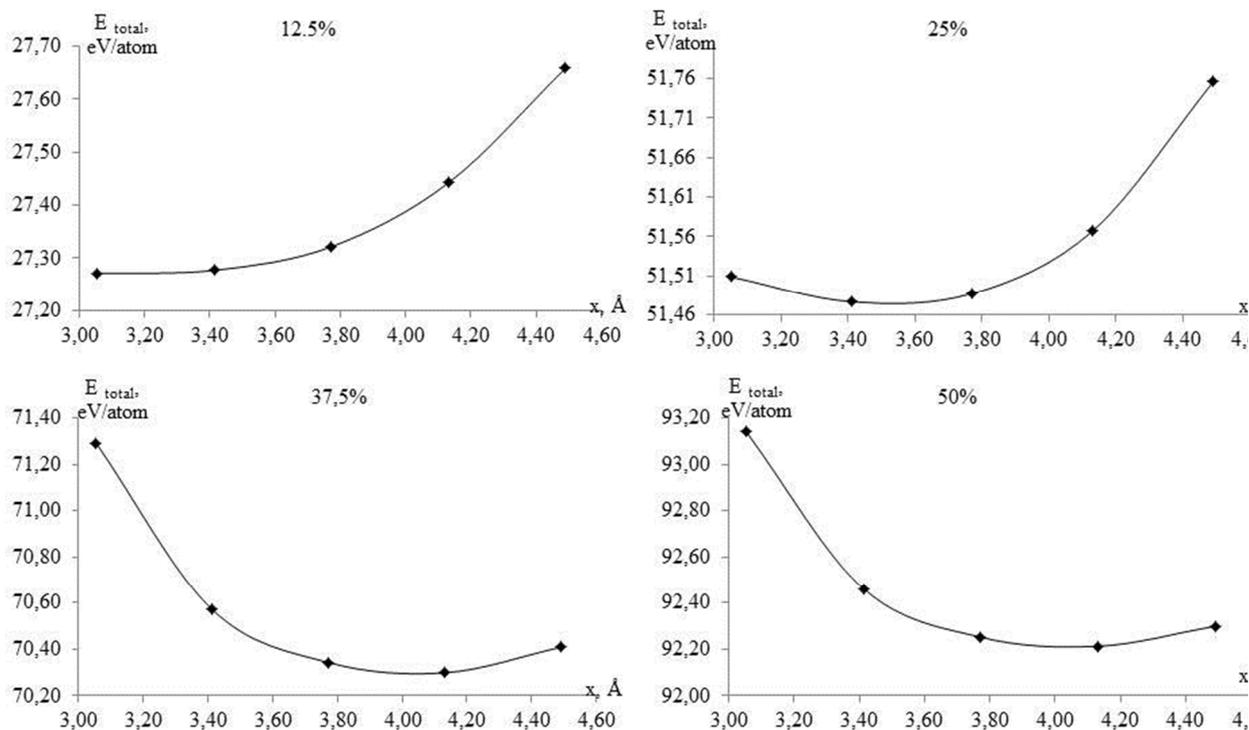


Fig. 2. Graph of the migration energy reliefs of Li atoms at degrees of filling of the SnS₂ layer from 12.5 to 50 %.

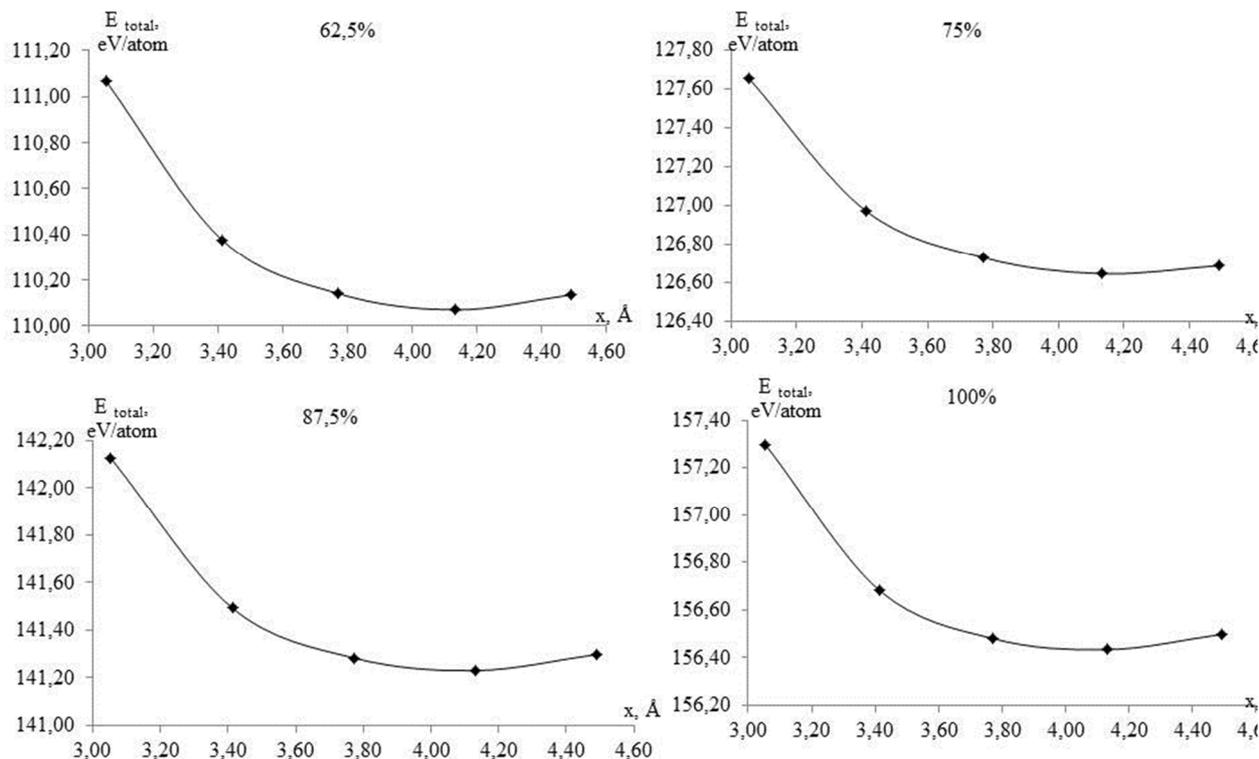


Fig. 3. Graph of the migration energy reliefs of Li atoms at degrees of filling of the SnS₂ layer from 62.5 to 100 %.

spatial migration (fig. 1, b), the total energy was calculated by the formula (10) thus generating the energy relief along the migration trajectory of Li atoms. The length of migration trajectory was 1.44 Å and a

displacement step was 0.36 Å. The reference level of energy on the energy relief graphs was taken to be equal to (-391.02 eV/atom) the value of the total energy of the system at zero filling of the layer SnS₂. From graph in

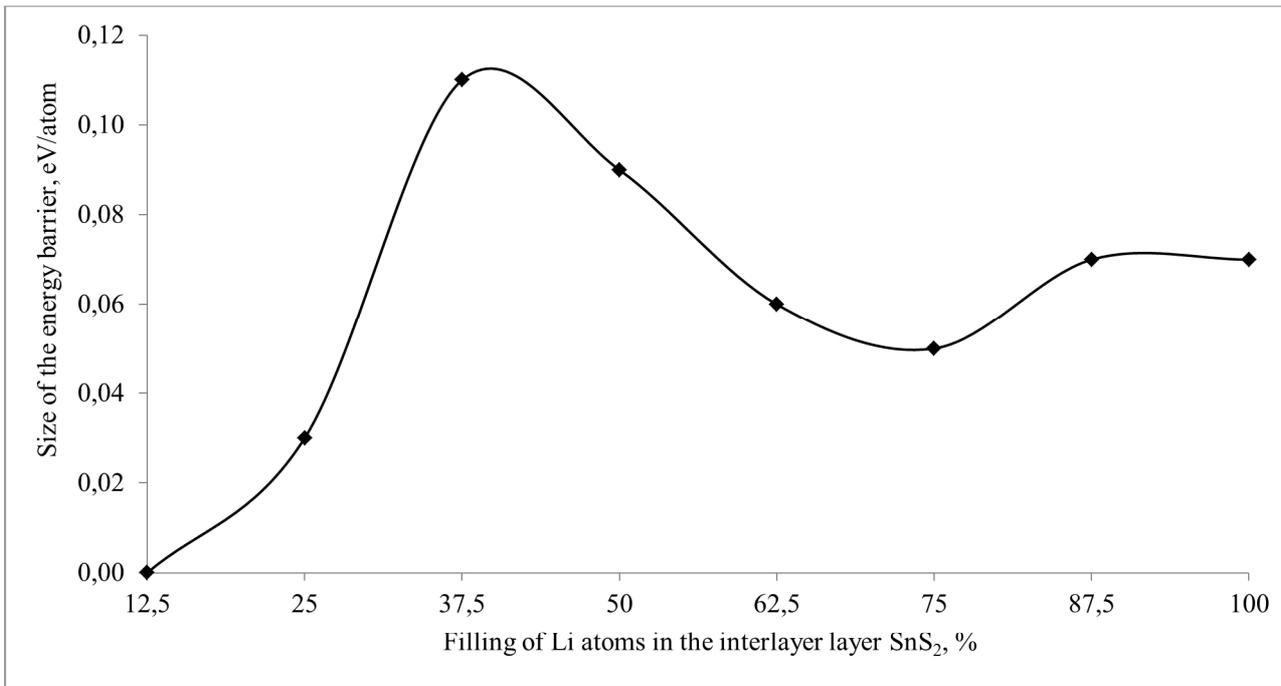


Fig. 4. Graph of dependence of the size energy barrier on the filling of Li atoms in the interlayer SnS₂ layers.

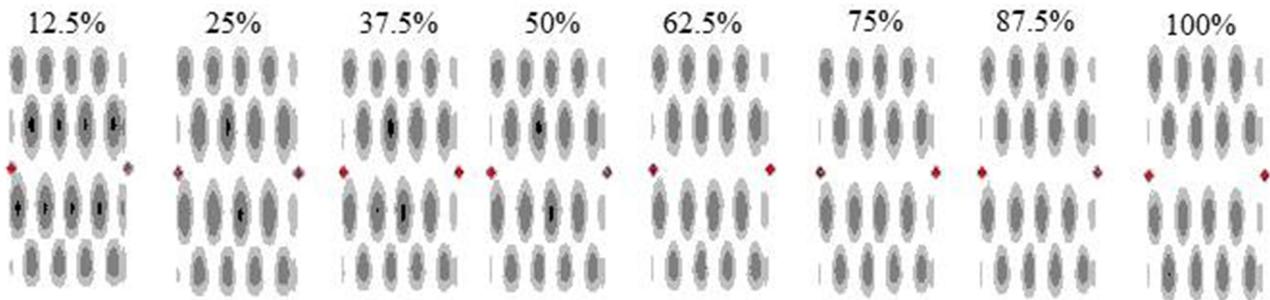


Fig. 5. The (110) cross sections of the spatial distributions of the density of valence electrons for the filling of the interlayer SnS₂ layers by Li atoms at degrees of fullness in 12.5 %, 25 %, 37.5 %, 50 %, 62.5 %, 75 %, 87.5 %, 100 % from left to right.

Fig.2 and Fig.3, it is seen some growth of the total energy of the system from 27.3 eV/atom to 157.3 eV/atom with the increase in the number of Li atoms in the SnS₂ layer

Fig. 2 shows the energy curves in the migration of two Li atoms from each other at different fillings of the interlayer layer with Li atoms. The motion of the Li atoms was accompanied by the overcoming of energy barriers. The magnitude of these energy barriers depended on the degree of filling of the SnS₂ layer with metal atoms. The value of the barrier was determined by the difference between the minimum and maximum values on the energy relief curve.

Migratory energy reliefs of Li atoms were similar in the presence of SnS₂ layer at 12.5 - 25 % (fig. 2), and the other – at fullness from 37.5 % and more (fig.2, 3). For the first group it is clear that at the final step of the locus of the motion of Li atoms (fig. 2) the value of total energy rapidly increased. For the second group (fig. 2, 3) the total energy decreased.

Analysis of the energy barriers that arise in the path

of the motion of Li atoms in the stratum SnS₂ (table 1, fig. 4) shows that their changes with the degree of filling of the stratum are no monotonically. At filling in 37.5 %, 50 % motion of atoms was accompanied by the collapse of 0.1 eV/atom energy barriers. With an increase in filling of 62.5 %, 87.5 % and 100 % the barriers decreased to a 0.65 eV/atom value. From the analysis of the graphs (fig. 4) we were able to conclude that the layer of SnS₂ is optimally filled with Li atoms of 75 % when atoms in motion practically do not consume of energy.

The presence of significant energy barriers in the migratory locus of Li atoms in the SnS₂ layer to 37.5 % filling can be explained by the interaction of Li atoms with the SnS₂ surface layer that consisted of sulphur atoms. The presence of such interaction was confirmed by the form of sections of spatial distributions of the density of valence electrons for the mentioned degrees of filling (fig. 5). By the intensity of gray color, it is evident that a greater density of valence electrons occurred in the region of sulphur atoms that are close to the Li atoms. Starting from the filling of the interlayer layer at 62.5 %

Table 1

Dependence of the size of the energy barrier on the filling of Li atoms in the interlayer SnS₂ layers

Filling of Li atoms in the interlayer SnS ₂ layers, %	Size of the energy barrier, eV/atom
12.5	0.00
25.0	0.03
37.5	0.11
50.0	0.09
62.5	0.06
75.0	0.05
87.5	0.07
100.0	0.07

or more, the density of valence electrons did not have such features.

Conclusions

Applying the methods of the functional of electron density and *ab initio* pseudopotential, we carried out

computational experiments. We have obtained the spatial distributions of the density of valence electron, the energy barriers of migration of Li atoms in the interlayer of SnS₂. Such a transfer was investigated at various degrees of filling of the interlayer space of SnS₂ of metal atoms.

It was established that with increasing number of metal in the interlayer space of SnS₂, the total energy of atomic system was increased. The motion of Li atoms was accompanied by the overcoming of energy barriers. Their size depended on the degree of filling of the SnS₂ layer with metal atoms. The optimum filling of the SnS₂ layer with the Li atoms in 75 % was recorded. With some fullness, the motion of Li atoms was accompanied by the least energy costs.

The processes occurring inside the layer SnS₂ during the migration of Li atoms were determined by the interaction of metal atoms with each other, which was filled with layer, as well as by the interaction of Li atoms with a surface layer of SnS₂, consisting of sulphur atoms.

Prikhozha Yu.O. - post-graduate student of the department of physics and methods of its teaching;
Balabai R.M. - Doctor of Physical and Mathematical Sciences, Professor of the Department of Physics and Methods of its teaching.

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Інтеркаляція атомів Li в анод акумулятора, виконаного із SnS₂: розрахунки із перших принципів

Криворізький державний педагогічний університет, Кривий Ріг, Україна, 50086, prihozhaya.yuliya93@gmail.com

Методами функціоналу електронної густини та псевдопотенціалу із перших принципів розраховано просторові розподіли густини валентних електронів та їх перетини, енергетичні бар'єри міграції атомів Li в міжшаровому прошарку аноду акумулятора, виконаного із SnS₂ при різній наповненості його атомами Li. Встановлено, що рух атомів Li супроводжувався доланням енергетичних бар'єрів, величина яких залежала від ступеня наповнюваності прошарку SnS₂ атомами металу. Зафіксовано оптимальну наповненість прошарку SnS₂ атомами Li в 75 %, при якій рух атомів Li супроводжувався найменшими енергетичними затратами.

Ключові слова: анод акумулятора, атоми Li, плівки SnS₂, функціонал електронної густини, псевдопотенціал із перших принципів, енергетичні рельєфи міграції.