

Computer Simulation of the Negative Electrode Operation in Lithium Ion Battery: Galvanostatics, the Problem of Calculating Working Parameters

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Abstract—The work of the negative electrode (anode) of a lithium-ion battery operating in the galvanostatic discharge mode is simulated. Attention was focused on formulating the complete mathematical description of processes occurring on the anode. The most serious complication is associated with taking into account the diffusion limitation arising at the extraction of lithium atoms from grains of the active substance (intercalating agent). The analytical relationship is found between the average lithium concentration in the intercalator grain and the lithium concentration on the contact surface between the intercalator grains and the electrolyte grains. Algorithms of computer-assisted calculations are developed that allow the anode characteristics to be found. The following anode working parameters are determined: the active layer thickness, the complete discharge time, the specific electric capacity, and the final potential at the active layer/inter-electrode space boundary. Calculations of the working parameters are carried out in the following two versions: for anodes with a thin active layer (imitation of processes occurring in an individual intercalator grain) and for anodes with the active layer of the optimal thickness. The procedure of selecting the reasonable discharge current, i.e., its maximum value at which virtually all lithium atoms can be removed from the active intercalator grain, is shown.

Keywords: lithium-ion rechargeable battery, negative electrode (anode), galvanostatic discharge mode, computer stimulations, model of isometric cubic grains of two types, anode with a thin active layer, anode with the active layer of the optimal thickness, active intercalator grains, problem of diffusion limitations

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1. FORMULATION OF THE PROBLEM

The studies on the development of efficient and economically acceptable versions of lithium-ion batteries (LIB) were carried out for two decades. Attempts to describe theoretically the operation of such systems were made in the early 1990s in the pioneering studies [1, 2]. This direction of theoretical investigations was taken up by several scientists and, on the whole, can be characterized as the “mathematical simulation” of lithium-ion batteries. This approach involves the following three parts: (1) writing a system of equation to describe the operation of LIB electrodes, (2) computations according to this system of equations, and (3) the discussion of the obtained solutions.

Unfortunately, in the process, a large number of questions on the nature of processes that occur in the LIB electrodes remain open. For example, the following questions can be posed.

(1) What should we take as the theoretical optimal volume concentration of active substance grains (intercalator grains) in the anode active layer?

(2) What optimal set of the volume concentrations of components should the cathode active layer (three-component system) include?

(3) What size (the degree of dispersion of the active mass) should the active substance grains have?

(4) In the active mass of electrodes, not every intercalator grain can be supplied with electrons and ions. Hence, the intercalator grains should be divided into the following two classes: active (that can take part in the electrochemical process) and passive. The fraction of electrochemically active intercalator grains must be found.

This list of questions can be continued. Obviously, these questions cannot be solved within the framework of “mathematic models” only. This is why here we pass to a new direction we have proposed for studying the lithium-ion batteries, namely, the “computer simulations” of active layers of LIB electrodes, i.e., to com-

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puter-assisted studies of the structural and functional characteristics of models of active layers of electrodes.

Moreover, the “computer simulations” of LIB electrodes should include three consecutive preliminary research stages. First of all (the first stage of computer simulations), the model of the electrode active layer should be formulated. The electrode active mass (for the anode) is the sum of active substance (intercalator) micrograins and electrolyte (e.g., polymer) micrograins, bound together with a small fraction of the binding agent. These micrograins (below referred to as grains) are of different shapes and size distributions but in the first approximation can be characterized by a certain average size. The latter value will be the main measure of the degree of dispersion of components of the electrode active mass. Thus, the “model of isometric grains” emerges.

Now, the shape of grains should be discussed. Usually it is believed that intercalator grains represent spheres. However, the sphere models cannot be used for the active layer, because any packing of spheres has voids (intersphere gaps), whereas according to the conventional technology of preparation of the active mass for LIB electrodes, the porosity should apparently be close to zero. Second, according to the model of spheres, the contact surface between the intercalator grains and the electrolyte grains on which the electrochemical process occurs apparently represents the sum of surfaces of geometrical points. Hence, the real contact surface is zero.

In light of aforementioned, for characterization of the active layer, the proposed model of isometric cubic grains should be preferred over the model of isometric spheres. The packing of cubes has zero porosity and a considerable (non-zero) surface on which the electrochemical process can occur.

The grain size is on the micron level, the active layer thickness is on the level of hundreds of microns. Therefore, the studied model cube that imitates the electrode (anode) active layer should be sufficiently large. Its volume must comprise $100 \times 100 \times 100 = 10^6$ grains. It is impossible to study the structural properties of this cube without using a computer; hence, the new method is called the “computer simulations”.

In the model cube, the so-called percolation clusters arise [3, 4]. They provide the delivery of electrons (along the electronic percolation cluster that involves intercalator grains) and ions (along the ionic percolation cluster that consists of electrolyte grains) throughout the electrode active layer. This is why studying the percolation problems forms the second stage of computer simulations.

Besides the computer-assisted studies of the percolation properties of the model of isometric cubic grains, the calculations (the third stage of computer simulation) of the effective coefficients of electro and mass transfer (electronic and ionic conductivity, diffusion coefficient, etc.) that enter the equations describ-

ing the processes in the electrode active layers should be carried out.

The computer simulations of the operation of the LIB negative electrode (anode) were already carried out in our earlier studies [4, 5]. There, the model of isometric cubic grains of two types, namely, intercalator grains and electrolyte grains, was studied as follows.

Neglecting the presence of the binding agent, we had the evident condition

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

where g is the volume fraction of the anode active layer accounted for the intercalator (e.g., graphite) grains, g_i is the active layer fraction accounted for electrolyte.

It was assumed that all intercalator and electrolyte grains were the same and represented microcubes with the edge length L . Thus, by carrying out the percolation computations in terms of the isometric grain model, we dealt with the cubic lattice of points [3].

The ionic and electronic percolation clusters are formed upon reaching the percolation threshold if the volume concentrations of the corresponding grains have reached a certain value, g^* or g_i^* . In the cubic lattice of points we study, the percolation threshold was found to be equal to $g^* = g_i^* = 0.298$ [6]. However, as was demonstrated in [7], the properly operating percolation clusters appeared later, i.e., for $g \geq 0.35$ and $g_i \geq 0.35$. Thus, taking into account condition (1), the region of reasonable values of parameter g (the concentration of intercalator grains) for which the anode discharge is possible confines within

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

Not every intercalator grain is capable of taking part in the electrochemical process. As was mentioned above, the intercalator grains are divided into the active grains with the concentration g^* ($g^* < g$) and passive grains with the concentration $g - g^*$. A grain can be called active if it contacts the electronic percolation cluster with at least one of its facets. Obviously, for an intercalator active grain, the maximum number of facets in contact with an ionic percolation cluster is 5. The 6th facet is necessary for the grain contact with the electronic percolation cluster.

Everything mentioned above forms the basis that allows us to pass to the final goal of our studies, the calculations of optimal working parameters of the LIB anode, i.e., the estimation of the anode active layer thickness, its discharge time, its specific capacity, and the final potential at the active layer/interelectrode space interface.

Here, the central problem of the LIB theory arises. This problem is not concerned with writing the system of equation (this is easy) but with solving this system. The difficulty lies in the fact that two simultaneous interrelated processes occur in both the space and the time, namely, the depletion of intercalator grains

(at the anode discharge), i.e., the diffusional removal of lithium atoms, and the redistribution of the anode potential along the active layer thickness, i.e., the process associated with ohmic complications. The more detailed discussion of the arising problems is shown below.

2. SYSTEM OF EQUATIONS FOR THE ANODE ACTIVE LAYER

In the initial moment ($t = 0$), all intercalator grains are filled with lithium atoms up to the concentration c_0 and then, at the anode discharge, the concentration of lithium atoms decreases. The average lithium concentration in intercalator grains $\check{c} = c/c^*$, where c^* is the maximum possible concentration.

The current density j generated at the contact of the ionic and electronic percolation clusters is as follows:

$$j = i_0[(1 - a_s)^{1/2} a_s^{1/2}] \{e^\eta - e^{-\eta}\}, \quad (3)$$

where a_s is the reduced value of the concentration of lithium atoms on in intercalator active grains at their surface in contact with electrolyte grains, i_0 is the exchange current, η is the reduced value of polarization

$$\eta = F[E - U]/2RT, \quad (4)$$

where E is the anode potential. At open circuit, the anode potential

$$U = -0.16 + 1.32 \exp(-3\check{c}). \quad (5)$$

Below, we assume that the lithium ion concentration in intercalator active grains is confined within $0.0 < \check{c} < c_0 = 0.7$ [8].

Based on the law of conservation of lithium ion flows in electrolyte, we can obtain the equation for the polarization η in the anode active layer

$$d^2 \eta / d\hat{y}^2 = [(1 - a_s)^{1/2} a_s^{1/2}] \{e^\eta - e^{-\eta}\}, \quad (6)$$

where $\hat{y} = y/L_{\text{ohm}}$ is the reduced coordinate, L_{ohm} is the characteristic ohmic length

$$L_{\text{ohm}} = (2RTk^*k/FSi_0)^{1/2}, \quad (7)$$

k is the specific conductivity of electrolyte, k^* is the conductivity of lithium ions in the percolation ionic cluster (dimensionless value), S is the specific surface of the contact between the electronic and ionic percolation clusters. For the galvanostatic discharge mode, the boundary conditions for equation (6) are as follows:

$$(-I_{\text{ohm}})d\eta/d\hat{y} = I = \text{const} \quad \text{for } y = 0, \quad (8)$$

$$d\eta/d\hat{y} = 0 \quad \text{for } y = \Delta, \quad (9)$$

where Δ is the anode active layer thickness, I is the discharge current density; the characteristic ohmic current

$$I_{\text{ohm}} = (2RTk^*kSi_0/F)^{1/2}. \quad (10)$$

The process of extraction of lithium ions from the intercalator grains is described by the following equation:

$$d\check{c}/dt^{**} = -[(1 - a_s)^{1/2} a_s^{1/2}] \{e^\eta - e^{-\eta}\}, \quad (11)$$

where $\check{c}(y, t)$ is the active-layer-volume-averaged concentration of lithium atoms at time t in the anode active layer section with coordinate y . The shown current value of the discharge time t^{**} is as follows:

$$t^{**} = t/\tau, \quad (12)$$

where τ , the characteristic discharge time, is determined as follows

$$\tau = g^*Fc^*/Si_0. \quad (13)$$

The initial condition for Eq. (11) is

$$\check{c} = c_0 \quad \text{for } t = 0. \quad (14)$$

Thus, it would seem obvious that the set of Eqs. (6) and (11) allows one to follow the polarization variations in time and in every point of the anode active layer

$$\psi = FE/2RT, \quad (15)$$

and also the variations of the lithium atom concentration \check{c} averaged over the volume of intercalator active grains.

However, this can be done only if we know the lithium ions concentration on the surface of intercalator active grains a_s that enters the right parts of Eqs. (6) and (11). Thus, the system of Eqs. (6) and (11) is incomplete. The relationship between a_s and \check{c} must be found. Here, a necessity arises to consider the problem of diffusion limitations that appear when lithium atoms are extracted from the intercalator active grain.

3. INTERCALATOR ACTIVE GRAIN

The intercalator grain was usually represented as a sphere surrounded on all sides with electrolyte. It was assumed that, first, any intercalator grain can take part in the electrochemical process (the grains are not divided into active and passive) and, second, the whole spherical surface of the intercalator grain is electrochemically active.

However, it was shown [5] that in the model of isometric cubic grains of two type, (the LIB anode), only a part of the external surface of active intercalator grains contributes into the electrochemical process. Moreover, the electrochemically active areas are distributed in an intricate fashion over the active grain surface.

A simplified model of the intercalator active grain structure and also of the process of diffusion removal of lithium atoms during the discharge was proposed [5]. It was shown that the real process of diffusion of lithium atoms is quasi-one-dimensional rather than three-dimensional. This occurs because the process of lithium atom removal from the intercalator active grain turns out to be similar to a process of lithium atoms diffusion in a flat layer with the thickness L . This can be observed if one of the surfaces of this layer is closed for the exchange so that the electrochemical process of lithium atom conversion to lithium ion occurs on the opposite side.

According to the model of the intercalator active grain, the distribution of the reduced concentration $a = c/c^*$ along the x coordinate in the active layer obeys the equation

$$da/dt^* = d^2a/dz^2, \quad (16)$$

where the reduced coordinate z in the intercalator layer with thickness L

$$z = x/L, \quad (17)$$

and the current value of the reduced time has the form

$$t^* = t/\tau^*, \quad (18)$$

where τ^* is the characteristic time determined by the expression

$$\tau^* = L^2/D, \quad (19)$$

where D is the diffusion coefficient of lithium atoms in the intercalator grain.

Let us list the initial and boundary conditions for Eq. (16). We have

$$\dot{c} \equiv c_0 \quad \text{for } t = 0, \quad (20)$$

on the intercalate layer surface closed for exchange

$$da/dz = 0 \quad \text{for } z = 0, \quad (21)$$

on the intercalate layer surface in contact with electrolyte grains (the conditions of equality of flows of lithium atoms and ions),

$$da/dz = -\lambda[(1 - a_s)^{1/2} a_s^{1/2}] \{e^\eta - e^{-\eta}\} = B, \quad (22)$$

for $z = 1$,

where parameter

$$\lambda = L\tilde{n}i_0/FDc^* = (\tilde{n}i_0/Fc^*)(L/D). \quad (23)$$

The significance of the presence of the parameter \tilde{n} in the expression for λ should be stressed. This parameter means the average number of electrochemically active facets in the active intercalator grains. According to calculations [5], \tilde{n} varies from 3.55 facets for $g = 0.35$ to 1.91 facets for $g = 0.65$.

The analytical solution of Eq. (16) with boundary conditions (21) and (22) has the following form:

$$a(z, t^*) = c_0 + B \left(t^* + \frac{3z^2 - 1}{6} + \frac{2}{\pi^2} \right. \\ \left. \times \sum_{k=1}^{\infty} (-1)^{k+1} \frac{\cos(k\pi z)}{k^2} \exp(-k^2 \pi^2 t^*) \right). \quad (24)$$

4. SOLVING THE PROBLEM OF ESTIMATION OF ANODE WORKING PARAMETERS

As mentioned above, the difficulty of estimating the anode working parameters lied in the fact that two interrelated processes occur simultaneously in space and in time. The discharge of a lithium-ion battery is accompanied by the depletion of intercalator grains (the decrease in the lithium atom concentration), while the restructuring of the anode potential distribution along the active layer thickness is associated with the ohmic limitations with respect to the transport of lithium ions in the electrolyte. Each of these processes is characterized by its own characteristic time.

The characteristic time of restructuring of the potential distribution τ is determined by Eq. (13) and the characteristic time of diffusion removal of lithium atoms from an intercalator grain τ^* is determined by condition (19).

Let us compare these times. Let us introduce a parameter

$$\alpha = \tau^*/\tau = L^2 Si_0 / Dg^* Fc^* = (LSi_0/g^* Fc^*)(L/D). \quad (25)$$

Below, the anode active mass is assumed to be characterized by the following parameters: $k = 10^{-3} \Omega^{-1} \text{ cm}^{-1}$, $i_0 = 10^{-4} \text{ A/cm}^2$, $L = 10^{-4} \text{ cm}$, $c^* = 3 \times 10^{-2} \text{ g-mol/cm}$, $D = 10^{-10} \text{ cm}^2/\text{s}$.

In [5], the problem of selecting the optimum value g_{opt} for the fraction of intercalator grains in the anode active layer, i.e., such a value of parameter g for which the specific anode capacity could reach its maximum. It was found that the optimal fraction of intercalator grains should not coincide with its maximum permissible value $g = 0.65$ (condition (2)) but be smaller $g = g_{\text{opt}} = 0.4$. The latter value corresponds to a fraction of intercalator active grains $g^* = 0.348$, the reduced specific surface of the contact between the electronic and ionic percolation clusters on which the electrochemical reaction occurs $SL = 1.167$, and the specific conductivity of lithium ions in the percolation ionic cluster $k^* = 0.231$.

All these data will be used in the further estimations and calculations of the anode working parameters. First of all, let us assess the parameter α . For $g = g_{\text{opt}} = 0.4$, we have $\alpha = 0.116$.

A general assumption can be made. Thus, insofar as the factor on the right side of relationship (25) $(LSi_0/g^* Fc^*) = 10^{-7} \text{ cm/s}$ and the parameter α should

be at least $\alpha \leq 0.1$, we can assume that the inequality $L/D \leq 10^6$ is true for those anodes for which the characteristic times τ^* and τ are related as $\tau^* \ll \tau$. It also deserves mention that with the decrease in the grain size L , for L tending to nanosizes (Eq. (25)), the parameter α continues to decrease.

Thus, we assume that there is a sufficiently large region of grain sizes L and diffusion coefficients D in which the following inequality is fulfilled

$$\alpha \ll 1. \quad (26)$$

From the physical viewpoint, this expression means the following: the diffusion process in an active intercalator grain is fast while the process of potential variation in the anode active layer (Eq. (6)) is slow. Let us use this fact. We will solve the posed problem in two steps. First, let us solve Eq. (16) with boundary conditions (21) and (22). Let us find the relationship between \check{c} and a_s and then pass to calculations with the system of equations (6) and (11).

It is reasonable to assume that if condition (26) is true, the current density j changes slowly as compared with diffusion in an active grain; hence, the parameter B in boundary condition (22) can be assumed as constant. In an intercalator grain, the distribution (24) is observed. By integrating the left side of Eq. (24) throughout the intercalator layer thickness, we can find how the volume-averaged concentration of lithium ions in the active grain \check{c} varies in time. The latter relationship can be found according to the following formula:

$$\check{c} = c_0 + Bt^*. \quad (27)$$

If in Eq. (24) we take $z = 1$, then the time variations of the lithium atom concentration on the front-face (in contact with the electrolyte) of the intercalator active grain a_s can be found as follows:

$$a_s = c_0 + B \left(t^* + \frac{1}{3} - \frac{2}{\pi^2} \sum_{k=1}^{\infty} \frac{\exp(-k^2 \pi^2 t^*)}{k^2} \right). \quad (28)$$

Now we consider more closely Eq. (28). Let us consider the case of $\alpha \ll 1$. As we pass to calculations according to the system of Eqs. (6) and (11), the fast diffusion processes in the active intercalator grain characterized by the time of the order of magnitude of τ^* give way to the slow processes characterized by the times of the order of magnitude of τ . The reduced time t^* in Eq. (28) becomes very large $t^* \sim \tau/\tau^* = 1/\alpha \gg 1$. Therefore, we can neglect the last term in Eq. (28) (the term containing exponents) as compared with the sum $(t^* + 1/3)$. The whole sum of exponents in Eq. (28) virtually vanishes; moreover, the sooner the smaller the parameter α .

Now we subtract equality (28) (without exponents) from equality (27) to obtain

$$\check{c} = a_s - B/3. \quad (29)$$

Taking into account the definition of B (22), we finally have

$$\check{c} = a_s + (\lambda/3)[(1 - a_s)^{1/2} a_s^{1/2}] \{e^\eta - e^{-\eta}\}. \quad (30)$$

Thus, we have obtained an important result. The problem of calculating the anode working parameters can be solved for anodes with the fulfilled criterion $\alpha \ll 1$ or, which is the same, the fulfilled inequality $(L/D) \leq 10^6$. The problem of finding the distributions of the lithium atom concentration \check{c} and the reduced polarization η throughout the active layer thickness is reduced to finding the joint solution of Eqs. (6) and (11) supplemented with condition (30).

It is also expedient to assess the parameter λ . Assuming that for $g = g_{\text{opt}} = 0.4a\bar{n} = 3.35$ [5], we find that $\lambda = 0.116$. Thus, we have an additional small parameter λ . The latter, like parameter α , decreases linearly with the changes in the grain size L (Eq. (23)). It is the smallness of parameter λ that allowed the calculations of the system of Eqs. (6) and (11) to be carried out in [5] under the assumption that the following equality is fulfilled in place of condition (30):

$$\check{c} = a_s. \quad (31)$$

5. WORKING PARAMETER OF THE ANODE WITH A THIN ACTIVE LAYER

First of all, we study the operation of intercalator active grains for the simplest operation mode, i.e., the anode discharge. Let us consider an anode with a very thin active layer [4]. It is assumed that the following criterion is fulfilled:

$$\Delta \ll L_{\text{ohm}} = (2RTk^*k/FSi_0)^{1/2}. \quad (32)$$

For the anode active layer thickness Δ much lower than the characteristic ohmic length, the values \check{c} and ψ are constant along the active layer thickness, namely, all intercalator active grains make equal contributions to the anode discharge process. In fact, it is possible to analyze the operation of an individual active grain of the intercalator.

According to [5], the most favorable conditions of anode operation are as follows: $g = 0.4 L_{\text{ohm}} = 31.46 \mu\text{m}$. This is why in further consideration, for condition (32) to be fulfilled, the anode active layer thickness is assumed to be $\Delta = 3 \mu\text{m}$. The anode active mass is the sum of three layers of a mixture of the intercalator and electrolyte grains. In the thin active layer, the following condition is fulfilled:

$$I = Sj\Delta = Si_0[(1 - a_s)^{1/2} a_s^{1/2}] \{e^\eta - e^{-\eta}\} \Delta. \quad (33)$$

Insofar as the ohmic limitations in an anode with a thin layer are virtually absent, there is no need to carry out calculations according to Eq. (6) because the reduced polarization is constant

$$\eta = \text{const}, \quad (34)$$

In place of Eq. (11), we have the following simple equation:

$$d\check{c}/dt^{**} = -\beta, \quad (35)$$

where

$$\beta = I/Si_0\Delta, \quad (36)$$

Its solution is as follows:

$$\check{c} = c_0 - \beta t^{**}, \quad (37)$$

where c_0 is the initial concentration of lithium atoms in the intercalator active grain. Furthermore, the condition (30) is fulfilled, which now should be written as

$$\check{c} = a_s + (\lambda/3)\beta. \quad (38)$$

By subtracting equality (38) from equality (37), we obtain

$$c_0 - a_s = \beta(\lambda/3 + t^{**}). \quad (39)$$

Then, the reduced time of anode discharge t^{***} is found from Eq. (39) by assuming that $a_s = 0$.

$$t^{***} = c_0/\beta - \lambda/3 = (c_0/\beta)[1 - (\lambda\beta/3c_0)]. \quad (40)$$

The specific capacity of the anode

$$\begin{aligned} C &= It^{***}\tau = g^*Fc^*c_0\Delta[1 - (\lambda\beta/3c_0)] \\ &= C^*[1 - (\lambda\beta/3c_0)], \end{aligned} \quad (41)$$

where $C^* = g^*Fc^*c_0\Delta$ is the maximum possible specific capacity of the anode. Like the discharge time (Eq. (40)), the specific capacity falls to zero when β becomes equal to

$$\beta = \beta^* = 3c_0/\lambda, \quad (42)$$

or, in other words, when the discharge current reaches the maximum possible value

$$I = I^* = 3c_0S\Delta i_0/\lambda = 3S\Delta F D c^* c_0/L\tilde{n}. \quad (43)$$

In the physical sense, this means that with the attainment of the maximum current I^* , the intercalator active grains can no longer donate lithium atoms. Immediately after the current is switched on, the concentration of lithium atoms on the grain surface a_s falls to zero, while the anode potential at the active layer/interelectrode space interface tends to infinity.

In the scale of values of parameter β , yet another important value $\beta = \beta^{**}$ can be singled out (correspondingly, the additional characteristic current value $I = I^{**}$ is introduced). For example, we assume that for this β value, the intercalator active grains are freed from lithium atoms by 95%. Then, for $\beta < \beta^{**}$ (correspondingly, for the discharge currents $I < I^{**}$), we can assume that virtually all lithium atoms are already removed from the intercalator active grain.

Figure 1 shows the discharge current I as a function of two values, namely, the specific capacity C (curve 1) and the reduced discharge time t^{***} (curve 2) for an anode with a thin active layer. The anode thickness is small ~ 0.3 mC/cm². The specific capacity falls to zero

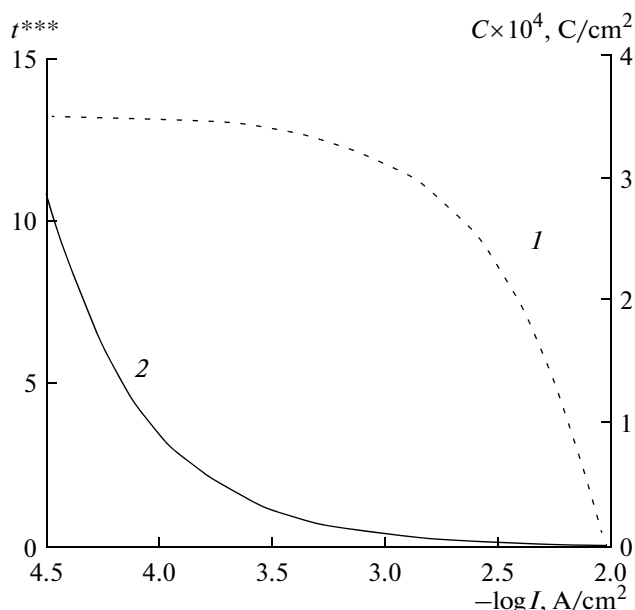


Fig. 1. Anode of a lithium-ion battery with a thin active layer (thickness $\Delta = 3$ μm). Dependences of (1) the specific capacity C and (2) the reduced value of discharge time t^{***} on the discharge current.

for $\beta^* = 18.1$ (for the discharge current $I^* = 6.34$ mA/cm²).

Figure 2 shows the dependence of the reduced capacity C/C^* on the parameter β , which was found from Eq. (41). In the curve, the values of parameters $\beta^* = 18.1$ and $\beta^{**} = 0.95$ are shown. They correspond to the discharge currents $I^* = 6.34$ mA/cm² and $I^{**} = 0.32$ mA/cm². For the current of 0.32 mA/cm², the anode discharge time is ~ 633 s.

It makes sense to see how the anodic potential E changes as the lithium ion concentration on the carrier active grain surface a_s varies from its initial value c_0 to zero. From the conditions (33), (34) and (36), it follows that

$$\begin{aligned} \eta &= \operatorname{arcsinh} \left\{ (I/2Si_0\Delta) / [(1 - a_s)^{1/2} a_s^{1/2}] \right\} \\ &= \operatorname{arcsinh} \left\{ (\beta/2) / [(1 - a_s)^{1/2} a_s^{1/2}] \right\}. \end{aligned} \quad (44)$$

Then, taking into account the definitions (4) and (5) and the relationship (38), we finally obtain

$$\begin{aligned} E &= (2RT/F) \operatorname{arcsinh} \left\{ (\beta/2) / [(1 - a_s)^{1/2} a_s^{1/2}] \right\} \\ &\quad - 0.16 + 1.32 \exp(-3[a_s + (\lambda\beta/3)]). \end{aligned} \quad (45)$$

Figure 3 shows the dependence of the potential E on the active layer/interelectrode space interface on the lithium atom concentration a_s on the surface of intercalator active grains for the following four values of parameter β : 18.1, 10, 5, and 0.95 (for the anode discharge currents I of 6.34, 3.5, 1.75, and 0.32 mA/cm², respectively) starting from β^{**} .

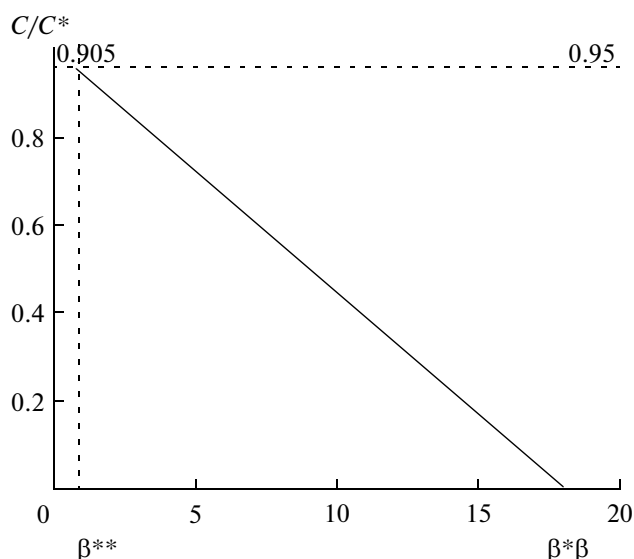


Fig. 2. Anode of a lithium-ion battery with a thin active layer (thickness $\Delta = 3 \mu\text{m}$). Dependence of the reduced capacity C/C^* on the parameter β . In the curve, the parameter values $\beta^* = 18.1$ and $\beta^{**} = 0.905$ are shown. The latter correspond to the discharge currents $I^* = 6.34 \text{ mA/cm}^2$ and $I^{**} = 0.32 \text{ mA/cm}^2$. $C^* = 0.21 \text{ C/cm}^2$.

Insofar as for $a_s = 0$, the potential difference becomes infinite, the infinitely small value, i.e., $a_s = 0.01$, was taken. The potential E corresponding to this concentration was designated as E^* . According to calculations, the potential E increases with a decrease in the lithium atom concentration on the grain surface a_s and its value does not exceed 1 V.

6. WORKING PARAMETERS OF AN ANODE WITH THE OPTIMAL THICKNESS

The algorithms of calculations based on the system of Eqs. (6) and (11) with the additional condition (30), which characterize the discharge of the LIB anode are shown in the Appendix in the end of the present paper. In the present section, we show the calculations of working parameters for an anode of the optimal thickness.

As in the case of the anode with a thin active layer (section 5), the concentration of intercalator grains in the anode active layer was chosen to provide the maximum specific capacity of the cathode [5]; it was assumed that $g = 0.4$. The values of all other parameters that characterize the anode with a thin active layer also remained unchanged. The discharge current density I (A/cm^2) was varied depending on the results of calculations carried out in the previous section. The following three values of discharge current density were taken: 1, 10, and 20 mA/cm^2 .

Figure 4 shows the dependence of the averaged concentration of lithium atoms in intercalator grains \check{c} (solid lines) and the concentrations of lithium atoms

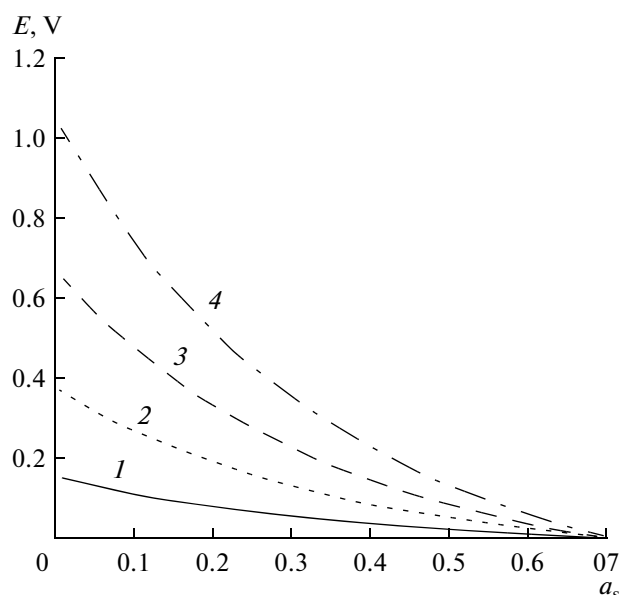


Fig. 3. Dependence of the anode potential E on the active layer/interelectrode space interface on the lithium atom concentration on the surface of intercalator active grains a_s for β : (1) 0.905, (2) 5, (3) 10, (4) 18.1 (correspondingly, the anode discharge currents I , mA/cm^2 : (1) 0.32, (2) 1.75, (3) 3.5, (4) 6.34).

on the surface of the intercalator active grain (dashed lines) on the reduced thickness of the anode active layer y/Δ . The discharge stops when the lithium atom concentration of the surface of an intercalator active grain reaches the threshold value arbitrary chosen as $a_s = 0.01$.

In Fig. 4, the concentration profile of lithium atoms in active grains is first constant and equal to $c_0 = 0.7$; later, the points of \check{c} vs. y/Δ curves are observed to descend (the active layer thickness $\Delta = 10^3 \mu\text{m}$). For the anode discharge current $I = 1 \text{ mA/cm}^2$ (Fig. 4a), the concentrations \check{c} and a_s virtually coincide. For the ten-fold increase in the discharge current $I = 10 \text{ mA/cm}^2$ (Fig. 4b), the \check{c} profile already lags behind the a_s profile. For $I = 20 \text{ mA/cm}^2$ (Fig. 4c), the difference between these curves becomes obvious.

The data shown in Figs. 4a–4c were obtained using the procedures described in [7]. They allow the optimal (effective) thickness of the anode active layer Δ^* to be assessed. The optimal thickness of the anode active layer is determined as follows. Based on the data of Fig. 4, all lithium to be discharged is collected (integration) and then the active layer section Δ^* which marks the point before which (from section $y = 0$ to $y = \Delta^*$) the collected lithium accounts for 90%, i.e., its amount that can be collected on this anode in the ideal case. This Δ^* value is precisely the reasonable optimal thickness of the active layer. In Fig. 4, the optimal anode thicknesses are marked with dashed vertical

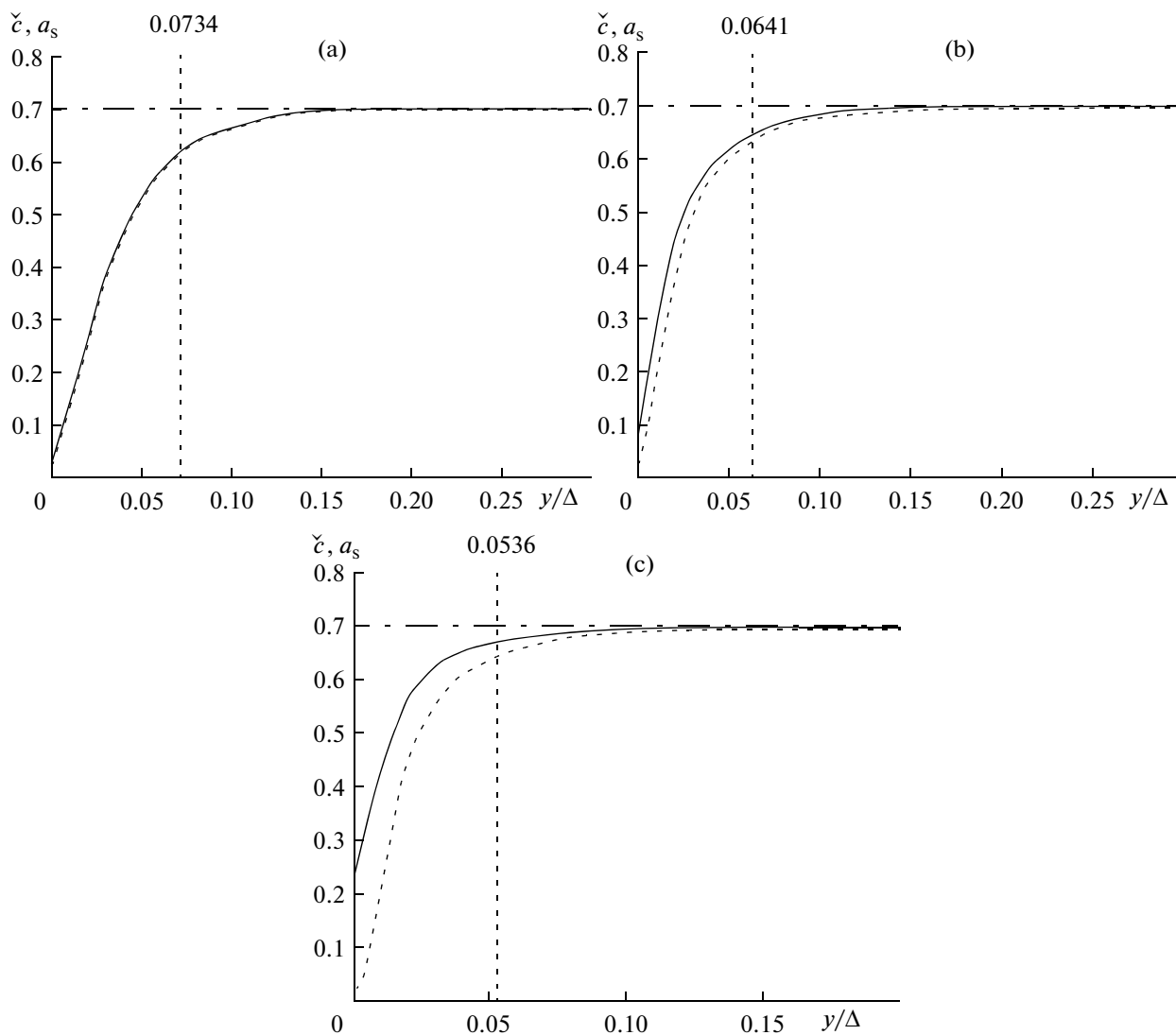


Fig. 4. Dependence of the average concentration of lithium atoms in the intercalator active grain \check{c} (solid lines) and the concentration of lithium atoms on the surface of an intercalator grain a_s (dashed lines) on the reduced value of the anode active layer thickness. Discharge current I , mA/cm²: (a) 1, (b) 10, (c) 20. $g = 0.4$.

line. Naturally, with the increase in the discharge current, the effective thickness Δ^* decreases. Table (the second column) shows the exact values of Δ^* for the three chosen currents of anode discharge.

Figure 5 shows the time variations of the averaged concentration of lithium atoms in graphite grains \check{c} (solid lines) and the lithium atom concentrations on the surface of intercalator active grains a_s (dashed lines) on the interface anode active layer/interelectrode space, for the same three discharge current values as in Fig. 4 (I , mA/cm²: (Fig. 5a) 1, (Fig. 5b) 10, (Fig. 5c) 20).

Once more, in agreement with condition (30), the difference between \check{c} and a_s increases with the increase in the anode discharge current. The anode discharge

time is determined as a moment when the a_s concentration reaches the value $a_s = 0.01$. As follows from the data in Figs. 5a–5c and the table (third column), as

Dependence of the optimal anode working parameters, namely, the active layer thickness Δ^* , the discharge time $t^{***}\tau$, the anode specific capacity C , and the final potential of the anode at the active layer/interelectrode space interface E^* on the discharge current density I . The volume concentration of intercalator grains $g = 0.4$

I , mA/cm ²	Δ^* , μm	$t^{***}\tau$, s	C , C/cm ²	E^* , V
1	73.2	2589.5	2.59	1.1
10	64.1	159.7	1.60	1.05
20	53.6	43.6	0.87	0.72

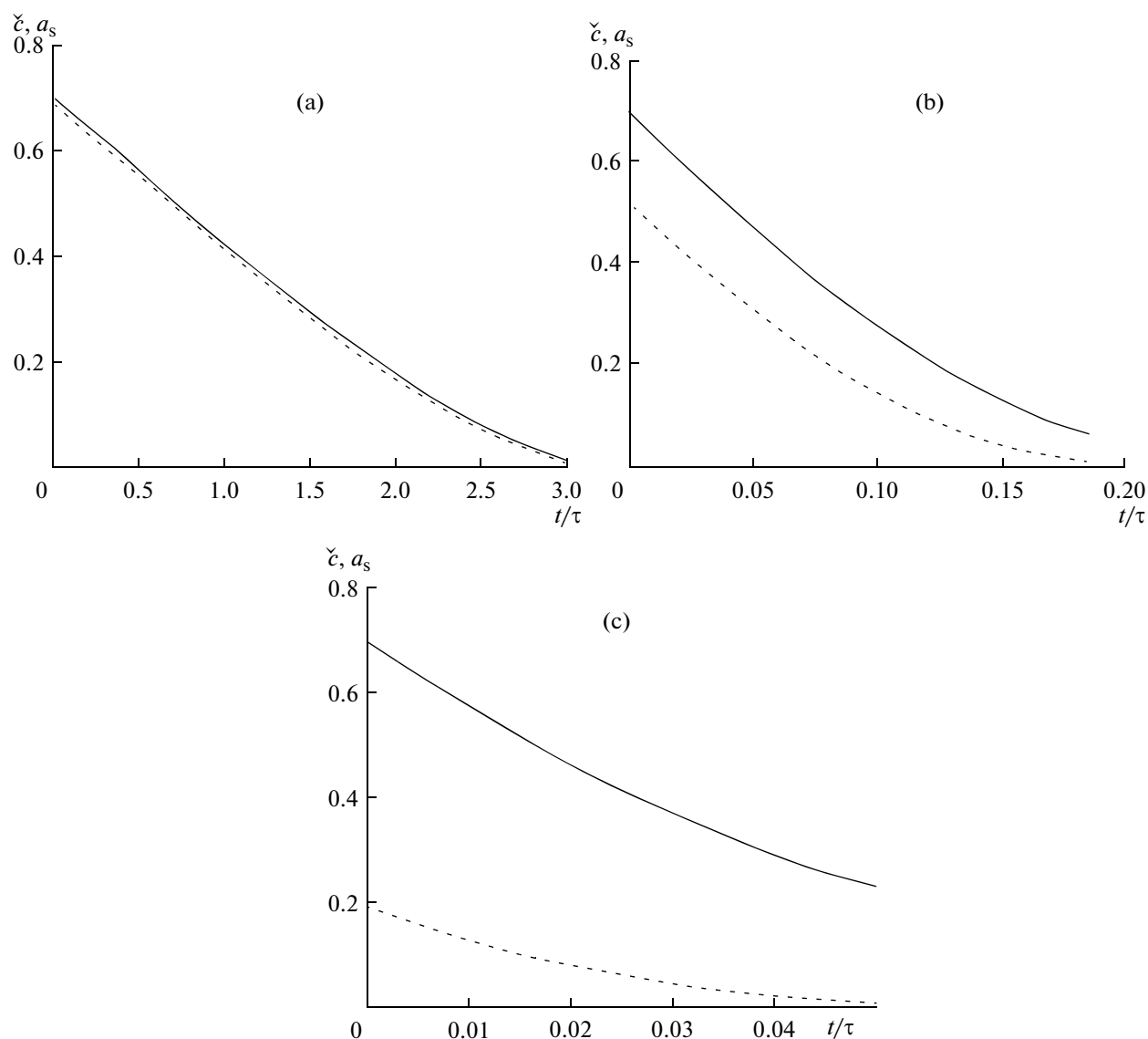


Fig. 5. The averaged concentration of lithium atoms in the intercalator active grain \bar{c} (solid lines) and the concentration of lithium atoms on the surface of an intercalator grain a_s at the anode active layer/interelectrode space interface (dashed lines) as a function of the reduce time. The discharge current I , mA/cm^2 : (a) 1, (b) 10, (c) 20. $g = 0.4$.

the discharge current increases the discharge time increases.

Due to the incomplete (for currents I , mA/cm^2 : 10 and 20) depletion of intercalator grains, the discharge-time–proportional specific capacity released by the LIB anode, which was assessed by a simple relationship $C = I^{***}\tau$ (the fourth column in table), also decreases.

Finally, in Fig. 6 and table (the last column), for the same three values of discharge current (1, 10, and 20 mA/cm^2), the dependence of the reduced discharge time of the LIB anode on the anode potential at the active layer/interelectrode space interface is shown.

7. THE CHOICE OF REASONABLE DISCHARGE CURRENT

It was found [5] that the discharge current I should not exceed a certain reasonable value I^* , otherwise the complete withdrawal of lithium atoms from the intercalator grains is impossible. This is why the discharge process should be organized in such a way that in the course of depletion of the intercalator active grains, the averaged concentration of lithium atoms \bar{c} and the lithium atom concentration on the surface of intercalator active grains a_s virtually coincided. This does not allow us to achieve considerable discharge currents, because lithium is removed by the diffusion mechanism and the diffusion coefficient D is very small. For

example, the diffusion coefficient of lithium in graphite D (cm²/s) was characterized as follows: 5×10^{-9} [9], 1.6×10^{-10} (at $T = 298$ K) [10], 2×10^{-10} [11], 3.9×10^{-10} [12], 1×10^{-11} [13]. In our estimates and calculations, we used the average value $D = 1 \times 10^{-10}$ cm²/s.

The diffusion current of lithium extracted from the intercalator can be assessed using the following simple formula:

$$j_d \sim F D c (\check{c} - a_s) / L. \quad (46)$$

As was shown in [5] by special calculations, the complete depletion of an intercalator active grain can be achieved only if the difference in Eq. (46) remains sufficiently small. We assume that the following criterion is fulfilled:

$$\check{c} - a_s \sim 0.01. \quad (47)$$

Then, according to Eq. (46), for intercalator grains of the micron size, $j_d \sim 9.65 \times 10^4 \times 10^{-10} \times 3 \times 10^{-2} \times 10^{-1} / 10^{-4} = 0.29$ mA/cm². Normally, the anode discharge current density should be approximately equal to this value ($I^* \sim 1$ mA/cm²), as was demonstrated by calculations carried out in Section 6 of this study. On the other hand, if we want to work with high current densities, then in Eq. (46), the diffusion coefficient should be increased and the grain size L should be decreased. For example, with these two quantities, i.e., $D = 1 \times 10^{-8}$ cm²/s and $L = 10$ nm, we have $j_d \sim 9.65 \times 10^5 \times 10^{-8} \times 3 \times 10^{-2} \times 10^{-1} / 10^{-6} = 0.29$ A/cm². The transition to nanosized grains and the enhanced value of diffusion coefficient can provide the operation at very high current densities.

The next question that requires answer is how we can achieve the fulfillment of criterion (47). The difficulty lies in the fact that, as was noted above, in LIB electrodes, two processes occur simultaneously. These are the depletion of intercalator active grains and the ohmic-limitation-determined (the supply of lithium ions to intercalator from electrolyte) gradual restructuring of the potential distribution along the active layer thickness. Each process has its own characteristic time.

For the complete withdrawal of lithium atoms from the intercalator active grains, it is necessary to make the process of concentration profile restructuring more mobile as compared with the process of changes in the potential distribution along the active layer thickness. Hence, the following criterion should be fulfilled:

$$\tau^* / \tau = (L S i_0 / g^* F c^*) (L / D) \leq 0.1. \quad (48)$$

Assuming that $SL = 1.167$, $i_0 = 10^{-4}$ A/cm², $g^* = 0.348$ ($g = 0.4$), $F = 9.65 \times 10^4$ C/g-mol, $c^* = 3 \times 10^{-2}$ g-mol/cm³, we can find that $L S i_0 / g^* F c^* \sim 10^{-7}$ cm s⁻¹. Thus, the two main parameters of intercalator active grains, i.e., their size L and the diffusion coefficient D must fulfill the following inequality:

$$(L / D) \leq 10^6. \quad (49)$$

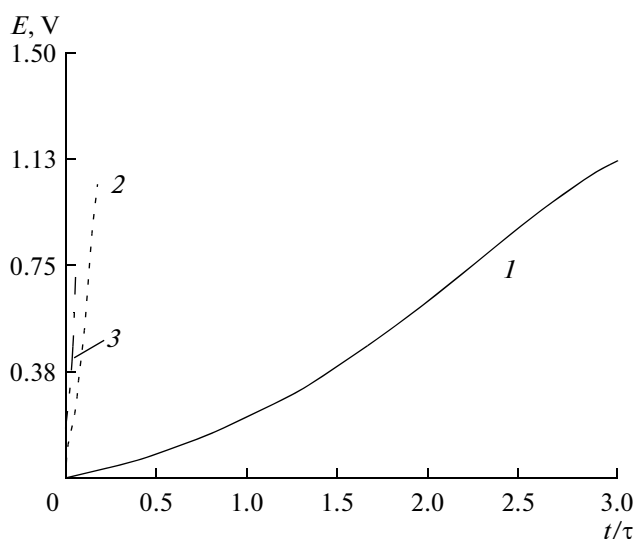


Fig. 6. Dependence of the LIB anode potential at the active layer/interelectrode space interface on the reduced time of discharge. Discharge current I , mA/cm²: (1) 1, (2) 10, (3) 20. $g = 0.4$.

Insofar as the intercalator grain size can apparently vary within 10^{-6} cm (10 nm) $\leq L \leq 10^{-3}$ cm (10 μ m), then condition (49) means that the diffusion coefficient D should not exceed the value $D = 10^{-12}$ cm²/s (for the minimum $L = 10^{-6}$ cm, $L/D = 10^{-6}/10^{-12} = 10^6$). Thus, we have solved the problem of calculation of anode working parameters only for the intercalator grains in which the diffusion coefficient of lithium atoms is sufficiently high so that the inequality $D \geq 10^{-12}$ cm²/s is fulfilled.

It also deserves mention that the diffusion coefficient has not only the minimum possible value $D = 10^{-12}$ cm²/s but also the maximum possible value $D = 10^{-8}$ cm²/s. Thus, by fixing the D value, we choose the admissible limits for the intercalator grain size L . For $D = 10^{-12}$ cm²/s, according to Eq. (49), the intercalator grains should have the size $L = 10^{-6}$ cm. For $D = 10^{-11}$ cm²/s, the intercalator grain size L should lie within $10^{-6} \leq L \leq 10^{-5}$ cm. For $D = 10^{-10}$ cm²/s, the intercalator grain size should fit the interval $10^{-6} \leq L \leq 10^{-4}$ cm. For $D = 10^{-9}$ cm²/s and $D = 10^{-8}$ cm²/s, the limits of admissible intercalator grain sizes are $10^{-6} \leq L \leq 10^{-3}$ cm.

Apparently, the condition of the complete extraction of lithium atoms from intercalator grains requires an additional limitation. Taking into account Eq. (46), the anode discharge current density I (A/cm²) should not exceed the reasonable critical value I^* equal to

$$I^* = j_d = F D c^* 0.01 / L. \quad (50)$$

Assuming that $F = 9.65 \times 10^4$ C/g-mol, $c^* = 3 \times 10^{-2}$ g-mol/cm³, then in place of Eq. (50), we have

$$I^* = 29(D/L) \text{ A/cm}^2. \quad (51)$$

This is why for the pair of values $D = 10^{-12}$ cm²/s and $L = 10^{-6}$ cm, the current $I^* = 0.029$ mA/cm². At the

same time, for the following pair of parameters: $D = 10^{-8} \text{ cm}^2/\text{s}$ and $L = 10^{-6} \text{ cm}$, the discharge current can rise to a considerable value, namely, $I^* = 0.29 \text{ A}/\text{cm}^2$.

8. CONCLUSIONS

In the computer simulations of the work of a negative electrode (anode) of a lithium-ion battery operating in the galvanostatic discharge mode, the attention was focused on formulating the complete mathematical description of processes occurring on the anode

In the process, the most serious complication was associated with taking into account of diffusion limitations that arise at the extraction of lithium ions from active substance (intercalator) grains. The analytical relationship was found between the average lithium concentration in the intercalator grain and the lithium concentration on the intercalator grain surface in contact with electrolyte grains.

Algorithms of computer-assisted calculations were developed that allowed determining of anode characteristics within the complete mathematical description of processes occurring on the anode. The main working parameters of the anode were estimated, namely, its active layer thickness, total discharge time, specific electric capacity, and the final value of its potential at the active layer/inter-electrode space interface.

The calculations of anode characteristics were carried out in the following two versions: for anodes with a thin active layer (imitation of processes that occur in an individual intercalator grain) and for anodes with an active layer of the optimal thickness.

Criteria limiting the values of the two most important parameters of an intercalator grain, namely, its size and the diffusion coefficient of lithium atoms in intercalator grain are formulated.

The procedure of selecting the reasonable discharge current density, i.e., a maximum value of this quantity for which virtually all lithium molecules can still be removed from the intercalator active grain, was described. As the discharge current increased further, only partial depletion of the intercalator active grain could occur.

DESIGNATIONS OF THE ANODE ACTIVE LAYER PARAMETERS FOR A LITHIUM-ION BATTERY

External Parameters

t is the current value of anode discharge time

$t^* = t/\tau^*$ is the reduced current time for the extraction of lithium atoms from the intercalator active grain

τ^* is the characteristic time for the process of lithium atom extraction from the intercalator active grain

$t^{**} = t/\tau$ is the reduced current time for the anode discharge process

τ is the characteristic time of anode discharge

t^{***} is the reduced time of anode discharge

C , C/cm^2 is the specific capacity of the anode

R is the gas constant

$T = 293 \text{ K}$ is the anode working temperature

Δ is the anode active layer thickness

Δ^* is the optimal thickness of the anode active layer

\bar{n} is the average number of electrochemically active facets of an intercalator active grain

Electrochemical Kinetic Parameters

$F = 9.65 \times 10^{-4} \text{ C}/\text{mol}$ is the Faraday number

I , A/cm^2 , is the anode discharge current

j , A/cm^2 , is the electrochemical reaction current density

i_0 is the exchange current

η is the reduced polarization

ψ is the reduced potential of the anode

E is the anode potential

E^* is the final anode potential at the active layer/inter-electrode space interface

U is the open-circuit potential of an intercalator grain

L_{ohm} is the characteristic ohmic length

I_{ohm} , A/cm^2 , is the characteristic ohmic current

y is the anode active layer coordinate

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

Parameters of Anode Active Layer Structure

g is the volume concentration (fraction) of intercalator grains

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

g_i is the volume fraction of electrolyte grains

L is the size of intercalator and electrolyte grains

S , cm^{-1} is the specific surface of the contact between electronic and ionic percolation clusters

Parameters of Intercalator Grain Structure

c is the grain-volume-averaged concentration of lithium atoms

c^* is the maximum possible lithium concentration in the intercalator grain

$\check{c} = c/c^*$ is the lithium atom concentration averaged over the intercalator grain volume

c_0 is the initial amount of lithium atoms in an intercalator grain

Parameter Determining the Diffusion Processes in an Intercalator Grain

a is the reduced concentration of lithium atoms in the intercalator active grain

a_s is the reduced concentration of lithium atoms on the intercalator grain surface

$z = x/L$ is the reduced coordinate in the intercalator grain

$\alpha = \tau^*/\tau$ is the constant determining the mode of lithium atom extraction from the intercalator grain

B is the constant that determines the mode of extraction of lithium atoms from the intercalator grain

χ is the parameter determining the mode of lithium atom extraction from the intercalator grain

Parameters Determining the Processes of Mass and Electro Transfer

D is the diffusion coefficient of lithium atoms in intercalator grains

k is the specific conductivity of electrolyte

k^* the conductivity (dimensionless) of lithium ions in the percolation ionic cluster

APPENDIX

Algorithms of Computer-Assisted Calculations

In solving the system of equations (6), (11) with condition (30), it is assumed that up to the moment when the overall current I is switched on, the concentration of atoms $c_0 = a_s$, $\eta = 0$. In the moment the circuit is closed $t = 0$ (in the beginning of discharge), in the anode active layer, a certain distribution of reduced polarization appears, which is defined as the solution of the following equation

$$\begin{aligned} & d^2\eta(0)/d\hat{y}^2 \\ &= [(1 - a_s(0))a_s(0)]^{1/2} \{e^{\eta(0)} - e^{-\eta(0)}\}, \end{aligned} \quad (6a)$$

At the same time, on the surface of contact between the active graphite grains and the electrolyte grains, the reduced concentration of lithium atoms a_s takes a value determined by the root of equation (30):

$$\begin{aligned} c_0 = a_s(0) - (\lambda/3)[(1 - a_s(0))a_s(0)]^{1/2} \\ \times \{e^{\eta(0)} - e^{-\eta(0)}\}. \end{aligned} \quad (30a)$$

This self-consistent problem was solved by the method of successive approximations, namely, in the first approximation, it was assumed that $a_{s1}(0, y) \equiv c_0$ and the $\eta_1(0, y)$ distribution was found from Eq. (6a). With the found $\eta_1(0, y)$ values, the a_s values were calculated in the next approximation as a root of Eq. (30a)

$$\begin{aligned} & a_{s2}(0, y) \\ &= \{2c_0 + Z_1([4c_0(1 - c_0) + Z_1]Z_1)^{1/2}\}/2(1 + Z_1), \end{aligned}$$

where

$$Z_1 = [2\lambda \sinh(\eta_1(0, y))/3]^2.$$

Then, the iterations continued until the following equality was fulfilled:

$$\begin{aligned} & a_{s, n+1}(t = 0, y = 0) - a_{s, n}(t = 0, y = 0) \\ & < \varepsilon a_{s, n}(t = 0, y = 0). \end{aligned}$$

In calculating $a_s(0, 0)$, we restricted ourselves to the value $\varepsilon = 0.001$.

After the determination of the starting values $\check{c}(0)$, $a_s(0, y)$, $\eta(0, y)$, the nonstationary equations (6a) and (11a) were solved numerically by the Euler method [14] in the time-space lattice points. The integration of Eq. (11a) over time was carried out with a sufficiently small step dt . In each time moment, the values of all quantities were calculated in m "reference" points ($m = 0, 1, \dots, m_{\max}$) that divided the anode active layer into m_{\max} domains. In the chosen time interval dt , the lithium atom concentration in moments $t_{N+1} = t_N + dt$ were calculated based on the formula

$$\begin{aligned} & \check{c}(t_{N+1}, y_m) = \check{c}(t_N, y_m) \\ & - dt \{ [1 - a_s(t_N, y_m)] a_s(t_N, y_m) \}^{1/2} \\ & \times 2 \sinh \{ \eta(t_N, y_m) \}, \end{aligned}$$

where

$$\begin{aligned} a_s(t_N, y_m) = \{ 2\check{c}(t_N, y_m) + Z_N \{ [4\check{c}(t_N, y_m) \\ \times (1 - \check{c}(t_N, y_m)) + Z_N] Z_N \}^{1/2} \} / 2(1 + Z_N) \end{aligned}$$

and

$$Z_N = [2\lambda \sinh(\eta_1(t_N, y_m))/3]^2,$$

The reduced polarization was found as the solution of equation

$$\begin{aligned} & d^2\eta(t_N, y)/d\hat{y}^2 = [(1 - a_s(t_N, y))a_s(t_N, y)]^{1/2} \\ & \times 2 \sinh \{ \eta(t_N, y) \} \end{aligned} \quad (6b)$$

with boundary conditions

$$d\eta(t_N, y)/d\hat{y} = -I/I_{\text{ohm}} = \text{const} \quad \text{for } y = 0, \quad (8a)$$

$$d\eta(t_N, y)/d\hat{y} = 0 \quad \text{for } y = \Delta. \quad (9a)$$

The numerical solution of Eq. (6b) was found by using the applied program package Maple [15]. The integration of Eq. (11a) over time was finished in a moment when the reduced concentration of lithium a_s reached a value lower than 0.01.

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