

# Computer Simulation of Negative Electrode Operation in Lithium–Ion Battery: Galvanostatic Discharge, Active Intercalating Agent Grains, Role of Diffusion Limitations

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**Abstract**—Computer simulation of the negative electrode (anode) operation in a lithium–ion battery under galvanostatic discharge mode is performed. The amount of active intercalating agent grains that may take part in the electrochemical process is calculated. Special attention was paid to evaluation of diffusion limitations arising under recovery of lithium atoms from an intercalating agent grains related to the low value of the diffusion coefficient of lithium atoms  $D$ . It is shown that the common model of a spherical intercalating agent grain, when its whole outer surface participates in an electrochemical process, contradicts the model of equally-sized cubic grains studied in this work. It is found that the average amount of electrochemically active faces of active intercalating agent grains varies in the range of 1.91 to 3.55. A new model of the structure and depletion of an intercalating agent grain is suggested. The process of full depletion of intercalating agent grains may be implemented in the case when they either have rather small dimensions  $L$ , more specifically, if the  $L/D$  ratio is low, or if the anode discharge current density  $I$  is sufficiently low. The optimum working anode parameters are calculated under the condition of reaching full depletion of intercalating agent grains: active layer depth, discharge time, specific electric capacitance and final anode potential at the active layer/inter-electrode space interface.

**Keywords:** lithium–ion battery, negative electrode (anode), galvanostatic discharge mode, active intercalating agent grains, role of diffusion limitations, computer simulation, model of equally sized grains of two types, percolation theory, intercalation

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## 1. PROBLEM STATEMENT

In [1], methods of computer modeling were used to calculate the characteristics of a lithium–ion battery working in the galvanostatic discharge mode according to the model of equally sized grains. The active anode material consisted of active material (intercalating agent) grains, their volume fraction being  $g$ , and grains of electrolyte, their volume fraction being  $g_i$ . The presence of binder in the active anode material was neglected, therefore

$$g + g_i = 1. \quad (1)$$

Grains of electrolyte and intercalating agent grains have a similar form and represent microcubes with edge length  $L$ . Thus, from the standpoint of the percolation theory, one has to deal with a cubic lattice in the model of equal-sized grains [2]. The 3D model of the active anode material was assumed to be a model cube with the conventional size of  $N_s \times N_s \times N_s = N_s^3$ . A model cube must have microscopic dimensions. This means that the cathode active layer depth  $\Delta$  must be, as

it usually is in actual reality, of much larger size than that of separate grains  $L$ .

The channels for supply or removal of lithium ions or electrons are the ionic (of grains of electrolyte) and electronic (of intercalating agent grains) percolation clusters formed in the anode active material. Each of these represents a set of interconnected grains of one kind or another. Percolation clusters extend to the whole active anode layer depth.

Percolation clusters are formed after percolation threshold is reached if the bulk concentrations of the corresponding grains reach the given value:  $g^*$  or  $g_i^*$ . In a cubic lattice we deal with, the percolation threshold, as shown in [3], is  $g^* = g_i^* = 0.298$ . However, fully functioning percolation clusters, as shown in [4], are formed later: at  $g \geq 0.35$  and at  $g_i \geq 0.35$ . Thus, with account for condition (1), the range of reasonable values for parameter  $g$  at which anode discharge may occur lies in the range of

$$0.35 < g < 0.65. \quad (2)$$

Not each intercalating agent grain can take part in the electrochemical process. The intercalating agent

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grains must be divided into two classes [4]: active grains with concentration  $g^*$  and inactive grains with concentration  $g - g^*$ . The term "active grain" may be used only for a grain that at least on one of its 6 faces contacts the ionic percolation cluster and at least on one of its faces contacts the electronic percolation cluster. If at least one of these two requirements is not fulfilled, the grain is apparently inactive.

A fault of work [1] was as follows: 1. No separation of intercalating agent grains to active and inactive ones was performed. 2. The role of diffusion limitations appearing as a result of recovery of lithium atoms from intercalating agent grains was in no way taken into account.

The faults of paper [1] are eliminated in this study. Special attention is given to the role played by diffusion of lithium atoms in the intercalating agent grains. Criteria are found that must be fulfilled in order to consider diffusion limitations in intercalating agent grains negligible.

## 2. CHOICE OF OPTIMUM INTERCALATING AGENT CONCENTRATION

Firstly, let us not take into account the effect of diffusion limitations in the process of recovery of lithium atoms from intercalating agent grains. Under these conditions, let us focus our efforts on establishing the fraction of active intercalating agent grains and determining the optimum concentration of intercalating agent grains in the active anode material.

In the galvanostatic anode discharge mode, the triads of values (fractions of active intercalating agent grains  $g^*$ , specific contact surface area  $S$  of the electronic and ionic percolation clusters on which the electrochemical reaction occurs, and specific conductivity of lithium ions in the percolation ionic cluster  $k^*$ ) are sufficient for determination of its operating characteristics.

Of course, full characterization of the anode active material also requires data presented in Table 1. It contains the following:  $k$  is the specific conductivity of electrolyte,  $D$  is the diffusion coefficient of lithium atoms in intercalating agent grains,  $i_0$  is the exchange current,  $c^*$  is the maximum possible concentration of lithium ions in intercalating agent grains. The choice of these particular values presented in Table 1 was discussed in [1].

There are three characteristic quantities in the galvanostatic anode discharge theory:

the characteristic ohmic length

$$L_{\text{ohm}} = (2RTkk^*/FSi_0)^{1/2}, \quad (3)$$

where  $R$  is the gas constant,  $T$  is the absolute temperature,  $F$  is the Faraday's number;

characteristic ohmic discharge current

$$I_{\text{ohm}} = (2RTkk^*Si_0/F)^{1/2}; \quad (4)$$

characteristic discharge time

**Table 1.** Initial parameters of the active anode material

$k, \text{Ohm}^{-1} \text{cm}^{-1}$	$D, \text{cm}^2/\text{s}$	$i_0, \text{A}/\text{cm}^2$	$L, \text{cm}$	$c^*, \text{g-m}/\text{cm}^3$
$10^{-3}$	$10^{-10}$	$10^{-4}$	$5 \times 10^{-4}$	$3 \times 10^{-2}$

**Table 2.** Dependence of characteristics of the active anode material on the bulk concentration of intercalating agent grains  $g$  and concentration of grains of solid polymer electrolyte  $g_i$

$g$	$g_i$	$g^*$	$SL$	$k^*$
0.35	0.65	0.247	0.907	0.304
0.4	0.6	0.348	1.197	0.231
0.45	0.55	0.416	1.325	0.166
0.5	0.5	0.470	1.362	0.109
0.55	0.45	0.509	1.325	0.061
0.6	0.4	0.524	1.197	0.026
0.65	0.35	0.459	0.907	0.0061

$$\tau = g^*Fc^*/Si_0. \quad (5)$$

Algorithms of computer calculations allowing determining the dependence of the  $g^*$ ,  $SL$ , and  $k^*$  values on the active anode material composition (on the  $g$  and  $g_i$  values) were discussed in [4]. The calculation results are presented in Table 2. As follows from definition (1), if the value of any parameter  $g$  or  $g_i$  is fixed, the other parameter also becomes fixed. Table 2 is arranged to that the main parameter is the bulk concentration (fraction) of intercalating agent grains  $g$ .

The data of Table 2 pose the question as to the choice of the optimum composition of the active anode material. It would seem that one must aim at the active material with high concentrations of intercalating agent grains  $g$  and therefore high values of the fraction of active intercalating agent grains  $g^*$  (the lower half of Table 2). However, in this case, conductivity of electrolyte in the active anode layer  $k^*$  will be very low (the last column of Table 2).

The order of magnitude of  $k \approx 10^{-3} \text{Ohm}^{-1} \text{cm}^{-1}$  [5] and product  $kk^*$  as shown by the data of Table 2, may even decrease to  $kk^* \sim 10^{-5} \text{Ohm}^{-1} \text{cm}^{-1}$ . Therefore, one should aim at choosing the maximum values of  $kk^*$  (the upper half of Table 2).

The problem of choosing the optimum  $g_{\text{opt}}$  for the fraction of the intercalating agent grains in the anode active layer may be explained at a particular example. Let us estimate how specific electric capacitance  $C$  of the anode changes under variation of  $g$ . It may be approximately estimated according to the obvious formula:

$$C = Fc^*g^*c_0L_{\text{ohm}} \sim g^*(k^*/S)^{1/2}. \quad (6)$$

**Table 3.** Dependence of characteristic ohmic length  $L_{\text{ohm}}$ , characteristic ohmic current  $I_{\text{ohm}}$ , and characteristic anode discharge time  $\tau$  on the fraction of intercalating agent grains  $g$

$g$	$L_{\text{ohm}}, \mu\text{m}$	$I_{\text{ohm}}, \text{mA}/\text{cm}^2$	$\tau, \text{s}$
0.35	93.5	1.64	4072
0.4	70.7	1.65	4316
0.45	56.9	1.47	4650
0.5	45.4	1.21	5103
0.55	34.5	0.89	5680
0.6	23.7	0.56	6476
0.65	13.3	0.23	7575

**Table 4.** Dependence of the specific electric capacitance of anode  $C$  on the bulk concentration of intercalating agent grains  $g$

$g$	$C, \text{C}/\text{cm}^2$
0.35	4.68
0.40	4.99
0.45	4.80
0.50	4.32
0.55	3.56
0.60	2.52
0.65	1.24

Again, analyzing the data of Table 2 confirms the inconsistency of requirements towards the choice of the values for the set of three parameters,  $g^*$ ,  $S$ , and  $k^*$ .

Let us do the following to find the approximate value of the optimum specific electric capacitance  $C_{\text{opt}}$ . Let us calculate according to formulas (3)–(5) the dependence of characteristic ohmic length  $L_{\text{ohm}}$ , characteristic ohmic current  $I_{\text{ohm}}$ , and characteristic anode discharge time  $\tau$  on the fraction of intercalating agent grains  $g$ . These data are presented in Table 3.

Using the data of Table 3 and assuming that the initial filling degree of intercalating agent grains by lithium atoms is  $\check{c} = c_0 = 0.7$ , one can calculate the dependence of cathode capacitance  $C$  on the fraction of intercalating agent grains according to formula (6). These data are presented in Table 4. They allow making an important conclusion that the optimum loading the active anode material by intercalating agent grains must be not the maximum allowable value of  $g = 0.65$ , but the lower value of  $g = g_{\text{opt}} = 0.4$ . At  $g = 0.4$ , the cathode capacitance reaches the maximum value of  $C = C_{\text{opt}} = 4.99 \text{ C}/\text{cm}^2$ .

### 3. SYSTEM OF EQUATIONS FOR ACTIVE ANODE LAYER

To calculate the value of specific electric capacitance and other working parameters of the anode not approximately but exactly, one must have a system of equations describing the processes in the active layer in time and space.

At the initial time moment (at  $t = 0$ ), all intercalating agent grains are filled by lithium atoms up to the concentration of  $c_0$ . Then, in the course of anode discharge, the concentration of lithium atoms starts decreasing. The reduced lithium concentration averaged by the intercalating agent grain volume  $\check{c} = c/c^*$ , where  $c^*$  is the maximum possible concentration.

Let us assume that current density  $j$  generated at the interface of the ionic and electronic clusters takes the form of:

$$j = i_0 [(1 - a_s)^{1/2} a_s^{1/2}] \{e^\eta - e^{-\eta}\}, \quad (7)$$

where  $a_s$  is the reduced concentration of lithium in the intercalating agent grains on the contact surface between the active intercalating agent grains and grains of electrolyte in the ionic percolation cluster,  $i_0$  is the exchange current, and reduced polarization

$$\eta = F[E - U]/2RT, \quad (8)$$

where  $E$  is the potentials of the intercalating agent and electrolyte, accordingly, and the open-circuit potential of a lithium-ion battery is [6]:

$$U = -0.16 + 1.32 \exp(-3\check{c}). \quad (9)$$

An equation for polarization  $\eta$  may be obtained on the basis of the law of conservation of lithium ion fluxes in electrolyte (in grains of the ionic percolation cluster):

$$d^2\eta/d\hat{y}^2 = [(1 - a_s)^{1/2} a_s^{1/2}] \{e^\eta - e^{-\eta}\}, \quad (10)$$

where  $\hat{y} = y/L_{\text{ohm}}$  is the reduced coordinate and  $L_{\text{ohm}}$  is the characteristic ohmic length determined by expression (3). The boundary conditions for equation (10) in the case of galvanostatic discharge mode take the form of:

$$-I_{\text{ohm}} d\eta/d\hat{y}^2 = I = \text{const} \quad \text{at } y = 0, \quad (11)$$

$$d\eta/d\hat{y} = 0 \quad \text{at } y = \Delta, \quad (12)$$

where  $I_{\text{ohm}}$  is the characteristic ohmic current determined by expression (4),  $I$  is the discharge current density.

The process of a decrease in the concentration of lithium atoms in intercalating agent grains (in the electronic percolation cluster) is described by the following equation:

$$d\check{c}/dt^* = -[(1 - a_s)^{1/2} a_s^{1/2}] \{e^\eta - e^{-\eta}\}, \quad (13)$$

Here,  $\check{c}(y, t)$  is the concentration of lithium atoms averaged by the intercalating agent grain volume. The meaning of the rightmost part of equation (13) is a decrease in the concentration of lithium atoms in the intercalating agent grains, as they are oxidized to lithium ions and pass into the ionic percolation cluster.

The reduced time coordinate  $t$  takes the form of:

$$t^* = t/\tau, \quad (14)$$

where  $\tau$  is the characteristic time determined by expression (5). The initial condition for equation (13) is:

$$\check{c} = c_0 \quad \text{at } t = 0. \quad (15)$$

Thus, the set of equations (10) and (13) allows tracing the changes in the reduced anode potential in the active anode layer:

$$\psi = F[E]/2RT \quad (16)$$

on the basis of the active layer depth and concentrations of lithium atoms  $\check{c}$  averaged by the intercalating agent grain volume. But this is true only in the case when the functional relationship between the  $\check{c}$  and  $a_s$  quantities is known. For example, if one may assume that the concentration of lithium atoms on the surface of the intercalating agent grain (equations (10) and (13)) is equal to the average concentration  $\check{c}$  of lithium atoms in an intercalating agent grain. That is, if the following equality is true:

$$a_s = \check{c}. \quad (17)$$

Physically, this condition means that diffusion limitations for removal of lithium atoms in an intercalating agent grain are negligible and they may be not taken into account.

#### 4. MODEL OF ACTIVE INTERCALATING AGENT GRAIN

Let us now analyze the processes occurring within an individual intercalating agent grain. Usually, this intercalating agent is represented in the form of a sphere [7] that is surrounded by electrolyte on all sides. It is tacitly assumed that the whole spherical grain surface participates in the electrochemical process.

As will be shown below, the actual situation is much more complicated. In the considered model of equally sized grains of two types, in which the grains have the form of cubes and only a part of 6 faces of the active intercalating agent grain, from 1 to 5, may be adjacent to grains of electrolyte and may participate in the electrochemical process. And this circumstance must also be taken into account in calculations of the working parameters of a lithium-ion battery anode.

It is necessary to know how the number of electrochemically active faces  $n_i$  on which the electronic and ionic percolation clusters contact each other and aver-

**Table 5.** Dependence of the number of electrochemically active faces  $n_i$  and average number of such faces for active intercalating agent grains  $n$  on the fraction of intercalating agent grains  $g$

$g$	$n_1$	$n_2$	$n_3$	$n_4$	$n_5$	$c$
0.35	7657	31933	71850	88162	47617	3.55
0.40	17791	58772	107949	110576	53020	3.35
0.45	33871	90329	133672	112390	45984	3.11
0.50	60093	125886	148138	101143	34507	2.84
0.55	982247	159734	147791	81067	22365	2.55
0.60	149536	179530	127208	54954	12292	2.24
0.65	191316	154417	80902	27363	4872	1.91

age number of such active faces  $\bar{n}$  on the active intercalating agent grains changes under variation in the anode active material composition.

The value of  $\bar{n}$  was calculated according to the obvious formula:

$$\bar{n} = (1n_1 + 2n_2 + 3n_3 + 4n_4 + 5n_5)/\sum n_i, \quad (18)$$

Summation in the denominator of the rightmost part of formula (18) is performed from 1 to 5.

The result of percolation calculations of the dependence of  $n_i$  and  $\bar{n}$  on the fraction of intercalating agent grains  $g$  is presented in Table 5. It shows that on the average, only a part of faces of a cubic active intercalating agent grain, from 3.55 faces at  $g = 0.35$  to 1.91 faces at  $g = 0.65$ , takes part in the electrochemical process.

Thus, a number of important circumstances come to light:

(1) The concept of all intercalating agent grains being able to participate in the electrochemical process is incorrect. Only a part of them, the active intercalating agent grains, participate in the anode discharge.

(2) Not the whole outer surface of active intercalating agent grains participates in the discharge process. The electrochemically active fraction of active grains is distributed in a complex way over the grain surface, as shown by the data of Table 5.

Due to a high conventional character of the concepts as to the intercalating agent grain as of a sphere of a microcube, it appears very complicated and inef-

ficient to take into account all the small details and high diversity of the results of computer calculations collected in Table 5 in the studied model of cubic grains of two types. It is necessary to suggest a simplified to the utmost diffusion process model in an active intercalating agent grain. Let us do it.

Firstly, let us take into account that there is always a face on an active intercalating agent grain, let us denote it as a "closed" face through which electrons are supplied into this grain. There is always contact between the neighboring intercalating agent grains within the electronic percolation cluster. The contact face of these intercalating agent grains is apparently electrochemically inactive, "closed".

Secondly, there are, on the average, other faces, from one to three (the data for  $\bar{n}$  in Table 5) that are also electrochemically inactive faces on an active intercalating agent grain. They are also closed for removal of lithium atoms, they hinder diffusion from an active grain of lithium atoms in the planes parallel to the surface of a "closed" active grain face. Therefore, they on the whole contribute to imparting quasi-unidimensional character to the process of lithium atom recovery from an active grain. In fact, the diffusion flux of lithium atoms in an active intercalating agent grain mainly occurs in the direction perpendicular to the "closed" active grain face.

Thirdly, one must take into account existence of a "variable size window" through which the largest part of lithium atoms basically leaves the active grain. Such a "window" consists of electrochemically active faces of an active intercalating agent grain, from two to three and a half faces (the data for parameter  $\bar{n}$  in Table 5).

With account for the above, one may suggest a simplified pattern of recovery of lithium atoms from an active grain. Let us assume that such a process is similar to the process occurring in the course of diffusion of lithium atoms in a planar layer with thickness  $L$  under the condition that one of the layer surfaces is closed of exchange of lithium atoms and an electrochemical process occurs on the opposite side. Here-with, there is an additional condition that the area of the "window" on the surface of which the electrochemical process occurs depends on the fraction of intercalating agent grains  $g$ .

The effective surface area of this "window" for each active intercalating agent grain is  $\bar{n}$  times higher than surface area  $L^2$ . Thus, exchange current  $i_0$  on its electrochemical side must be replaced by product  $i_0\bar{n}$  in the model of a planar layer with thickness  $L$ .

## 5. SYSTEM OF EQUATIONS FOR ACTIVE INTERCALATING AGENT GRAIN

According to the above active grain model, we will assume that distribution of reduced concentration  $a = c/c^*$  in the grain corresponds to the following equation:

$$da/dt^{**} = d^2a/dz^2, \quad (19)$$

where reduced coordinate  $z$  in the intercalating agent layer with thickness  $L$  is

$$z = x/L, \quad (20)$$

and the reduced time coordinate takes the form of

$$t^{**} = t/\tau^*, \quad (21)$$

where  $\tau^*$  is the characteristic time determined by the following expression:

$$\tau^* = L^2/D, \quad (22)$$

where  $D$  is the diffusion coefficient of lithium atoms in an intercalating agent grain.

Equation (19) may be written in a form more convenient for full calculations of the working anode characteristics:

$$\alpha da/dt^{**} = d^2a/dz^2, \quad (23)$$

where constant

$$\alpha = \tau^*/\tau = L(LS)i_0/Dg^*Fc^*. \quad (24)$$

Let us write down the initial and boundary conditions for equation (23). We have:

$$a \equiv c_0 \text{ при } t = 0, \quad (25)$$

on the surface of the intercalating agent layer closed for exchange of lithium atoms,

$$da/dz = 0 \text{ at } z = 0, \quad (26)$$

on the surface of an intercalating agent layer contacting with grains of electrolyte (condition of equality of fluxes of lithium atoms and ions):

$$-\chi da/dz = [(1 - a_s)^{1/2} a_s^{1/2}] \{e^\eta - e^{-\eta}\} \text{ at } z = 1, \quad (27)$$

where parameter

$$\chi = FDe^*/L\bar{n}i_0. \quad (28)$$

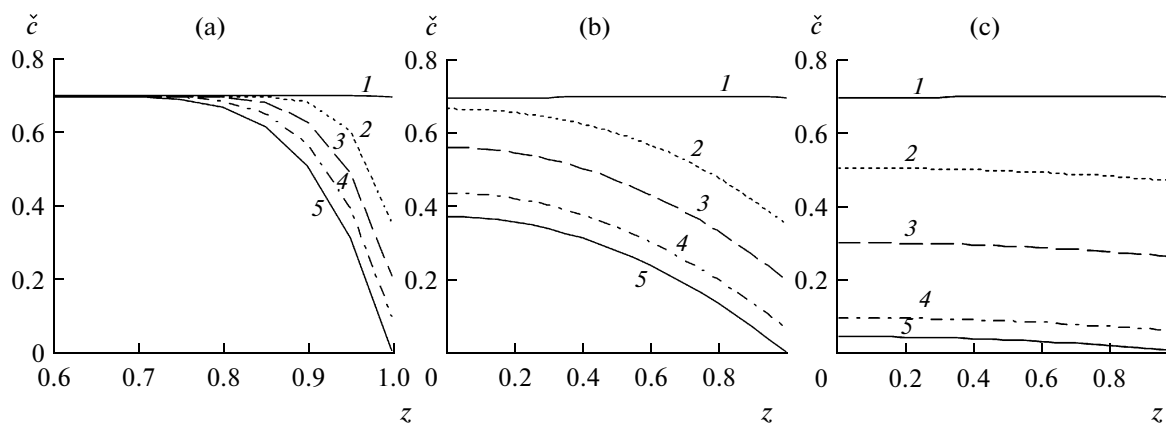
Let us stress the importance of parameter  $\bar{n}$  in the expression for  $\chi$ .

## 6. CHARACTERISTICS OF ANODE WITH THIN ACTIVE LAYER

The nearest problem is to envisage the relationship between the concentration of lithium atoms on the surface of intercalating agent grain  $a_s$  and average concentration of lithium atoms in the whole intercalating agent grain bulk  $\check{c}$ . One must formulate conditions at which equation (17) is true and therefore diffusion limitations in active intercalating agent grains may be assumed negligible.

Let us analyze the functioning of active intercalating agent grains in the simplest form. Let us consider one of the possible specific modes of galvanostatic anode discharge, mode 3 in the terms of work [1]. (Anode Mode with Thin Active Layer). Let us assume that the following criterion is fulfilled:

$$\Delta \ll L_{\text{ohm}} = (2RTk^*k/FSi_0)^{1/2}. \quad (29)$$



**Fig. 1.** Distribution of the lithium atom concentration in an active intercalating agent grain in different time points of anode discharge with a thin active layer (variation of parameter  $L/D$ ). (a)  $\alpha = 0.579$ ,  $B = -7.44$ ;  $t^*$ : (1) 0, (2)  $1 \times 10^{-3}$ , (3)  $2 \times 10^{-3}$ , (4)  $3 \times 10^{-3}$ , (5)  $4 \times 10^{-3}$ . (b)  $\alpha = 0.0579$ ,  $B = -0.744$ ;  $t^*$ : (1) 0, (2)  $1 \times 10^{-2}$ , (3)  $2 \times 10^{-2}$ , (4)  $3 \times 10^{-2}$ , (5)  $3.5 \times 10^{-2}$ . (c)  $\alpha = 0.00579$ ,  $B = -0.0744$ ;  $t^*$ : (1) 0, (2)  $1.6 \times 10^{-2}$ , (3)  $3.2 \times 10^{-2}$ , (4)  $4.8 \times 10^{-2}$ , (5)  $5.2 \times 10^{-2}$ .  $c_0 = 0.7$ .

Anode active layer thickness  $\Delta$  is much lower than the characteristic ohmic length. Then one may assume that the  $\check{c}$  and  $\psi$  values are constant through the active layer depth: all active intercalating agent grains contribute equally to the anode discharge process. In fact, we analyze the functioning of an individual active intercalating agent grain.

According to the data of Table 3, characteristic ohmic length  $L_{\text{ohm}} = 70.35 \mu\text{m}$  under the most favorable conditions of anode operation at  $g = 0.4$ . Therefore, we will assume further to fulfill condition (29) that the anode active layer thickness  $\Delta = 10 \mu\text{m}$ . In view of the data of Table 1, this means that  $\Delta = 2L$ . The anode active material consists of only two layers of the mixture of intercalating agent and electrolyte grains.

The physical meaning of the rightmost part of equation (13) is the value of discharge current  $I$  divided by the anode active layer thickness  $\Delta$ . Current  $I$  is constant, as the galvanostatic mode is considered. Therefore, the following equality is fulfilled:

$$-(g^*Fc^*\Delta/\tau)d\check{c}/dt^* = I = \text{const.} \quad (30)$$

With account for definition (5), we have:

$$-Si_0\Delta d\check{c}/dt^* = I = \text{const.} \quad (31)$$

By integrating (30) and assuming that the initial filling of the intercalating agent grain by lithium atoms in it  $\check{c} = c_0 = 0.7$ , we find that

$$\check{c} = c_0 - (I/Si_0\Delta)t^* = c_0 - It/g^*Fc^*\Delta \quad (32)$$

and the discharge time of an anode with a thin active layer

$$t^{***} = c_0(Si_0\Delta/I)\tau = c_0g^*Fc^*\Delta/I. \quad (33)$$

Let us estimate discharge time value  $t^{***}$ . According to the data of Table 3, characteristic ohmic current  $I_{\text{ohm}} = 1.65 \text{ mA/cm}^2$  at  $g = 0.4$  is several units of

$\text{mA/cm}^2$ . Let us assume further that discharge current density  $I = 3 \text{ mA/cm}^2$ . Therefore,  $t^{***} = 0.7 \times 0.348 \times 9.6510^4 \times 310^{-2} \times 10^{-3}/310^{-3} = 235 \text{ s}$ . Reduced discharge time  $t^{***}/\tau = c_0(Si_0\Delta/I) = 5.45 \times 10^{-2}$ .

In reality, intercalating agent grains may be depleted both fully and partially due to diffusion limitations. Let us show this using results of specific calculations.

With account for equations (13) and (30), we obtain the relationship between  $a_s$  and  $\eta$

$$[(1 - a_s)^{1/2}a_s^{1/2}] \{e^\eta - e^{-\eta}\} = I/Si_0\Delta. \quad (34)$$

Now, boundary condition (27) changes:

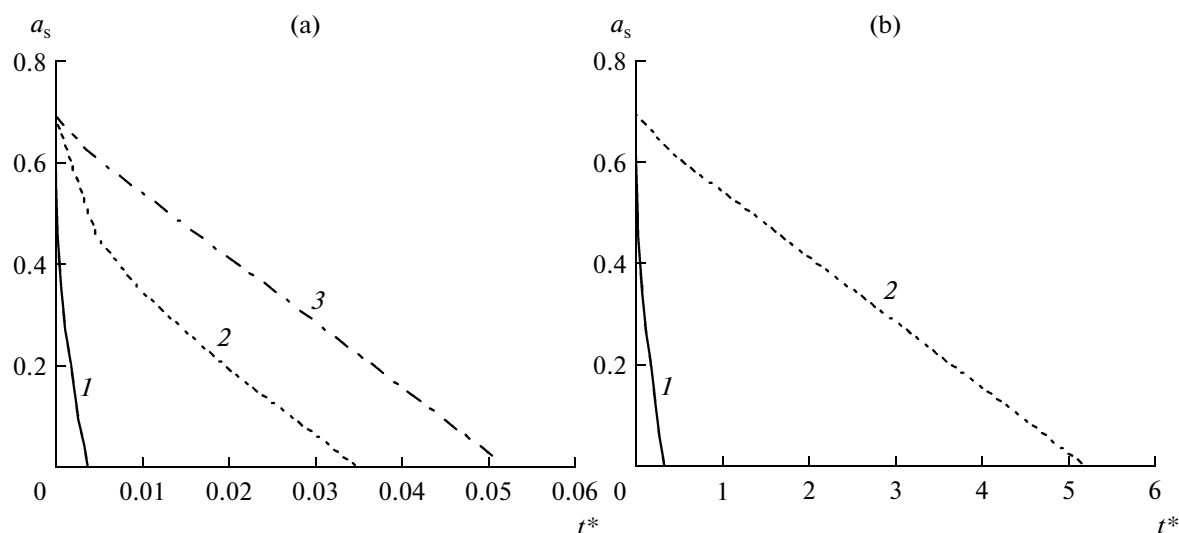
$$da/dz = -I\tilde{n}L/FDc^*S\Delta = B. \quad (35)$$

An analytic solution for equation (23) takes the form of [8, 9]:

$$a(z, t^*) = c_0 + B \left( \frac{t^*}{\alpha} + \frac{3z^2 - 1}{6} \right) + \frac{2}{\pi^2} \sum_{k=1}^{\infty} (-1)^{k+1} \frac{\cos(k\pi z)}{k^2} \exp\left(-\frac{k^2\pi^2 t^*}{\alpha}\right). \quad (36)$$

Let us estimate parameters  $\alpha$  (formula (24)) and  $B$  (formula (35)) in expression (36) and allowing calculating concentration distribution of lithium atoms in an active intercalating agent grain. The result is that if  $g = 0.4$ ,  $L = 5 \times 10^{-4} \text{ cm}$ ,  $SL = 1.167$ ,  $i_0 = 10^{-4} \text{ A/cm}^2$ ,  $D = 10^{-10} \text{ cm}^2/\text{s}$ ,  $g^* = 0.348$ ,  $F = 9.65 \times 10^4 \text{ C/g.-m.}$ ,  $c^* = 3 \times 10^{-2} \text{ g.-m./cm}^3$ , then parameter  $\alpha = 0.579$ ; if  $I = 3 \text{ mA/cm}^2$ ,  $\tilde{n} = 3.35$  (the data of Table 5),  $\Delta = 10^{-3} \text{ cm}$ , then parameter  $B = -7.44$ .

The pattern of distribution of lithium atoms in an intercalating agent grain at  $\alpha = 0.579$  and  $B = -7.44$  is presented in Fig. 1a. It shows the process of depletion of an intercalating agent grain at different time



**Fig. 2.** Variation with time  $t^*$  of the lithium atom concentration on the face (at  $z = 1$ ) of the active intercalating agent grain  $a_s$ . (a) (1)  $\alpha = 0.579$ ,  $B = -7.44$ ; (2)  $\alpha = 0.0579$ ,  $B = -0.744$ , (3)  $\alpha = 0.00579$ ,  $B = -0.0744$ . (b) (1)  $I = 0.3 \text{ mA/cm}^2$ ,  $\alpha = 0.579$ ,  $B = -0.744$ , (2)  $I = 0.03 \text{ mA/cm}^2$ ,  $\alpha = 0.579$  and  $B = -0.0744$ .  $c_0 = 0.7$ .

moments of discharge of an anode with a thin active layer. One can see how the concentration distribution profile for lithium atoms through the grain depth decreases in time. The process of lithium atom recovery from a grain must be over when the concentration at the face intercalating agent grain surface (at  $z = 1$ ) decreases to zero. In Fig. 1a, this moment is reached at  $t^{***}/\tau = 4 \times 10^{-3}$ .

Integration of the rightmost part of formula (36) through the depth of an intercalating agent grain allows finding that volume-average concentration of lithium atoms in an active intercalating agent grain  $\check{c}$  changes in time. It appears that this value may be evaluated using the formula:

$$\check{c} = c_0 + (B/\alpha)t^* = c_0 - (g^* I \tilde{n} / S^2 L \Delta i_0) t^*. \quad (37)$$

Fig. 1a shows for the moment of discharge stop  $\check{c} = 0.7 - (0.744/0.579) \times 410^{-3} = 0.65$ . Thus, only a small fraction of lithium atoms stored in active intercalating agent grains is used in the discharge process.

Obviously, the lower the diffusion coefficient of lithium atoms in active intercalating agent grains  $D$  and the higher the grain size (parameter  $L$ ), the higher the diffusion limitations. Therefore, in order to intensify the process of recovery of lithium atoms from the active intercalating agent grains, it is desirable to decrease the  $L/D$  ratio in expressions for parameters  $\alpha$  and  $B$ . Let us assume that this ratio decreased by an order of magnitude. Let  $\alpha = 0.0579$  and  $B = -0.744$ . The pattern of concentration distribution of lithium atoms in an active intercalating agent grain at different time moments is presented for this case in Fig. 1b. It can be seen that in this case, already a significant

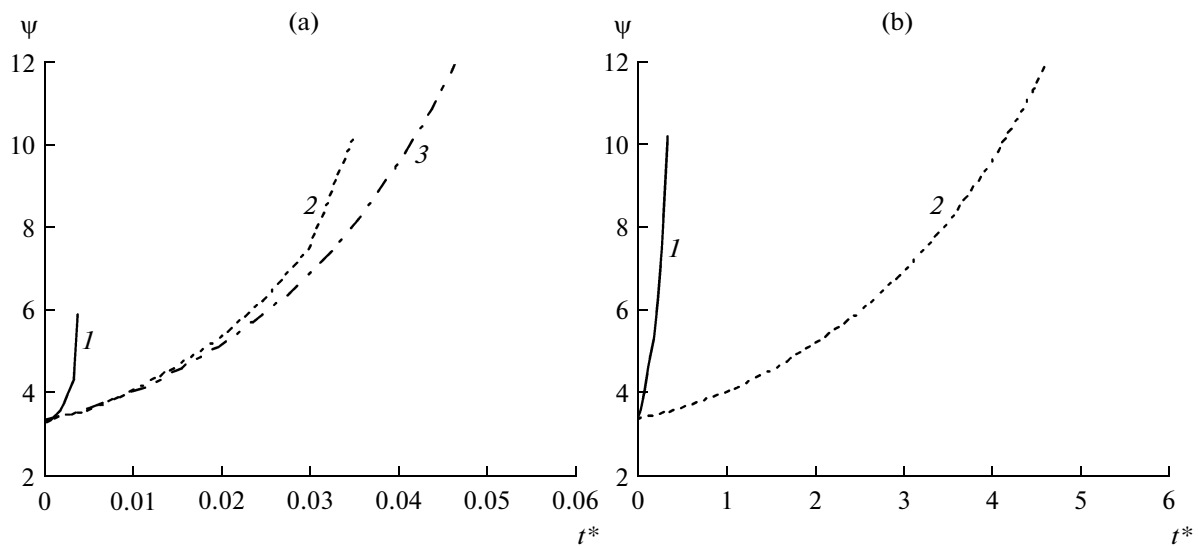
amount of lithium atoms stored in intercalating agent grains is used in the discharge process. Fig. 1b shows for the moment of discharge stop  $\check{c} = 0.7 - (0.744/0.0579) \times 3.510^{-2} = 0.25$ .

One can achieve practically full depletion of an active intercalating agent grain under the anode discharge process, if the  $L/D$  ratio value is decreased by yet another order of magnitude. Let  $\alpha = 0.00579$  and  $B = -0.744$ . Then the pattern of concentration distribution of lithium atoms in an active intercalating agent grain at different time moments is presented for this case in Fig. 1c. This time, an approximately uniform distribution of lithium atom concentration through the grain depth is observed. And Fig. 1c shows for the moment of discharge stop  $\check{c} = 0.7 - (0.744/0.00579) \times 5.2 \times 10^{-2} = 0.03$ . Thus, the content of the intercalating agent grain may be discharged nearly fully.

At a decrease in parameter  $L/D$ , the discharge process duration also increases. If one assumes  $z = 1$  in formula (36), one can determine how the concentration of lithium atoms on the face surface of an active intercalating agent grain  $a_s$  changes in time. Namely,

$$a_s = c_0 + B \left( \frac{t^*}{\alpha} + \frac{1}{3} - \frac{2}{\pi^2} \sum_{k=1}^{\infty} \frac{\exp(-k^2 \pi^2 t^*/\alpha)}{k^2} \right). \quad (38)$$

the dependence of  $a_s$  on  $t^*$  for the three cases just analyzed above is presented in Fig. 2a. The values of parameters  $\alpha$  and  $-B$ : curve 1: 0.579 and 7.44; curve 2: 0.0579 and 0.744; curve 3: 0.00579 and 0.0744. The anode discharge with a thin active layer stops, accordingly, at time moments:  $t^{***}/\tau = 4 \times 10^{-3}$ ,  $3.5 \times 10^{-2}$ ,  $5.2 \times 10^{-2}$ . If parameter  $L/D$  is decreased further, the



**Fig. 3.** Dependence of the anode potential value at the active anode layer/ interelectrode space interface  $\psi$  on time  $t^*$ . (a) (1)  $\alpha = 0.579$ ,  $B = -7.44$ ; (2)  $\alpha = 0.0579$ ,  $B = -0.744$ , (3)  $\alpha = 0.00579$ ,  $B = -0.0744$ . (b) (1)  $I = 0.3$  mA/cm<sup>2</sup>,  $\alpha = 0.579$ ,  $B = -0.744$ , (2)  $I = 0.03$  mA/cm<sup>2</sup>,  $\alpha = 0.579$  and  $B = -0.0744$ .  $I/Si_0\Delta = 12.85$ .  $c_0 = 0.7$ .

full depletion of the intercalating agent grain may be achieved. Such a limiting characteristic discharge time for an anode with a thin active layer is determined by formula (33) and is  $t^{***}/\tau = 5.45 \times 10^{-2}$ .

There is a fundamental difference between formulas (32) and (37). Formula (32) assumes full depletion of the intercalating agent active grain, while formula (37), together with condition (38) allowing determining the time when recovery of lithium atoms from the active grain stops implies only partial depletion of the intercalation agent grain.

Let us see now how the reduced difference in the intercalating agent/electrolyte potentials at the active anode layer/interelectrode space interface  $\psi$  changes in time. Let us solve equation (34) for reduced polarization  $\eta$ .

$$\eta = \operatorname{arcsinh}\left(\frac{I}{2Si_0\Delta\sqrt{(1-a_s)a_s}}\right). \quad (39)$$

With account for relationships (8), (9), and (37), we finally obtain the expression for reduced potential  $\psi$  in a thin anode active layer under partial depletion of active intercalating agent grains

$$\psi = \operatorname{arcsinh}\left(\frac{I}{2Si_0\Delta\sqrt{(1-a_s)a_s}}\right) + \frac{1.32 \exp\left[-3\left\{c_0 + \frac{B}{\alpha}t^*\right\}\right] - 0.16}{2RT/F}. \quad (40)$$

There is yet another parameter of the problem in formula (40):  $I/Si_0\Delta$ . It is  $IL/SLi_0\Delta = 3 \times 10^{-3} \times 5 \times 10^{-4}/1.167 \times 10^{-4} \times 10^{-3} = 12.85$ . The calculation

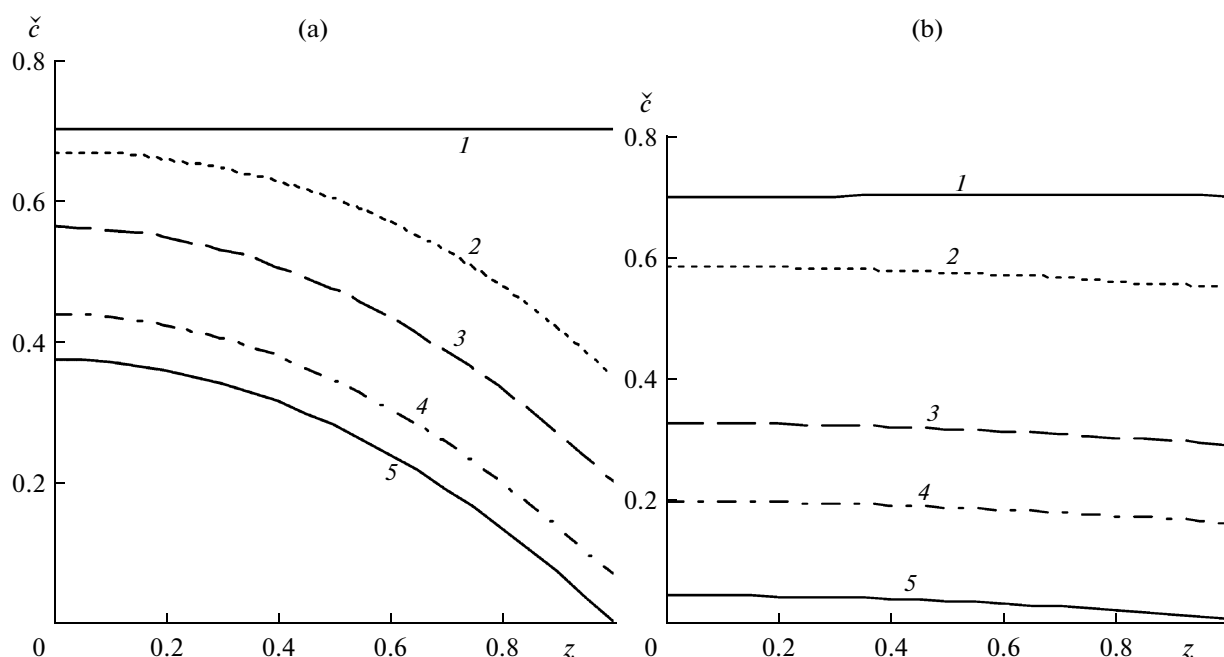
result for the dependence of  $\psi$  on  $t^*$  is presented in Fig. 3a. The difference in potentials ( $2RT/F$ )  $\psi$  ranges one Volt.

Not only the value of parameter  $L/D$  is important for discussion as to whether active intercalating agent grains are fully or partially depleted of lithium atoms. Let us start decreasing anode discharge current  $I$  entering the expression for parameter  $B$  (formula (35)) fixing the value of parameter  $L/D$ .

Let us consistently replace the earlier chosen current value  $I = 3$  mA/cm<sup>2</sup> first to  $I = 0.3$  mA/cm<sup>2</sup> and then to  $I = 0.03$  mA/cm<sup>2</sup>. The pattern of the decrease in time of the amount of lithium atoms in the intercalating agent grains for these two cases (with parameters  $I = 0.3$  mA/cm<sup>2</sup>,  $\alpha = 0.579$ ,  $B = -0.744$  and parameters  $I = 0.03$  mA/cm<sup>2</sup>,  $\alpha = 0.579$  and  $B = -0.0744$ ) is presented in Fig. 4. And if only 0.25 of the grain volume filled by lithium atoms remains in the grain under current  $I = 0.3$  mA/cm<sup>2</sup> (Fig. 4a), then the grain volume filled by lithium atoms decreases to 0.03 under current  $I = 0.03$  mA/cm<sup>2</sup> in the grain at the moment of discharge stop (Fig. 4b).

The discharge time also increases fast at a decrease in the discharge current value (Fig. 2b). It grows from  $t^* = 0.35$  at current  $I = 0.3$  mA/cm<sup>2</sup> to  $t^* = 5.2$  at current  $I = 0.03$  mA/cm<sup>2</sup>. Herewith, a smoother increase in time in the value of reduced difference in intercalating agent/electrolyte potentials at the active anode layer/interelectrode space interface  $\psi$  occurs (curves 1 and 2 in Fig. 3b).

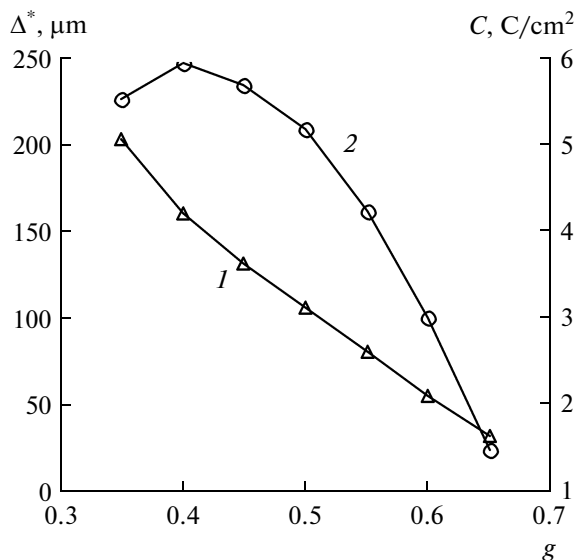




**Fig. 4.** Distribution of the lithium atom concentration in an active intercalating agent grain in different time points of anode discharge with a thin active layer (variation of discharge current density value  $I$ ). (a)  $I = 0.3 \text{ mA/cm}^2$ ,  $\alpha = 0.579$ ,  $B = -0.744$ ;  $t^*$ : (1) 0, (2) 0.1, (3) 0.2, (4) 0.3, (5) 0.35. (b)  $I = 0.03 \text{ mA/cm}^2$ ,  $\alpha = 0.579$ , and  $B = -0.0744$ ;  $t^*$ : (1) 0, (2) 1, (3) 3, (4) 4, (5) 5.2.  $c_0 = 0.7$ .

## 7. CALCULATION OF ANODE WORKING PARAMETERS (COMPLETE ABSENCE OF ACTIVE GRAINS)

Thus, in the case of the lithium-ion battery in the studied anode for which the initial active material parameters are presented in Table 1, one can achieve



**Fig. 5.** Dependence of the working parameters of the anode on the bulk concentration of intercalating agent grains in the active layer: (1) active layer thickness, (2) specific electric capacitance.  $I = 0.01 \text{ mA/cm}^2$ .

practically full recovery of lithium atoms from the intercalating agent grains under discharge can be achieved using two methods. Either the grain edge length is decreased to nanosize, when the anode active material with the grains with  $L = 5 \times 10^{-6} \text{ cm} = 50 \text{ nm}$  and below is used instead of  $L = 5 \times 10^{-4} \text{ cm}$  (Table 1). Or the discharge current value is consistently used: instead of the initially chosen current of  $I = 3 \text{ mA/cm}^2$ , the currents of  $I = 0.03 \text{ mA/cm}^2$  and below are used.

Let us choose the second method. And in order to obtain with confidence 100% of lithium atom recovery from the intercalating agent grain under anode discharge, let us decrease the discharge current value even further down to the value of  $I = 0.01 \text{ mA/cm}^2$ . In this case, one may already use the system of equations of (10) and (13), for which equality (17) is true to calculate the working anode parameters.

The results of calculation of the working anode parameters under the discharge current value of  $I = 0.01 \text{ mA/cm}^2$  are presented in Fig. 5 and in Table 6, namely, the dependence on the bulk intercalating agent concentration of the active layer of the lithium-ion battery anode is presented for the four parameters: anode active layer depth  $\Delta^*$  (curve 1 in Fig. 5), anode full discharge time  $t^{****}$ , specific electric capacitance  $C$  (curve 2 in Fig. 5), and finite difference of the electrolyte/intercalating agent potentials at the anode active layer/interelectrode space interface  $E^*$ .

As already pointed out above (approximate estimates of the anode working parameters performed in section 2, the data of Table 4), the anode working

parameters reach optimum values at the concentration of intercalating agent grain of  $g = g_{\text{opt}} = 0.4$ . Such an anode has the optimum thickness of  $\Delta^* = 160 \mu\text{m}$ , discharge time  $t^{****} = 5.95 \times 10^5 \text{ s}$ , specific capacitance of  $5.94 \text{ C/cm}^2$ , finite anode potential at the anode active layer/interelectrode space interface ( $E^*$ ) = 1.12 V.

## 8. CONCLUSIONS

Intercalating agent grains in the anode active material fall into two classes: active and inactive. The former can take part in the electrochemical process, while the latter cannot. The paper presents calculations of the amount of active intercalating agent grains in the anode active material.

Special attention in this research was paid to estimation of the value of diffusion limitations appearing after extraction of lithium atoms from an active intercalating agent grain which are related to the smallness of the diffusion coefficient of lithium atoms  $D$ , which results in incomplete consumption of lithium atoms stored in the active grain. It was shown that the universally accepted model of a spherical intercalating agent grain, its external surface participating in the electrochemical process, deviates from the actual situation in the terms of the studied anode active layer model. It was calculated using the model of equal-sized cubic grains how the average number of electrochemically active faces of active intercalating agent grains  $\tilde{n}$  is changed under variation of the intercalating agent grain fraction in the active material. Variation of the bulk concentration of intercalating agent grains  $g$  in the range of  $0.65 \geq g \geq 0.35$  results in variation of parameter  $\tilde{n}$  in the range of 1.91 to 3.55.

A new model of depletion is suggested for an active intercalating agent grain. The diffusion process of lithium atom extraction from the grain is assumed to be one-dimensional, so that the character of lithium atom concentration distribution in an intercalating agent grain can be calculated using simple enough formulas.

The process of active intercalating agent grain depletion may lead to two results: either lithium atoms remain in the grain or the grain is completely free of them. The second variant is naturally more attractive from the practical viewpoint. It may be implemented in the case when the intercalating agent grains either have rather small dimensions  $L$ , more specifically, if the  $L/D$  ratio is low, or if the anode discharge current density  $I$  is sufficiently low.

It was shown that the amount of unused lithium atoms in an active intercalating agent grain falls at a decrease in parameters  $L/D$  and  $I$ .

Under the condition of full depletion of active intercalating agent grains, working parameters of the lithium-ion battery anode were calculated: anode active layer thickness  $\Delta^*$ , anode full discharge time

**Table 6.** Dependence of the working anode parameters on the bulk concentration of intercalating agent grains  $g$ . Discharge current density  $I = 0.01 \text{ mA/cm}^2$

$g$	$\Delta^*, \mu\text{m}$	$t^{****} \times 10^{-5}, \text{s}$	$C, \text{C/cm}^2$	$E^*, \text{V}$
0.35	203	5.53	5.53	1.12
0.40	160	5.94	5.94	1.12
0.45	131	5.69	5.69	1.12
0.50	106	5.17	5.17	1.12
0.55	81	4.23	4.23	1.12
0.60	55	3.01	3.01	1.12
0.65	31	1.48	1.48	1.12

$t^{****}$ , specific electric capacitance  $C$ , and finite potential at the anode active layer/interelectrode interface  $E^*$ .

It was shown that the optimum bulk concentration of intercalating agent grains is  $g = 0.40$ . Then the anode is characterized by the following parameters at the discharge current density of  $I = 0.01 \text{ mA/cm}^2$  (under full depletion of active intercalating agent grains):  $\Delta^* = 160 \mu\text{m}$ ,  $t^{****} = 5.94 \times 10^5 \text{ s}$ ,  $C = 5.94 \text{ C/cm}^2$ ,  $E^* = 1.12 \text{ V}$ .

## DESIGNATIONS FOR PARAMETERS OF ANODE ACTIVE LAYER OF LITHIUM-ION BATTERY

### External Parameters

$t$  is the current discharge time of the anode  
 $t^* = t/\tau$  is the reduced discharge time of the anode  
 $t^{**}$  is the reduced characteristic time of the extraction process of lithium atoms from an intercalating agent grain  
 $t^{***}$  is the discharge time of the anode active grain  
 $t^{****}$  is the anode discharge time after full depletion of its active grains  
 $\tau$  is the characteristic discharge time of the anode  
 $\tau^*$  is the characteristic time of the extraction process of lithium atoms from an intercalating agent grain  
 $C, \text{C/cm}^2$ , is the specific electric capacitance of the anode  
 $R$  is the gas constant  
 $T = 293 \text{ K}$  is the working temperature of the anode  
 $\Delta$  is the thickness of the anode active layer  
 $\Delta^*$  is the optimum active layer thickness

### Parameters of the Electrochemical Kinetics of the Process of Oxygen Reduction on Platinum

$F = 9.65 \times 10^4 \text{ C/mol}$  is the Faraday number  
 $I, \text{A/cm}^2$  is the anode discharge current  
 $j, \text{A/cm}^2$  is the current density of the electrochemical reaction  
 $i_0$  is the exchange current

$\eta$  is the reduced polarization

$\psi$  is the reduced anode potential

$E$  is the anode potential

$E^*$  is the finite anode potential at the active layer/interelectrode space interface

$U$  is the open circuit potential of the lithium–ion battery

$L_{\text{ohm}}$ , cm, is the characteristic ohmic length

$I_{\text{ohm}}$ , A/cm<sup>2</sup>, is the characteristic ohmic current

$y$  is the coordinate of the anode active layer

$\hat{y} = y/L_{\text{ohm}}$  is the reduced coordinate in the anode active layer

#### *Structure Parameters of the Active Layer and Active Intercalating Agent Grain*

$g$  is the bulk concentration (fraction) of intercalating agent grains

$g^*$  ( $g^* < g$ ) is the fraction of intercalating agent active grains

$g_i$  is the bulk concentration (fraction) of grains of electrolyte

$L$  is the average diameter of grains of intercalating agent and electrolyte

$S$ , cm<sup>-1</sup>, is the specific contact surface area between electron and ion percolation clusters

$\check{c}$  is the concentration of lithium atoms averaged by the intercalating agent grain volume

$c^*$  is the maximum possible concentration of lithium atoms in an intercalating agent grain

$\check{c} = c/c^*$  is the reduced concentration of lithium atoms averaged by the intercalating agent grain volume

$\check{c} = c_0$  is the initial degree of filling of intercalating agent by lithium atoms

#### *Parameters Determining the Diffusion Process in the Active Intercalating Agent Grain*

$a$  is the reduced concentration of lithium atoms in an active intercalating agent grain

$a_s$  is the reduced concentration of lithium on the intercalating agent grain surface

$z = x/L$  is the reduced coordinate in an active intercalating agent grain

$\alpha = \tau^*/\tau$  is the constant determining the extraction mode of lithium atoms from an intercalating agent grain

$B$  is the constant determining the extraction mode of lithium atoms from an intercalating agent grain

$\chi$  is the parameter determining the extraction mode of lithium atoms from an intercalating agent grain

#### *Parameters Determining the Processes of Material and Electric Transfer*

$D$  is the diffusion coefficient of lithium atoms in intercalating agent grains

$k$  is the specific conductivity of electrolyte

$k^*$  is the specific conductivity of lithium ions in the percolation ion cluster in the active cathode layer

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