

Computer Simulation of Operation of Lithium-Ion Battery: Galvanostatics, Central Problem of Theory, Calculation of Characteristics of Thin Active Layers with Low Diffusion Coefficients

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Abstract—Computer simulation of lithium-ion battery operating in the galvanostatic discharge mode was performed. Special attention was paid to the complete mathematical description of the processes proceeding in the active layers of electrodes. The central problem of the theory of lithium-ion batteries is a possibility of analyzing two processes proceeding concurrently in space and time: the recovery or filling of active substance (intercalating agent) grains with lithium atoms and redistribution of electrode potentials over the active layer width, which is caused by the ohmic limitations. A new approach to the central problem is proposed. It is based on comparing the characteristic times of two main processes proceeding in the electrodes. Here, the diffusion coefficient of lithium atoms in the intercalating agent grains is of critical importance. Two ranges of diffusion coefficients (high and low diffusion coefficients) can be recognized. The merits and drawbacks of the electrodes exhibiting high and low diffusion coefficients are discussed. The calculations of the working parameters of the electrode (by the example of the anode) are performed for the active layers with low diffusion coefficients. The active layer thickness, complete discharge time, specific electric capacitance, and final potential at the active layer/interelectrode space interface are determined.

Keywords: lithium-ion battery, galvanostatic discharge mode, computer simulation, model of equally sized cubic grains, active intercalating agent grains, ranges of high and low diffusion coefficients, electrodes with a thin active layer, calculation of anode operation parameters

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1. STATEMENT OF PROBLEM

The computer simulation of the operation of anode and cathode of lithium-ion battery has already been performed in [1–4]. We will remind briefly the approaches to calculating characteristics of lithium-ion battery electrodes proposed earlier [1–4]. The models of equally sized cubic grains of two types (in the anode active layer) and three types (in the cathode active layer) were studied.

Ignoring the presence of binding agent, the following obvious condition for anode can be written:

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

where g is a fraction of anode active layer volume occupied by the intercalating agent grains and g_i is a fraction of active layer occupied by the electrolyte. For the cathode, the following condition is true:

$$g + g_i + g_e = 1, \quad (2)$$

where g_e is the bulk concentration of the grains of electron-donor material.

It was assumed that all grains of intercalating agent and electrolyte are identical microcubes with edges L . Thus, within the model of equally sized grains, the percolation calculations are performed for the cubic lattice (the site-problem) [5].

The ionic and electronic percolation clusters form in the active layers of the electrodes upon reaching the percolation threshold, if the bulk concentrations of the corresponding grains reach certain values: g^* , g_i^* , and g_e^* . In the cubic lattice, the percolation threshold is $g^* = g_i^* = g_e^* = 0.298$ [6]. However, as it was demonstrated earlier [2], fully functioning percolation clusters arise later: at $g \geq 0.35$, $g_i \geq 0.35$, and $g_e \geq 0.35$. Thus, with regard for conditions (1) and (2), the range of reasonable values of parameter g (the concentration of

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intercalating agent grains), at which the anode can discharge completely, is as follows:

$$0.35 \leq g \leq 0.65. \quad (3)$$

For the cathode, the corresponding condition is as follows:

$$0 \leq g \leq 0.3. \quad (4)$$

Not every intercalating agent grain can take part in the electrochemical process. The intercalating agent grains are classified as active grains with concentration g^* ($g^* < g$) and inactive grains with concentration $g - g^*$. A grain, which comes in contact with an ionic percolation cluster by at least one face and comes in contact with an electronic percolation cluster by at least one face, can be denoted active. Obviously, an active intercalating agent grain can come in contact with an ionic percolation cluster by 5 faces at the most. The 6th face is required for the contact of intercalating agent grain with an electronic percolation cluster.

The above basis allows us to pass to the goals of the study: to calculate optimal working parameters of lithium-ion battery electrodes, namely, optimal active layer thickness, discharge time, specific electric capacitance, and final potential at the active layer/interelectrode space interface.

Here, the central problem of the theory of lithium-ion batteries arises. The system of equations can be easily written, but is difficult to solve. The point is that two parallel interrelated processes proceed in the active electrode layers in space and time: the diffusion of lithium atoms in the intercalating agent grains and the redistribution of potentials over the anode active layer width, which is caused by the ohmic limitations. It is difficult to correlate these processes. This problem is discussed in detail below.

2. SYSTEM OF EQUATIONS FOR ACTIVE ELECTRODE LAYER

Let us write a system of equations describing the processes proceeding in the active layer of lithium-ion battery electrode in space and time. Specifically, for anode, at the initial instant of time (at $t = 0$), all intercalating agent grains are filled with lithium atoms to the concentration c_0 ; then, during the anode discharge, the concentration of lithium atoms decreases. The reduced average concentration of lithium atoms in the intercalating agent grains is $\check{c} = c/c^*$, where c^* is the highest possible concentration.

The current density j , which is generated at the interface between the ionic percolation cluster (an aggregate of interconnected electrolyte grains) and electronic percolation cluster (an aggregate of interconnected intercalating agent grains), is as follows:

$$j = i_0[(1 - a_s)^{1/2} a_s^{1/2}] \{e^\eta - e^{-\eta}\}, \quad (5)$$

where a_s is the reduced concentration of lithium atoms in the active intercalating agent grains near the surface

of their contact with the electrolyte grains and i_0 is the exchange current.

The reduced electrode polarization is as follows:

$$\eta = F[E - U]/2RT, \quad (6)$$

where E is the electrode potential. The open-circuit potential of the anode can be as follows [7]

$$U = -0.16 + 1.32 \exp(-3\check{c}). \quad (7)$$

As for the cathode, the equation for potential U can be, for example, as follows [8]:

$$U = 6.515 + 2.3192\check{c} - 5.3192\check{c}^{1/2} + 0.41082 \times \exp[200(0.44 - \check{c})] - 0.24247 \exp[60(\check{c} - 0.99)]. \quad (8)$$

For the anode, we can suppose that the concentration of lithium atoms in the active intercalating agent grains falls within the range $0.0 < \check{c} < c_0/c^* = 0.7$ [7].

For the cathode, $0.45 \check{c} < 1.0$ [8].

From the law of conservation of lithium ion fluxes in the electrolyte (in the grains of ionic percolation cluster), the equation for polarization η in the active electrode layer can be obtained:

$$d^2\eta/d\hat{y}^2 = [(1 - a_s)^{1/2} a_s^{1/2}] \{e^\eta - e^{-\eta}\}, \quad (9)$$

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

$$L_{\text{ohm}} = (2RTk^*k/FSi_0)^{1/2}, \quad (10)$$

k is the electrolyte conductivity, k^* is the conductivity of lithium ions in the percolation ionic cluster (dimensionless value), and S is a specific surface area of the contact between the electronic and ionic percolation clusters. In the case of galvanostatic electrode discharge mode, the boundary conditions for equation (9) are as follows:

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

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

where Δ is the thickness of electrode active layer, I is the discharge current density, and the characteristic ohmic current is

$$I_{\text{ohm}} = (2RTk^*kSi_0/F)^{1/2}. \quad (13)$$

For the anode, the recovery of lithium atoms from the active grains of intercalating agent is described by the following equation:

$$d\check{c}/dt^{**} = -[(1 - a_s)^{1/2} a_s^{1/2}] \{e^\eta - e^{-\eta}\}, \quad (14)$$

Here, $\check{c}(y, t)$ is the concentration of lithium atoms at the instant of time t in the section of anode active layer with coordinate y averaged over the volume of active intercalating agent grain. The right-hand side of equation (14) means the rate of recovery of lithium atoms from the intercalating agent grains. As a result of electrochemical process, lithium atoms convert into lith-

ium ions and pass to the ionic percolation cluster. The reduced current discharge time t^{**} is as follows:

$$t^{**} = t/\tau, \quad (15)$$

Here τ is the characteristic discharge time, which is defined as follows:

$$\tau = g^*Fc^*/Si_0. \quad (16)$$

The initial condition for equation (14) is

$$\check{c} = c_0/c^* \quad \text{at } t = 0. \quad (17)$$

Thus, the set of equations (9) and (14) seemingly enables one to follow the variation of reduced potential

$$\psi = FE/2RT, \quad (18)$$

and lithium atom concentration \check{c} with time in every point of electrode active layer. However, this can be done provided that the concentration of lithium atoms a_s , which is involved in the right-hand sides of equations (9) and (14), is known. Thus, the set of equations (9) and (14) appears to be incomplete. The relationship between a_s and \check{c} should be determined. Therefore, it is necessary to consider the problem of diffusion limitations arising in the intercalating agent grains.

Hereafter, for the sake of definiteness, we will study the anode; we keep in mind that similar processes occur on the cathode.

3. ACTIVE GRAIN OF INTERCALATING AGENT

An intercalating agent grain is commonly imagined as a sphere surrounded by the electrolyte. Therewith, it is commonly assumed that, firstly, any grain of intercalating agent can be involved in the electrochemical process (the intercalating agent grains are not divided into active and inactive grains) and, secondly, the entire spherical grain surface is electrochemically active.

However, earlier [3], it was shown that, within the model of equally sized cubic grains of two types (the anode of lithium-ion battery), actually, only a fraction of outer surface of active intercalating agent grains contributes to the electrochemical process. The electrochemically active areas are distributed in a complex manner over the outer surface of active grains.

A simplified model of structure of active grain of intercalating agent and the diffusion process proceeding in the grain during the discharge in it was proposed earlier [3]. It was shown that real diffusion of lithium atoms is quasi-one-dimensional rather than three-dimensional. The situation is as follows: the recovery of lithium atoms in the active grain of intercalating agent appears to be similar to the diffusion of lithium atoms in a plane layer of thickness L , provided that one surface of the layer is closed for the exchange with lithium atoms, whereas, at the opposite surface of the

layer, the electrochemical process of conversion of lithium atoms into lithium ions proceeds.

According to the model of intercalating agent grain [3], the distribution of the reduced concentration of lithium atoms $a = c/c^*$ along the coordinate x in the grain satisfies the following equation:

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

Here, z is the reduced coordinate in the intercalating agent layer with thickness L

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

and the reduced current time is

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

where τ^* is the characteristic time defined by the following equation:

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

Here, D is the diffusion coefficient of lithium atoms in the intercalating agent grain.

The initial and boundary conditions for equation (19) are as follows.

$$a \equiv c_0/c^* \quad \text{at } t = 0, \quad (23)$$

On the surface of intercalating agent layer closed for the exchange with lithium atoms:

$$da/dz = 0 \quad \text{at } z = 0, \quad (24)$$

On the surface of intercalating agent layer, which is in contact with the electrolyte grains, (the condition of equal fluxes of lithium atoms and ions):

$$da/dz = -\lambda \left[(1 - a_s)^{1/2} a_s^{1/2} \right] \{ e^\eta - e^{-\eta} \} = -\lambda j/i_0 \quad (25)$$

at $z = 1$,

where parameter

$$\lambda = (\tilde{n}i_0/Fc^*)(L/D). \quad (26)$$

It is very important that parameter \tilde{n} is involved in the expression for λ . It is an average number of electrochemically active faces of active intercalating agent grains. The percolation calculations showed that, in the cathode, \tilde{n} varies from 3.27 faces at $g = 0.05$ to 1.80 faces at $g = 0.30$ [2]; in the anode, it varies from 3.55 faces at $g = 0.35$ to 1.91 faces at $g = 0.65$ [3].

Equation (19) seemingly enables one to determine lacking relation between the concentrations a_s and \check{c} in the active intercalating agent grain. However, it emerges that, in the boundary condition (25), parameter B depends on the time and coordinate of intercalating agent grain location in the anode active layer. Thus, the processes in the intercalating agent grain depend on the redistribution of potentials over the active layer.

Table 1. The characteristics of anode active mass

$k, \Omega^{-1} \text{ cm}^{-1}$	$i_0, \text{ A/cm}^2$	$c^*, \text{ g-m/cm}^3$	g^*	ζ	k^*	n	c_0
10^{-3}	10^{-4}	3×10^{-2}	0.348	1.167	0.231	3.35	0.7

4. THE LINES OF ATTACK ON THE CENTRAL PROBLEM OF THE THEORY

An enormous amount of research has been devoted to the methods of calculating the working parameters of lithium-ion battery electrodes (see, for example, a review [9]). Unfortunately, the methods are rather complex and consume long computational time [10, 11]. Here, we propose a simplified time-saving procedure of calculating the electrode working parameters.

Assume that, in the boundary condition (25), parameter

$$B = -\lambda_j/i_0 = \text{const.} \quad (27)$$

Then, for equation (19) with the boundary conditions (24) and (25), the following analytical solution can be obtained:

$$a(z, t^*) = c_0/c^* + B \left(t^* + \frac{3z^2 - 1}{5} + \frac{2}{\pi^2} \sum_{k=1}^{\infty} (-1)^{k+1} \frac{\cos(k\pi z)}{k^2} \exp(-k^2 \pi^2 t^*) \right). \quad (28)$$

Integrating the right-hand side of equation (28) over the entire width of intercalating agent grain, we obtain the time variation of lithium atom concentration \check{c} averaged over the volume. It is found that \check{c} can be estimated by the following equation:

$$\check{c} = c_0/c^* + Bt^*. \quad (29)$$

Assuming that, in equation (28), $z = 1$, we can obtain the time variation of concentration a_s of lithium atoms on the face surface (which is in contact with the electrolyte) of active grain of intercalating agent:

$$a_s = c_0/c^* + B \left(t^* + \frac{1}{3} - \frac{2}{\pi^2} \sum_{k=1}^{\infty} \frac{\exp(-k^2 \pi^2 t^*)}{k^2} \right). \quad (30)$$

A set of conditions (29) and (30) enables us to determine the relationship between the concentrations \check{c} and a_s :

$$\check{c} = a_s - B \left\{ \frac{1}{3} - \left(\frac{2}{\pi^2} \right) \Sigma \left[\exp(-k^2 \pi^2 t^*) / k^2 \right] \right\}. \quad (31)$$

Thus, to calculate the working parameters of the electrode by using a set of equations (9), (14), and (31), it is necessary to determine the conditions, under which parameter B may be assumed to be constant (eq. (27)).

One more important point should be indicated. The diffusion in the active grain of intercalating agent and the process of redistribution of potentials over the active layer width are characterized by different characteristic times. The characteristic time of redistribution of potentials τ is determined by the condition (16), whereas the characteristic time of the diffusion in the intercalating agent grain τ^* is determined by the condition (22). Let us compare these times. The following parameter is introduced:

$$\alpha = \tau^*/\tau = L^2 Si_0/Dg^*Fc^* = (\zeta i_0/g^*Fc^*)(L/D), \quad (32)$$

where $\zeta = LS$.

Hereafter, assume that the active mass of the anode (this electrode is chosen for calculating the working parameters) is characterized by the values listed in Table 1.

Here, recall that, earlier [3], the problem of choosing an optimal g_{opt} for a fraction of intercalating agent grains in the active layer of the anode, at which a specific anode capacitance can reach the maximum value, was formulated and solved. It was found that not highest admissible value $g = 0.65$ (condition (3)), but a smaller value $g = g_{\text{opt}} = 0.4$ is the optimal fraction of intercalating agent grains. It corresponds to the fraction of active grains of intercalating agent $g^* = 0.348$, the reduced specific surface area of the contact between the electronic and ionic percolation clusters, at which the electrochemical reaction proceeds, $\zeta = SL = 1.167$, an average number of electrochemically active faces of active intercalating agent grain $\bar{n} = 3.35$, and a conductivity of lithium ions in the percolation ionic clusters $k^* = 0.231$. All these data will be used to estimate and calculate the working parameters of the anode.

First, factor $(\zeta i_0/g^*Fc^*)$ in equation (32) will be estimated. For $g = g_{\text{opt}} = 0.4 \times (\zeta i_0/g^*Fc^*) \approx 10^{-7}$ s/cm. Thus, instead of equation (32), we obtain:

$$\alpha = 10^{-7}(L/D). \quad (33)$$

Now, it is important to determine the ranges, where parameter α may be taken to be $\alpha \ll 1$ or $\alpha \gg 1$. Obviously, the dimension of intercalating agent grain cannot be smaller than the minimum value $L = 10^{-6}$ cm (10 nm). Substituting this value into (33), we obtain that $\alpha \leq 0.1$ provided that

$$D \geq 10^{-12} \text{ cm}^2/\text{s}. \quad (34)$$

Hereafter, this range of diffusion coefficient in the active grain of intercalating agent will be named the range of high D values.

It should be noted that high values prescribed for D require the estimation of highest admissible values of intercalating agent grain size L . According to (33), at $D = 10^{-12}$ cm²/s, the intercalating agent grain should strictly have a size $L = 10^{-6}$ cm. At $D = 10^{-11}$ cm²/s, L will fall into the range $10^{-6} \leq L \leq 10^{-5}$ cm. At $D = 10^{-10}$ cm²/s, L will fall into the range $10^{-6} \leq L \leq 10^{-4}$ cm. At $D = 10^{-9}$ cm²/s, L will fall into the range $10^{-6} \leq L \leq 10^{-3}$ cm; at $D = 10^{-8}$ cm²/s, L will fall into the range $10^{-6} \leq L \leq 10^{-2}$ cm.

Now we consider the range of low diffusion coefficients D , at which $\alpha \geq 10$. Clearly, here, the diffusion coefficient will satisfy the following inequality:

$$D \leq 10^{-13} \text{ cm}^2/\text{s}. \quad (35)$$

As for the size of intercalating agent grains, according to (33), at $D = 10^{-13}$ cm²/s, $L \geq 10^{-5}$ cm; at $D = 10^{-14}$ cm²/s and lower, the upper size of intercalating agent grain can be as large as is wished.

To calculate the working parameters of the anode, it is important to determine the ranges of D and L , where parameter α is large or, conversely, small. Let us consider the case that $\alpha \leq 0.1$. Physically, this means that the diffusion process in the active grain of intercalating agent proceeds with a high rate, whereas the potentials in the anode active layer vary slowly (equation (9)). We use this important fact. The problem will be solved in two steps. First, equation (19) with boundary conditions (24) and (25) will be solved, the relationship between \check{c} and a_s will be determined; then, we will pass to the calculation of system of equations (9) and (14).

At $\alpha \leq 0.1$, the processes in the active layer proceed with a low rate; therefore, we can suppose that the current density j varies slowly. Then, in accordance with the definition (25), we may believe that parameter B is constant (equation (27) is valid). Thus, for the anodes with high diffusion coefficients (condition (34)), equation (31) is valid. The algorithms of computer calculations and the computations of the working parameters are significantly simplified. An example of such calculations for the anodes was given earlier [12].

This brings up the question: What can be done for the anodes (and cathodes) with low diffusion coefficients (condition (35))? The answer is as follows. First, we invoke the fact that the galvanostatic mode of discharge of lithium-ion battery electrodes is considered. Then, also for the anodes with $D \leq 10^{-13}$ cm²/s (more precisely, for the anodes with $\alpha \geq 10$), which possess sufficiently thin active layer, the working parameters can be calculated rather simply.

5. THIN ACTIVE LAYERS

Now, an anode with a very thin active layer of thickness Δ is considered. Assume that the following criterion is true:

$$\Delta \ll L_{\text{ohm}} = (2RTk^*k/FSi_0)^{1/2}. \quad (36)$$

The thickness of anode active layer is much smaller than the characteristic ohmic length (equation (10)). Then, the values \check{c} , ψ , and j will be constant across the active layer width: all active grains of intercalating agent will make equal contributions to the anode discharge. Actually, here, it is possible to analyze the work of an individual active grain of intercalating agent.

In a thin active layer, obviously, the following condition is fulfilled:

$$I = Sj\Delta = Si_0[(1 - a_s)^{1/2} a_s^{1/2}]\{e^\eta - e^{-\eta}\}\Delta. \quad (37)$$

There are virtually no ohmic limitations in the anodes with a thin active layer; therefore, there is no need to perform the calculations by equation (9), the reduced polarization and reduced potential are constant, and, instead of equation (14), after straightforward transformations, the following simple equation is obtained:

$$d\check{c}/dt^{**} = -j/i_0 = -\beta, \quad (38)$$

where

$$\beta = I/Si_0\Delta = LI/\zeta i_0\Delta, \quad (39)$$

It has the solution

$$\check{c} = c_0/c^* - \beta t^{**}, \quad (40)$$

where c_0 is the initial concentration of lithium atoms in the active grain of intercalating agent.

We need also an equation for the anode potential E . With regard for equations (5)–(7), it takes the following form:

$$E = (2RT/F) \operatorname{arcsinh} \left\{ (\beta/2) / \left[(1 - a_s)^{1/2} a_s^{1/2} \right] \right\} - 0.16 + 1.32 \exp(-3\check{c}). \quad (41)$$

In what follows, an obvious (see equations (15), (21), and (32)) equation:

$$t^* = t^{**}/\alpha. \quad (42)$$

will be also useful.

Then, with regard for the set of equations (31), (40)–(42), we obtain the following systems of equations:

$$\check{c} = a_s + \lambda\beta \left\{ 1/3 - (2/\pi^2) \Sigma \exp(-k^2\pi^2 t^{**}/\alpha) / k^2 \right\}. \quad (43)$$

$$E = (2RT/F) \operatorname{arcsinh} \left\{ (\beta/2) / \left[(1 - a_s)^{1/2} a_s^{1/2} \right] \right\} - 0.16 + 1.32 \exp \left(-3 \left[a_s + \lambda\beta \left\{ 1/3 - (2/\pi^2) \Sigma \exp(-k^2\pi^2 t^{**}/\alpha) / k^2 \right\} \right] \right), \quad (44)$$

$$a_s = c_0/c^* - \beta t^{**} - \lambda\beta \times \left\{ 1/3 - (2/\pi^2) \Sigma \exp(-k^2\pi^2 t^{**}/\alpha) / k^2 \right\}. \quad (45)$$

Table 2. The data used for calculating the working parameters of anode with a thin active layer and a low diffusion coefficient

$D, \text{cm}^2/\text{s}$	L, cm	$\Delta, \mu\text{m}$	$L_{\text{ohm}}, \mu\text{m}$	α	λ	$C^*, \text{C}/\text{cm}^2$
10^{-13}	10^{-5}	0.995	9.95	11.58	11.57	0.07
10^{-13}	10^{-4}	3.15	31.5	115.8	115.7	0.222
10^{-14}	10^{-5}	0.995	9.95	115.8	115.7	0.07

Table 3. The reduced capacitance and reduced discharge time for various discharge currents

$I, \text{mA}/\text{cm}^2$	t^{***}	C/C^*
1×10^{-4}	701.2	1.0
1×10^{-3}	69.8	0.995
1×10^{-2}	6.68	0.953
1×10^{-1}	0.373	0.533
1.0	3.87×10^{-3}	0.055

II. If $\alpha \geq 1$,

$$\check{c} = a_s + \lambda\beta \left\{ \frac{1}{3} - \left(\frac{2}{\pi^2} \right) \Sigma \exp(-k^2\pi^2 t^*) / k^2 \right\}, \quad (46)$$

$$E = (2RT/F) \operatorname{arcsinh} \left\{ \frac{(\beta/2)}{\left[(1-a_s)^{1/2} a_s^{1/2} \right]} \right\} - 0.16 + 1.32 \exp \left(-3 \left[a_s + \lambda\beta \left\{ \frac{1}{3} - \left(\frac{2}{\pi^2} \right) \Sigma \exp(-k^2\pi^2 t^*) / k^2 \right\} \right] \right), \quad (47)$$

$$a_s = c_0/c^* - \alpha\beta t^* - \lambda\beta \times \left\{ \frac{1}{3} - \left(\frac{2}{\pi^2} \right) \Sigma \exp(-k^2\pi^2 t^*) / k^2 \right\}. \quad (48)$$

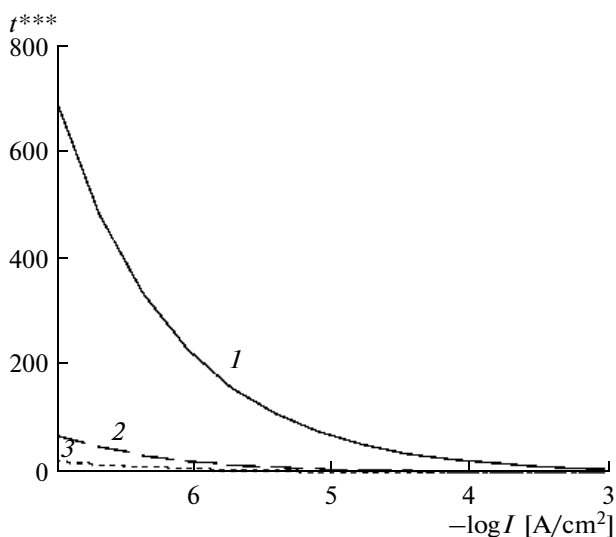


Fig. 1. The anode of lithium-ion battery with a thin active layer ($\Delta = 1 \mu\text{m}$ thick). The dependences of reduced discharge time t^{***} on the discharge current I ; $g = 0.4$; the parameters of intercalating agent grains: (1) $D = 10^{-13} \text{cm}^2/\text{s}$ and $L = 10^{-5} \text{cm}$; (2) $D = 10^{-14} \text{cm}^2/\text{s}$ and $L = 10^{-5} \text{cm}$; and (3) $D = 10^{-13} \text{cm}^2/\text{s}$ and $L = 10^{-4} \text{cm}$.

Obviously, in equations (43)–(45), among two parallel processes with times t^* and t^{**} , we are interested of slow process (t^{**}); in equations (46)–(48), the process with t^* appears to be slow.

6. CALCULATION OF WORKING PARAMETERS AT $\alpha \geq 1$

The set of equations (46)–(48) enables us to calculate the working parameters of anode with a thin active layer and a low diffusion coefficient of atoms in the active grain of intercalating agent. This can be done with the help of the data listed in Table 2. They are based on the set of data listed in Table 1, the definition of a thin active layer

$$\Delta = L_{\text{ohm}}/10 \quad (49)$$

and the equation that determines the maximum possible anode capacitance

$$C^* = g^* F c_0 \Delta. \quad (50)$$

Table 2 presents three versions of the couples of diffusion coefficient (the first column) and anode grain dimension (the second column). Obviously, the active layer thickness Δ (the third column) should exceed the anode grain dimensions; therefore, we cannot consider other versions of the couples of D and L presented in Table 2. However, this set will be sufficient to make important conclusions about the functioning of the electrodes with low diffusion coefficients.

First, based on equations (46)–(48), the time of complete anode discharge will be calculated. To do this, it is assumed that $a_s = 0$ in (48) and the discharge current I (correspondingly, parameter β , equation (39)) is varied. As a result, the reduced time of anode discharge $t^* = t^{***}$ (divided by τ^*) is obtained. Figure 1 gives the dependences of t^{***} on I for three couples of D and L .

The above calculation enables us to estimate the specific capacitance of anode by the following obvious equation:

$$C = I t^{***} \tau^*. \quad (51)$$

Figure 2 gives the dependences of reduced capacitance C/C^* on the discharge current I .

The capacitance increases from zero at high currents and reaches the limiting value in the current range $10^{-4} \leq I \leq 10 \text{ mA}/\text{cm}^2$. Table 3 shows the variation of t^{***} and C/C^* in this range.

It should be noted that the anode is thin and, therefore, its maximum possible specific capacitance is

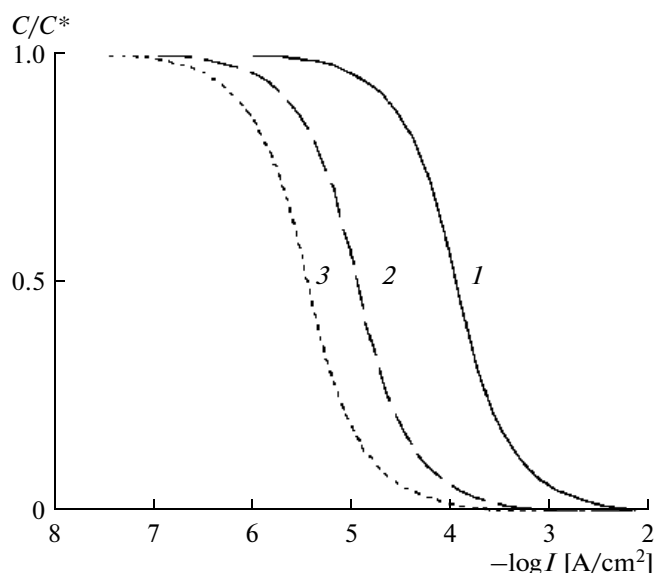


Fig. 2. The anode of lithium-ion battery with a thin active layer ($\Delta = 1 \mu\text{m}$ thick). The dependences of reduced specific capacitance C/C^* on the discharge current I ; $C^* = 0.07 \text{ C/cm}^2$; $g = 0.4$; the parameters of intercalating agent grains: (1) $D = 10^{-13} \text{ cm}^2/\text{s}$ and $L = 10^{-5} \text{ cm}$; (2) $D = 10^{-14} \text{ cm}^2/\text{s}$ and $L = 10^{-5} \text{ cm}$; and (3) $D = 10^{-13} \text{ cm}^2/\text{s}$ and $L = 10^{-4} \text{ cm}$.

small. The maximum capacitances $C_{\text{max}} = C^*$ for three couples of D and L are presented in Table 4.

The specific capacitance, as well as the discharge time, decrease to zero with increasing discharge current or, in other words, when the discharge current reaches the highest possible value I^* and parameter β reaches a value $\beta = \beta^*$. Physically, this means that, upon reaching the limiting current I^* , the active grains of intercalating agent lose their ability to donate lithium atoms. In the intercalating agent, immediately after switching-on the current, the concentration of lithium atoms on the grain surface a_s falls to zero, and the anode potential at the active layer/interelectrode space interface tends to infinity.

Figure 3 gives the dependences of C/C^* on the parameter β . One more important value $\beta = \beta^{**}$ can be recognized (correspondingly, one more characteristic current $I = I^{**}$ is introduced). For example, assume that at β^{**} , 95% lithium atoms are recovered from active grains of intercalating agent. Then, we can suppose that, at $\beta < \beta^{**}$ (correspondingly, at the discharge currents $I < I^{**}$), almost all lithium atoms are

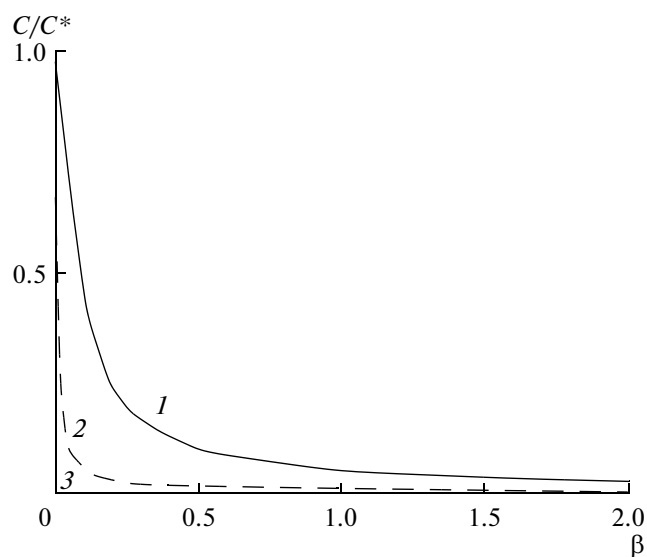


Fig. 3. The anode of lithium-ion battery with a thin active layer ($\Delta = 1 \mu\text{m}$ thick). The dependences of reduced specific capacitance C/C^* on the parameter β . A thin active layer; $g = 0.4$; the parameters of intercalating agent grains: (1) $D = 10^{-13} \text{ cm}^2/\text{s}$ and $L = 10^{-5} \text{ cm}$; (2) $D = 10^{-14} \text{ cm}^2/\text{s}$ and $L = 10^{-5} \text{ cm}$; and (3) $D = 10^{-13} \text{ cm}^2/\text{s}$ and $L = 10^{-4} \text{ cm}$.

already removed from active grains of intercalating agent. Table 4 lists all above values.

Figure 4 gives the dependences of averaged concentration of lithium atoms in the intercalating agent grains \check{c} (the dashed lines calculated by equations (46) and (48)) and the concentration of lithium atoms on the surface of active grain of intercalating agent a_s (solid lines) on the reduced time $t^* = t/\tau^*$. The anode discharge should be terminated, when the concentration of lithium atoms on the surface of active intercalating agent grains reaches an arbitrary chosen threshold value, for example, $a_s = 0.01$.

On Fig. 4, initially, the profile of concentrations of lithium atoms in the active grains \check{c} and a_s is constant ($c_0/c^* = 0.7$); then, the points of the plots of \check{c} vs. t^* and a_s vs. t^* start to descend. At a low anode discharge current $I = 10^{-2} \text{ mA/cm}^2$ (Fig. 4a), the concentrations \check{c} and a_s almost coincide; this enables one to recover virtually completely lithium atoms from active grains of intercalating agent. When the discharge current is raised by ten times (at $I = 3.162 \times 10^{-2} \text{ mA/cm}^2$,

Table 4. The maximum capacitances for three couples of D and L

$D, \text{ cm}^2/\text{s}$	$L, \mu\text{m}$	$I^*, \text{ mA/cm}^2$	β^*	$I^{**}, \text{ mA/cm}^2$	β^{**}	$C_{\text{max}}, \text{ C/cm}^2$
10^{-13}	10^{-5}	1×10^{-3}	0.861	1.1×10^{-5}	9.2×10^{-3}	0.07
10^{-13}	10^{-4}	3.5×10^{-5}	0.097	4.3×10^{-7}	1.2×10^{-3}	0.222
10^{-14}	10^{-5}	1.1×10^{-4}	0.096	1.1×10^{-6}	9.9×10^{-4}	0.07

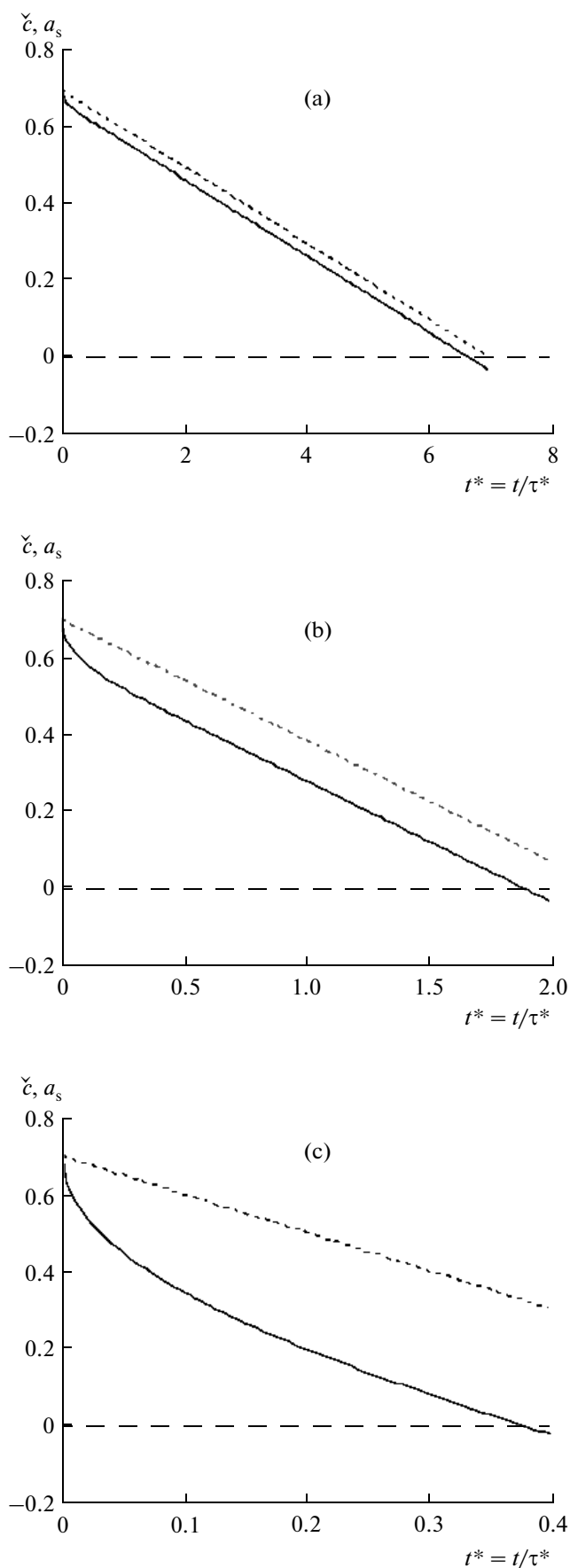


Fig. 4. The dependences of averaged concentration \check{c} of lithium atoms in the bulk of active intercalating agent grain (the dashed lines) and the concentration a_s of lithium atoms at the active intercalating agent grain/electrolyte interface (solid lines) on the reduced discharge time $t^* = t/\tau^*$. The discharge current I , mA/cm²: (a) 10^{-2} , (b) 3.162×10^{-2} , and (c) 10^{-1} . $g = 0.4$; the parameters of intercalating agent grains: (I) $D = 10^{-13}$ cm²/s and $L = 10^{-5}$ cm.

Fig. 4b), the \check{c} profile falls behind the a_s profile. At $I = 10^{-1}$ mA/cm² (Fig. 4c), the difference between the curves of \check{c} and a_s becomes substantial. Therefore, an intercalating agent grain is only partially free of lithium atoms.

It also makes sense to follow the variation of anode potential E with decreasing concentration of lithium atoms on the surface of active intercalating agent grain (a_s decreases from the initial value c_0 to zero). We now turn our attention to equation (47). Figure 5 gives the plots of E vs. a_s for two couples of D and L parameters and four values of parameter β in the range of β^* and β^{**} .

At $a_s = 0$, the potential difference tends to infinity (equation (5)); therefore, for example, $a_s = 0.1$ can be taken as the limiting small value (Fig. 5, vertical dashed lines). The calculations show (Figs. 5a and 5b) that potential E , first, slightly increases with decreasing concentration of lithium atoms on the grain surface a_s ; then, when a_s approaches zero, the potential begins to increase steeply. However, on the whole, the values of potential are not high, because we consider the anodes with a thin active layer.

Figure 6 shows the time dependences of anode potential E for the anode with a couple of parameters of active intercalating agent grain $D = 10^{-13}$ cm²/s and $L = 10^{-5}$ cm at several discharge currents I . The discharge current was varied from 10^{-4} to 10^{-1} mA/cm². The potential increases steeply when the discharge current approaches its limiting value, at which the intercalating agent grain loses its ability to donate lithium atoms during the discharge.

One more important remark should be made. The electrodes exhibiting high and low diffusion coefficients of lithium atoms in the intercalating agent grains are essentially different. The point is that, in view of equation (10) and equation $S = \zeta/L$, the electrode capacitance can be approximately estimated by the following evident relationship:

$$C \sim Fg^*c_0L_{\text{ohm}} \sim L^{1/2}. \quad (52)$$

As was noted above, in the electrodes with high D , the grain dimension L is limited above, whereas in the electrodes with low D , there is no restriction on L . Thus, for the electrodes with high D , their specific capacitance cannot be raised by increasing the grain dimension in the active layer. Therefore, in this case,

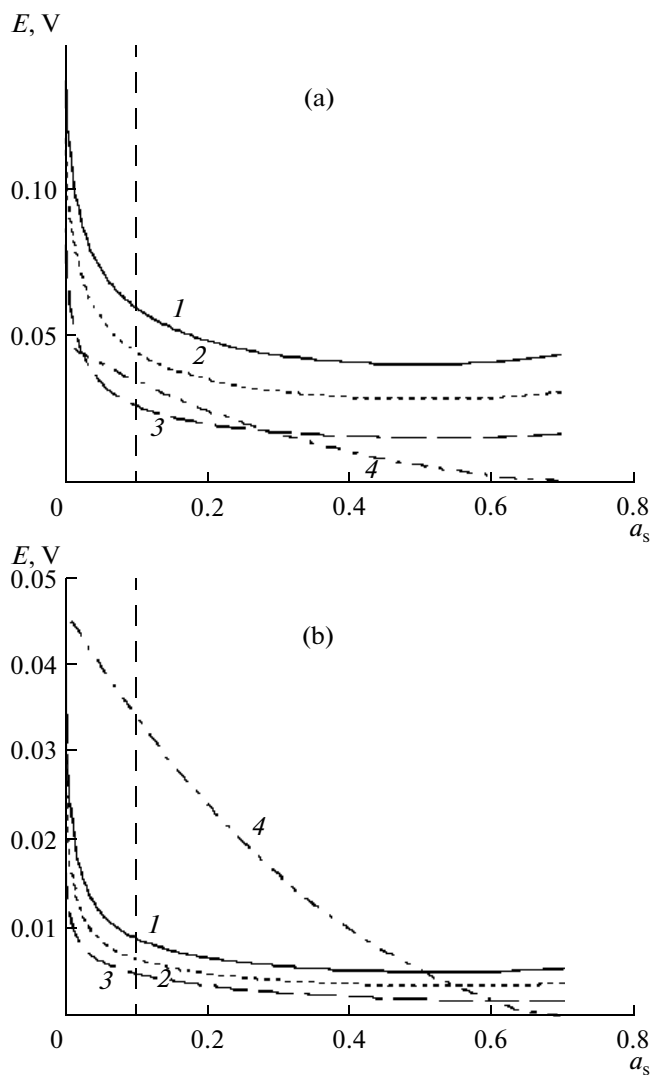


Fig. 5. The dependences of potential E of anode with a thin active layer on the concentration of lithium atoms on the surface of active intercalating agent grains a_s ; $g = 0.4$. The parameters of intercalating agent grains: (a) $D = 10^{-13}$ cm²/s and $L = 10^{-5}$ cm (β : (1) 0.861, (2) 0.577, (3) 0.293, and (4) 0.092) and (b) $D = 10^{-13}$ cm²/s and $L = 10^{-4}$ cm (β : (1) 9.7×10^{-2} , (2) 6.5×10^{-2} , (3) 3.3×10^{-2} , and (4) 1.2×10^{-3}).

the grain size is limited by approximately 10 μm (this problem was discussed in detail earlier [4]).

A completely different situation occurs in the electrodes with low D . Here, the growth of grains in the active layer is not limited. Therefore, the electrodes with a high specific capacitance can be obtained by raising parameter L . However, thereby, the discharge current in them will decrease with increasing L .

The matter is that the diffusion current j_d of lithium atoms recovered from the active intercalating agent grain can be estimated by the following simple relationship:

$$j_d \sim F D c^*(\check{c} - a_s)/L \sim D/L. \quad (53)$$

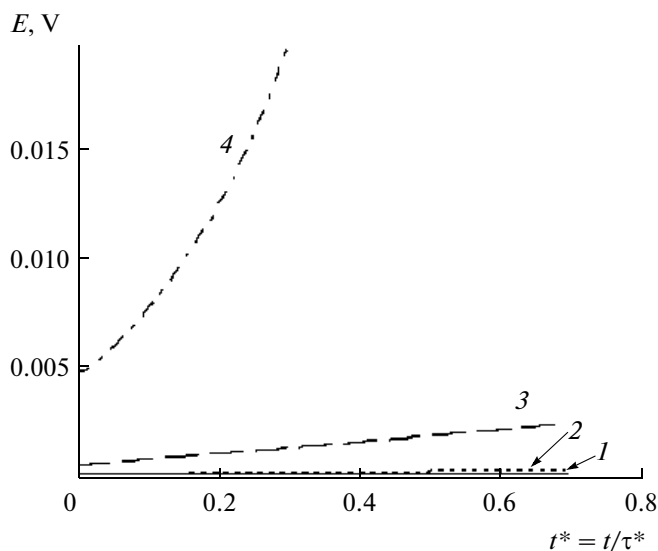


Fig. 6. The dependences of potential E of lithium-ion battery anode on the reduced discharge time $t^* = t/\tau$. The discharge current I , mA/cm²: (1) 10^{-1} , (2) 10^{-2} , (3) 10^{-3} , and (4) 10^{-4} ; $g = 0.4$; the parameters of intercalating agent grains: $D = 10^{-13}$ cm²/s and $L = 10^{-5}$ cm.

Therefore, in the electrodes with low D , an increase in L leads to an increase in the electrode capacitance (equation (52)); however, thereby, the discharge current I (equation (53)) will decrease significantly. The more so as the diffusion coefficient is very low.

The reverse situation is observed in the electrodes with high D . Here, an increase of capacitance due to an increase in the grain size is excluded; however, according to relationship (53), the discharge current can appear to be rather high owing to a high diffusion coefficient D .

7. CONCLUSIONS

Computer simulation of electrodes of lithium-ion battery operating in the galvanostatic discharge mode was performed. Special attention was paid to the complete mathematical description of the processes proceeding in the active layers of the electrodes.

The central problem of the theory of these systems is that two interrelated processes proceed in the active layers of electrodes concurrently in space and time: the diffusion of lithium atoms in the intercalating agent grains and redistribution of potentials over the electrode active layer width, which is caused by the ohmic limitations. It is rather difficult to correlate these processes.

An enormous amount of research has been devoted to the methods of calculating the working parameters of lithium-ion battery electrodes. Unfortunately, the methods are rather complex and consume long computational time. Here, we propose a simplified time-

saving procedure of calculating the electrode working parameters.

A new approach to the central problem is based on comparing the characteristic times of two main processes proceeding in the electrodes. Here, the diffusion coefficient of lithium atoms in the intercalating agent grains is of critical importance. Two ranges of diffusion coefficients (high and low diffusion coefficients) can be recognized.

The calculations of the electrode working parameters (by the example of the anode) are performed for thin active layers with low diffusion coefficients. The active layer thickness, complete discharge time, specific electric capacitance, and final potential at the active layer/interelectrode space interface are determined.

The merits and drawbacks of the electrodes exhibiting high and low diffusion coefficients are discussed.

In the electrodes with high diffusion coefficients, the size of intercalating agent grain is limited above, whereas in the electrodes with low diffusion coefficient, there are no restrictions on the grain size. Thus, in the first case, the electrode specific capacitance cannot be raised by increasing the grain size in the active layer. Therefore, in this case, the grain size is commonly limited by approximately 10 μm . However, the discharge current can be rather high due to a high diffusion coefficient.

A completely different, reverse situation occurs in the electrodes with low diffusion coefficients. Here, the growth of grains in the active layer is not limited. Therefore, the electrodes with a high specific capacitance can be obtained by raising grain size. However, the discharge current in them will decrease with increasing grain size. The more so as the diffusion coefficient is very low in this case.

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

External Parameters

t is the anode discharge time

$t^* = t/\tau^*$ is the reduced current time of the recovery of lithium atoms from an active intercalating agent grain

τ^* is the characteristic time of the recovery of lithium atoms from an active intercalating agent grain

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

τ is the characteristic anode discharge time

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

C , 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

Δ is the thickness of anode active layer

\bar{n} is an average number of electrochemically active faces of active intercalating agent grains

Parameters of Electrochemical Kinetics

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

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

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

i_0 is the exchange current

η is the reduced polarization

ψ is the reduced anode potential

E is the anode potential

U is the open-circuit potential of intercalating agent grain

L_{ohm} is the characteristic ohmic length

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

y is the coordinate in the anode active layer

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

Structure Parameters of Anode Active Layer

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

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

g_l is the bulk concentration of electrolyte grains

L is dimension of grain edges of intercalating agent and electrolyte

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

$\zeta = SL$ is the reduced specific area of contact surface between electronic and ionic percolation clusters

Structure Parameters of Intercalating Agent Grain

c is the concentration of lithium atoms averaged over the volume of intercalating agent grain

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

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

c_0 is the initial degree of filling of intercalating agent grains with lithium atoms

Parameters Determining the Diffusion Processes in an Intercalating Agent Grain

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

a_s is the reduced concentration of lithium atoms near the surface of intercalating agent grain

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

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

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

χ is the parameter determining the mode of recovery of lithium atoms from an intercalating agent grain

Parameters Determining Mass and Electric Transfer

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

k is the electrolyte conductivity

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

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