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Intercalation of Li Atoms in TaSe₂ Film's Anode with LiClO₄/PEO Polymer Electrolyte: First Principles Calculation

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Using the methods of electron density functional and pseudopotential from the first principles, the total energy, energy reliefs and migration barriers of Li atoms in the interlayer space of layers of anode material made of 2H-TaSe₂, 2H-TaSe₂ with molecules of polymer electrolytes LiClO₄, PEO and LiClO₄/PEO, charges on Se atoms limit the interlayer space 2H-TaSe₂, spatial distributions of valence electron density and their cross sections.

Keywords: anode of battery, Li atoms, 2H-TaSe₂ films, 2H-TaSe₂ with molecules of polymer electrolytes LiClO₄, 2H-TaSe₂ with molecules of polymer electrolytes PEO, 2H-TaSe₂ with molecules of polymer electrolytes LiClO₄/PEO, electron density functional, *ab initio* pseudopotential, energy reliefs of migration.

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Introduction and Statement of the Problem

To improve the anode properties of lithium-ion batteries based on transition metal dichalcogenides, they are supplemented with an ionic liquid, for example, a polymer electrolyte LiClO₄/PEO [1-11]. In order to minimize the disadvantages in the manufacture of such composites with a combination of different structures for anode materials, it is necessary to use in advance a computational experiment, which is based on quantum calculation from the first principles.

I. Methods and Models of Calculation

For a computational experiment according to the algorithm described in [12-14], atomic models of anodes were developed in the form of:

- two infinite monolayers 2H-TaSe₂;
- two infinite 2H-TaSe₂ monolayers with two molecules of polymer electrolyte LiClO₄ per primitive cell, located on the outer surfaces;

- two infinite 2H-TaSe₂ monolayers with two molecules of polymer electrolyte PEO per primitive cell, located on the outer surfaces;

- two infinite 2H-TaSe₂ monolayers with two molecules of polymer electrolyte LiClO₄/PEO per primitive cell, located on the outer surfaces.

To reproduce atomic models of TaSe₂ anodes with polymer electrolytes PEO, LiClO₄ with intercalated Li atoms in the layer between TaSe₂ monolayers, the technique of superlattice construction was used, which is described in [12-14]. The spatial structure of such a superlattice was tetragonal with a corresponding atomic basis that reproduced atomic models of anodes. To avoid interaction between the translated TaSe₂ films along the crystallographic axis *c*, a vacuum gap was used. For the developed models of LIB anodes, the total energy, energy reliefs and migration barriers of Li atoms in the interlayer layers of monolayers: 2H-TaSe₂, 2H-TaSe₂ with molecules of polymer electrolytes LiClO₄, PEO and LiClO₄/PEO, and charges on limiting the interlayer space, the spatial density distributions of valence electrons and their cross sections.

To estimate the energy relief of migration of Li atoms with a displacement step of 0.3111 Å along the interlayer layer of anode material (four atomic models of anodes) at different filling of 2, 4 and 6 Li atoms, the total energy of the corresponding model atomic configurations was calculated (Fig. 1). Thus, in our migration experiment, the intercalated Li atoms moved along the OY axis, which coincides with the crystallographic direction *ab* of the supercell. Figure 1

shows the probable migration path of two Li atoms in the opposite direction within the interlayer layer of two TaSe₂ monolayers infinite in the *ab* plane at different degrees of filling of the layer with Li atoms.

II. Results and Discussion

Figures 2-5 show the calculated energy reliefs that

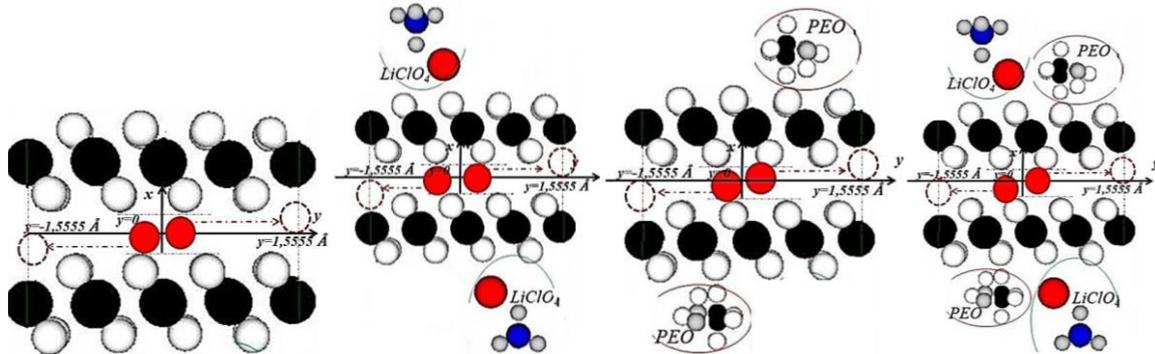


Fig. 1. The trajectory and direction of movement of intercalated Li atoms in the interlayer layers of anodes made of films 2H-TaSe₂ (a), 2H-TaSe₂ with molecules of polymer electrolyte LiClO₄ (b), 2H-TaSe₂ with polymer electrolyte PEO (c), 2H-TaSe₂ of polymer electrolytes LiClO₄/PEO (d).

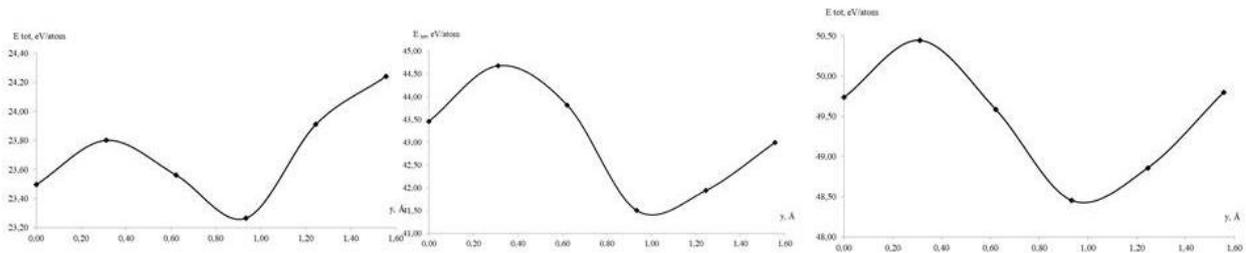


Fig. 2. Migratory energy reliefs of Li atoms in the TaSe₂ interlayer; TaSe₂, which already contains 2 intercalated Li atoms; TaSe₂, which already contains 4 intercalated Li atoms.

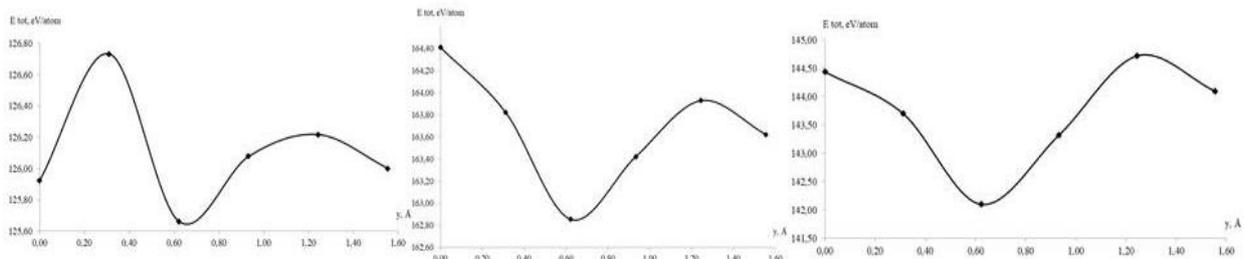


Fig. 3. Migratory energy reliefs of Li atoms in the TaSe₂ interlayer with LiClO₄ polymer electrolyte molecules; TaSe₂ with molecules of polymer electrolyte LiClO₄ containing already 2 intercalated Li atoms; TaSe₂ with molecules of polymer electrolyte LiClO₄ containing already 4 intercalated Li atoms.

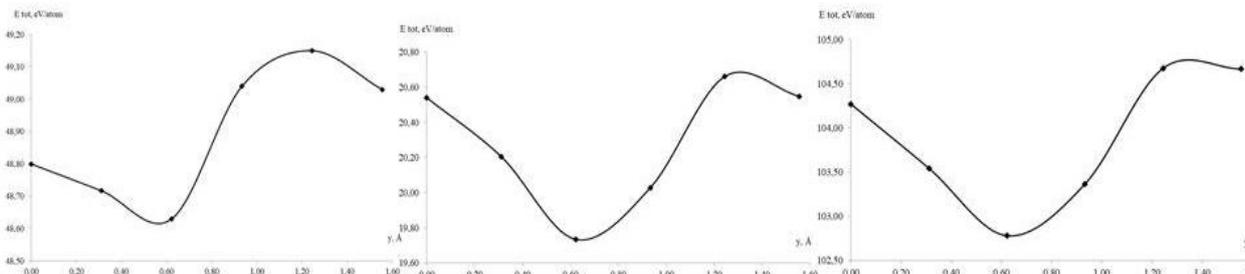


Fig. 4. Migratory energy reliefs of Li atoms in the TaSe₂ interlayer with PEO polymer electrolyte molecules; TaSe₂ with molecules of polymer electrolyte PEO containing 2 intercalated Li atoms; TaSe₂ with molecules of polymer electrolyte PEO containing 4 intercalated Li atoms.

accompanied the movement of intercalated Li atoms in the TaSe₂, TaSe₂ layers with molecules of polymer electrolyte LiClO₄, TaSe₂ with molecules of polymer electrolyte PEO, TaSe₂ with molecules of polymer electrolytes in LiClO₄/PEO 2, 4, 6 Li atoms. Thus, the graphs show that the movement of Li atoms along the OY axis in the interlayer spaces of pure TaSe₂ and TaSe₂ with added molecules of polymer electrolyte LiClO₄ or PEO there are several energy minima and maxima (Tab. 1), while the movement of metal atoms along the

interlayer space TaSe₂ with added molecules of polymer electrolytes LiClO₄/PEO in the same direction there is only one energy barrier.

Using the energy reliefs of the movement of intercalated Li atoms in the TaSe₂ interlayer with different composite additives (molecules of polymer electrolytes LiClO₄ or (and) PEO) and at different fillings with Li atoms, the energy barriers of migration of intercalated atoms were calculated.

The values of energy barriers during the movement

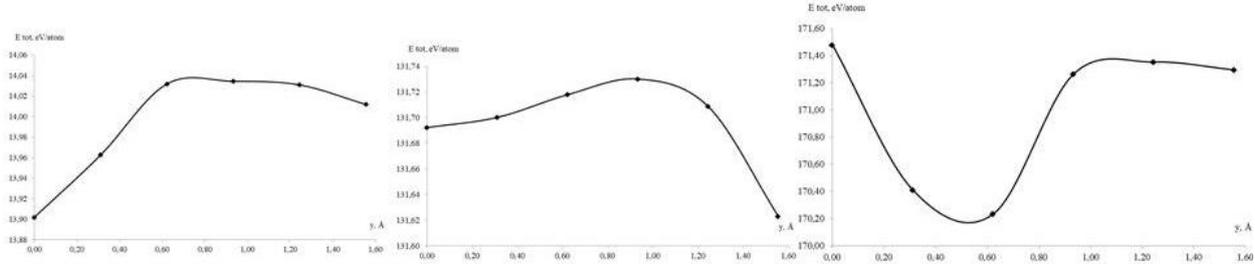


Fig. 5. Migratory energy reliefs of Li atoms in the interlayer of TaSe₂ with molecules of polymer electrolytes LiClO₄/PEO; TaSe₂ with molecules of polymer electrolytes LiClO₄/PEO, which already contains 2 intercalated Li atoms; TaSe₂ with molecules of polymer electrolytes LiClO₄/PEO, which already contains 4 intercalated Li atoms.

Table 1

The value of charges on Se atoms at the final step of migration of Li atoms ($y = 1,5555 \text{ \AA}$) depending on the type of anode material

Atom number Se	Charge, <i>ee</i>	Charge, <i>ee</i>	Charge, <i>ee</i>	Charge, <i>ee</i>
TaSe ₂				
	Empty layer	The filling of the layer with 2 Li atoms	The filling of the layer with 4 Li atoms	The filling of the layer with 6 Li atoms
2	4.020812	4.185801	4.149317	4.079412
5	4.011354	4.163270	4.117679	4.062081
7	4.029822	4.208887	4.213425	4.196816
10	4.014123	4.146755	4.008055	3.944986
11	4.014219	4.144442	4.011618	3.949930
14	4.029904	4.200690	4.217696	4.196820
16	4.007084	4.176107	4.133276	4.065615
19	4.002818	4.166039	4.112542	4.069962
TaSe ₂ with molecules of polymer electrolyte PEO				
2	5.019559	5.022983	5.000147	4.999738
5	4.643792	4.663858	4.786035	4.777329
7	4.964219	4.962260	4.944664	4.944675
10	4.924350	4.921297	4.902715	4.899896
11	4.922870	4.917670	4.905098	4.902763
14	4.962511	4.960387	4.941160	4.940439
16	4.991114	5.000878	5.022669	5.017344
19	4.101882	4.128461	4.541804	4.967250
TaSe ₂ with molecules of polymer electrolyte LiClO ₄				
2	5.026054	5.026522	5.027030	5.011385
5	4.998418	5.000552	5.000754	5.002060
7	4.973298	4.976433	4.978934	4.985447
10	4.994641	4.993887	4.992868	4.992471
11	4.993595	4.992768	4.991126	4.989834
14	4.975174	4.978789	4.982598	4.988096
16	4.968583	4.964526	4.968650	4.957053
19	4.977863	4.982581	4.979794	4.982013

Table 1(continuation)

TaSe ₂ with molecules of polymer electrolyte LiClO ₄ /PEO				
2	4.933664	4.940877	4.933436	4.952982
5	4.949544	4.951386	4.947882	4.958869
7	4.974578	4.970283	4.970103	4.970353
10	4.98726	4.984213	4.983985	4.984573
11	4.980834	4.979134	4.978905	4.978638
14	4.968501	4.964191	4.963547	4.964447
16	5.076402	5.095651	5.095085	5.099072
19	4.986552	5.005945	5.005730	4.996763

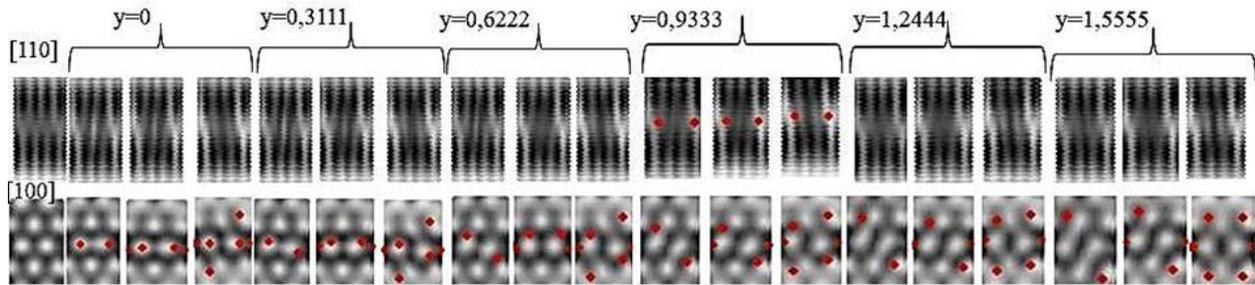


Fig. 6. The cross sections [110] and [100] of the spatial distributions of the valence electron density within a cell whose atomic basis simulates two TaSe₂ monolayers, with Li atoms intercalated into the interlayer space, at 2, 4, 6 atoms for $y = 0 - 1.5555 \text{ \AA}$.

of intercalated Li atoms in the interlayer of TaSe₂ with molecules of polymer electrolytes LiClO₄.PEO were 0.02 eV/atom, 0.04 eV/atom during movement in the empty layer and pre-filled with two Li atoms, respectively. Relatively low energy consumption is seen during the migration of Li atoms in the anode material TaSe₂ with molecules of polymer electrolyte PEO, along the y-axis in the trajectory corresponding to the range of movement between $y = 0.9333 - 1.2444 \text{ \AA}$. Here, the value of energy barriers is almost unchanged and is equal to 0.12 eV/atom, 0.11 eV/atom, and at $y = 1.5555 \text{ \AA}$ drops sharply to 0.01 eV/atom. The largest value of the energy barrier (6.47 eV/atom) during the migration of Li atoms in pure anode material TaSe₂ along the y-axis in the trajectory corresponding to the range of movement from $y = 0 \text{ \AA}$ to $y = 0.6222 \text{ \AA}$ with subsequent decline (0.94 eV/atom) at $y = 0.9333 - 1.5555 \text{ \AA}$.

There was an increase in the value of the energy barrier with increasing number of intercalated Li atoms that filled the interlayer space of all studied anode materials, except TaSe₂ with molecules of PEO polymer electrolyte during the migration of Li atoms in the areas $y = 0.9333 - 1.5555 \text{ \AA}$. Here, the total energy of the system significantly decreased to the value of 0.01 eV/atom. Thus, the presence of significant energy barriers at the initial steps of migration of Li atoms can be explained by the interaction of the inner layer of Se with Li atoms.

The total energy of the studied atomic systems, attributed to 1 atom, increases significantly with the increase in the number of atoms in the atomic basis of the primitive cell. Thus, the total energy of the system at the final step of the migration trajectory of Li atoms in the empty TaSe₂ layer was 24.24 eV/atom, whereas at the previous filling of the layer with 4 atoms - 49.80 eV/atom. A similar pattern was observed in the case of composite anodes: TaSe₂ with molecules of

polymer electrolytes LiClO₄ or (and) PEO.

Figures 6 show the cross sections [110] and [100] of the spatial distributions of the valence electron density within a cell.

From Fig. 6 on the intense gray color we see that the largest value of the electron density is in the region of interaction of Li atoms with the inner layer Se of TaSe₂ films, whereas in the unfilled interlayer space TaSe₂, the electron density is evenly distributed throughout the layer. Analyzing the cross sections [110] of the spatial distributions of the valence electron density within the cell, it is seen that as the intercalated Li atoms increase in the TaSe₂ interfilm space, the electron density falls more on the region within the y coordinate axis where the Li atom is located. From Tab.1 it is seen that the values of electric charges on Se atoms increase in the presence of polymer electrolyte molecules in TaSe₂ films.

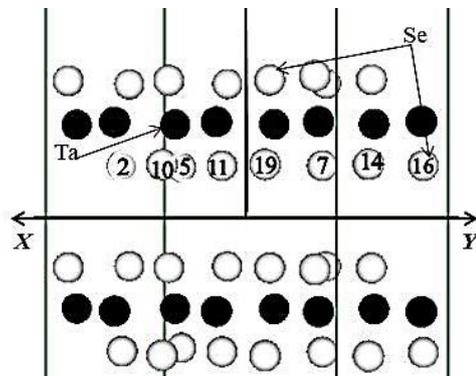


Fig. 7. Se 2H-TaSe₂ atoms bounding the interlayer space and their numbering within the primitive cell to calculate the effective charges.

From Fig. 8-9 we see that the distributions of the electron density in the neighborhoods with a radius of

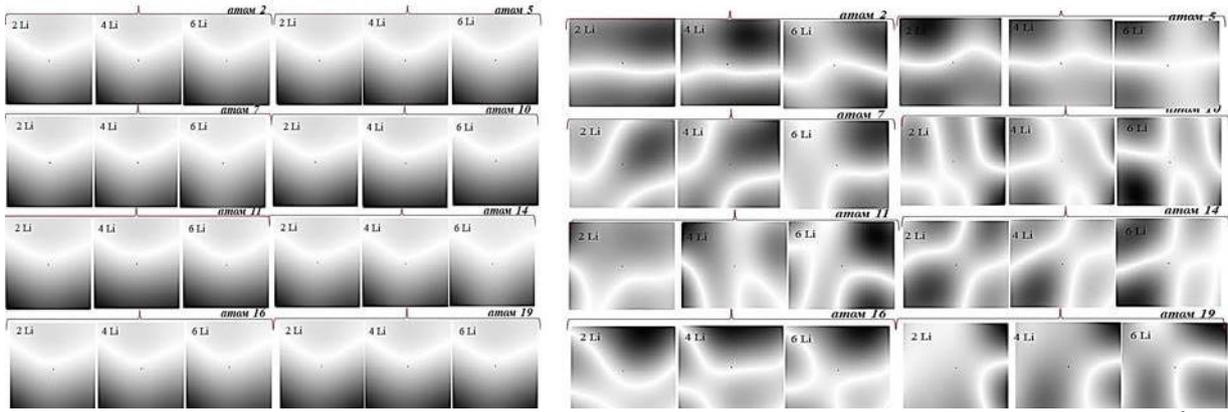


Fig. 8. Sections [110] of spatial distributions of valence electron density in environments with a radius of 1 Å Se atoms located in the inner part of the TaSe₂ film (left) and TaSe₂ film with molecules of the polymer electrolyte LiClO₄ (right), with different filling of metal atoms and location of mobile Li atoms at the final migration step ($y = 1.5555 \text{ \AA}$)

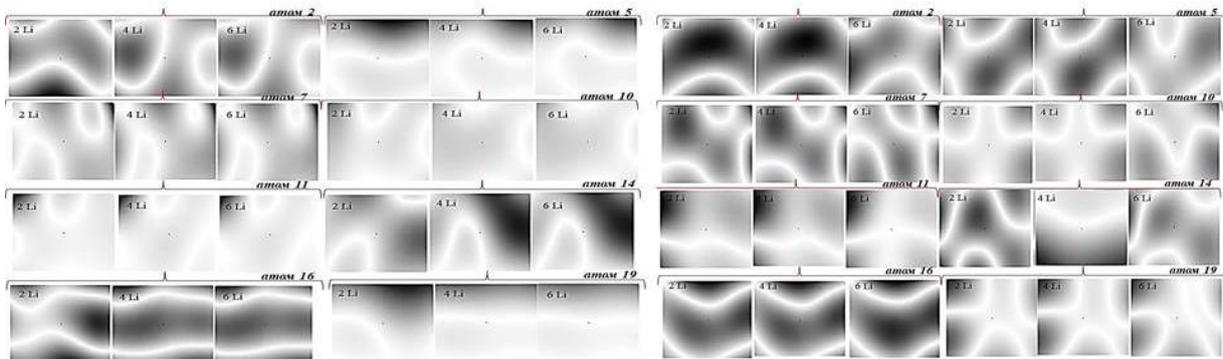


Fig. 9. Sections [110] of spatial distributions of valence electron density in environments with a radius of 1 Å Se atoms located in the inner part of the TaSe₂ film with PEO polymer electrolyte molecules (left) and of the TaSe₂ film with polymer electrolyte molecules LiClO₄ and PEO (right), intercalated in the interlayer layer of Li atoms at the final migration step.

1 Å of Se atoms located in the inner part of the TaSe₂ film, with different filling of the TaSe₂ layer with metal atoms was uniform. The location of the moving Li atoms was at the final migration step ($y = 1.5555 \text{ \AA}$) within the primitive cell. What can not be said about the studied anode material based on TaSe₂ with molecules of polymer electrolytes LiClO₄ or (and) PEO. Here, the electron density distribution had different configurations in the environments with a radius of 1 Å Se atoms depending on the degree of filling of the interlayer with Li atoms and the proximity of these Se atoms to PEO polymer electrolyte molecules (numbers 7, 14, 16 within the primitive cell).

The cross-sections [110] of the spatial distributions of valence electron densities in the vicinity of internal Se atoms for TaSe₂-based anode material with added molecules of polymer electrolyte LiClO₄ and with the addition of molecules of two types of electrolytes LiClO₄/PEO also have a non-uniform appearance. In this case, the form of the electron density distributions of the valence electrons changed little with varying degrees of filling of the TaSe₂ layer with Li atoms.

To better understand the physical mechanisms that accompany the motion of Li atoms in the interlayer space of the anode material and the redistribution of the valence electron charge of all atoms involved in the process, effective electric charges on the Se atoms of the

2H-TaSe₂ film were calculated.

Tab.1. show the values of effective electric charges calculated in the vicinity with a radius of 1 Å near the atomic backbones of Se with numbers 2, 5, 7, 10, 11, 14, 16, 19 (within the atomic basis), which teach interlayer layer of monolayers TaSe₂, TaSe₂ with molecules of polymer electrolyte LiClO₄, TaSe₂ with molecules of polymer electrolyte PEO, TaSe₂ with molecules of polymer electrolytes LiClO₄ and PEO. We see that the values of effective electric charges on Se atoms in the TaSe₂ film vary depending on the number of the Se atom, the position of the intercalated Li atom relative to the Se atom for which the effective electric charge was calculated and depending on the layer filling with Li atoms. In the anode material of the battery, to which a polymer electrolyte is added, the values of the charges on the Se atoms, with a change in the position of the Li atom, hardly change.

LiClO₄ and (or) PEO, the uniformity of electric charges on Se atoms is observed, which inevitably affects the energy consumption of migratory movements of Li atoms in the anode. This is confirmed by our calculations of energy barriers estimated by the movement of metal atoms along the interlayer space TaSe₂ with added molecules of polymer electrolytes LiClO₄ and PEO, which is almost monotonic in nature compared to other types of model anodes. Tab.1 shows that the values of

the effective charges calculated on the Se atoms, limiting the pure interlayer layer of TaSe₂ and the interlayer layer of TaSe₂ with molecules of polymer electrolytes LiClO₄ or (and) PEO differ by a value close to the value of 0.75 ee . The value effective charges on Se atoms in the anode made of pure TaSe₂ films was 4.05 ee , while for composite TaSe₂ anodes with molecules of polymer electrolytes LiClO₄ or (and) PEO this value increased to 4.8 ee .

Conclusions

Films of transition metal dichalcogenides, namely TaSe₂, TaSe₂ with polymer electrolyte LiClO₄/PEO, for anodes of lithium-ion batteries were studied by the methods of electron density functional and pseudopotential from the first principles. For the developed models of anodes of ion batteries it is calculated:

- total energy, energy reliefs and migration barriers of Li atoms in the interlayer layer of the battery anode, made of TaSe₂, TaSe₂ films with molecules of polymer electrolytes LiClO₄ or (and) PEO, with different filling of Li atoms;
- spatial distributions of valence electron density and their cross sections;

- charges on Se atoms of TaSe₂ films, which limit their interlayer space.

An increase in the value of the energy barrier with an increase in the number of intercalated Li atoms, which filled the interlayer space of all studied anode materials, except TaSe₂ with molecules of polymer electrolyte PEO during the migration of Li atoms. It was found that the values of effective electric charges on Se atoms in TaSe₂ film with composite additives are different and depend on the position of the Se atom relative to the polymer molecules, the position of the intercalated Li atom relative to the Se atom and the layer filling with Li atoms. In the anode of the battery based on TaSe₂ film with polymer electrolyte LiClO₄ and (or) PEO, uniformity of electric charges on Se atoms is observed, which limit the layer in which Li atoms move, which affects the energy consumption of migratory movements of Li atoms in the anode - it becomes monotonic.

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Ю.О. Прихожа, Р.М. Балабай

Інтеркаляція атомів Li в плівковий анод на основі 2H-TaSe₂ з полімерним електролітом LiClO₄/PEO: розрахунки із перших принципів

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Розраховано повну енергію, енергетичні рельєфи та бар'єри міграції атомів Li у міжшаровому просторі шарів анодного матеріалу, виконаного із 2H-TaSe₂, 2H-TaSe₂ з молекулами полімерних електролітів LiClO₄, PEO та LiClO₄/PEO, заряди на атомах Se 2H-TaSe₂, що обмежують міжшаровий простір, просторові розподіли густини валентних електронів та їх перетини. В основу комп'ютерного експерименту покладено метод функціоналу електронної густини та псевдопотенціалу із перших принципів.

Ключові слова: анод акумулятора, атоми Li, плівки 2H-TaSe₂, плівки 2H-TaSe₂ з молекулами полімерного електроліту LiClO₄, плівки 2H-TaSe₂ з молекулами полімерного електроліту PEO, плівки 2H-TaSe₂ з молекулами полімерних електролітів LiClO₄/PEO, функціонал електронної густини, псевдопотенціал із перших принципів, енергетичні рельєфи міграції.