

Computer Simulation of Negative Electrode Operation in Lithium–Ion Battery: Galvanostatic Discharge, Porous Electrode Model and Film Model

Yu. G. Chirkov^{a, z}, V. I. Rostokin^b, and A. M. Skundin^a

^aA. N. Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences, Moscow, Russia

^bNational Research Nuclear University “Moscow Engineer Technical Institute”, Moscow, Russia

Received May 17, 2010

Abstract—Computer simulation of the structure and methods of operation (galvanostatic discharge) of the negative electrode of a lithium–ion battery is performed. Two possible models of the active anode layer were compared. 1. The model of porous active layer (mixture of active substance grains with grains of electrolyte). Here, the electrochemical process occurs within a porous active layer. 2. The film model (constant–thickness layer) of pure active substance (intercalating agent) grains without admixture of grains of electrolyte. In this case, the electrochemical reaction occurs only on the planar active electrode layer/interelectrode space interface. In both cases, the optimum working parameters of anode active layers were calculated: porous active layer thickness (in the film model, this was the calculation parameter), duration of full anode discharge, specific electric capacitance and finite difference between the intercalating agent/electrolyte potentials at the active anode layer/interelectrode space interface. It is found that each of these two models has its advantages and faults. Specific electric capacitance C cannot exceed the values of the order of magnitude of 10 C/cm^2 when a porous active layer is used. Whereas in the film model, much higher values of C may be obtained: tens and even hundreds of C/cm^2 . On the other hand, in the case of anode discharge, the reasonable discharge current density value, its maximum value, at which practically full recovery of lithium atoms from active intercalating agent grains is still possible, proves to be by orders of magnitude higher in the case of an anode with a porous active layer, as compared with a film–type anode. Thus, in the case of development of electrode active layers of lithium–ion batteries, there is a possibility of choosing from two variants. There is the variant of an active film–type layer providing high capacitance values, but low discharge current density. Or there is another variant: a porous active layer with limited capacitance but then much higher values of discharge current density.

Keywords: lithium–ion battery, negative electrode (anode), galvanostatic discharge, computer simulation, model of equal–sized grains of two types, model of porous active layer, film–type model, calculation of the optimum working parameters of active anode layers

DOI: 10.1134/S1023193511030050

1. PROBLEM STATEMENT

In order to understand the processes occurring in electrodes of a lithium–ion battery, it is useful to compare the operation of their active layers with that of the active layers of the electrodes of a different chemical power source: a hydrogen–oxygen fuel cell with polymer electrolyte.

It is necessary to supply protons into the current generation region in an active layer of a fuel cell cathode, whereas the active layer of a battery anode requires supply of lithium ions for its discharge. An equation for polarization η in the anode active layer may be obtained on the basis of the law of conservation

of lithium ion fluxes in electrolyte (in grains of the ionic percolation cluster):

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

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

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

k is the specific conductivity of electrolyte, k^* is the conductivity of lithium ions in a percolation ionic cluster, S is the specific contact surface between the electronic and ionic cluster, i_0 is the exchange current. The boundary conditions for equation (1) in the case of the galvanostatic discharge mode take the form of:

$$-I_{\text{ohm}}d\eta/d\hat{y} = I = \text{const} \quad \text{at } y = 0, \quad (3)$$

$$d\eta/d\hat{y} = 0 \quad \text{at } y = \Delta, \quad (4)$$

^z Corresponding author: olga.nedelina@gmail.com (Yu.G. Chirkov).

Table 1. Initial parameters of the active material of a lithium–ion battery anode

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

Table 2. Dependence of specific electric capacitance of the anode C on the grain size in the active material L (porous active layer, model of equal–sized grains)

L , cm	C , C/cm ²
10^{-6}	7.3×10^{-2}
10^{-5}	0.23
10^{-4}	0.73
10^{-3}	2.30
10^{-2}	7.30

Δ is the thickness of the anode porous active layer, I is the discharge current, and characteristic ohmic current

$$I_{\text{ohm}} = (2RTk^*kSi_0/F)^{1/2}. \quad (5)$$

An equation similar by its form to (1) could also be written for the active layer of an fuel cell cathode. It would imply expressions for the characteristic ohmic length and characteristic ohmic current similar to definitions (2) and (5).

It is absolutely necessary to increase the specific contact surface S between the electronic and ionic clusters on which the electrochemical process occurs in the active layer of the fuel cell cathode, as the exchange current here is very low, $i_0 \sim 10^{-8}$ A/cm² (at the steady–state potential of 1.05 V). Also, to obtain significant overall current values (several A/cm²), it is necessary to have high characteristic ohmic current (definition (5)). This can be achieved, in particular, by developing surface area S in every possible way.

In fact, development of the surface area on which the electrochemical reaction occurs is the main purpose of organization of an active layer in the fuel cell cathode. The case is quite the opposite as regards the active layer of a lithium–ion battery anode. Here, an increase in S according to definition (2) causes a decrease in the characteristic ohmic length, hence decreasing the specific electric capacitance value of the anode C that may be approximately estimated using the obvious formula:

$$C = Fc^*g^*c_0L_{\text{ohm}} \sim g^*(k^*k/Si_0)^{1/2}, \quad (6)$$

here, c^* is the maximum possible concentration of lithium ions in an intercalating agent grain (active substance grain), g^* is the fraction of active intercalating agent grains [1], c_0 is the initial filling degree of intercalating agent grains by lithium atoms.

Thus, we see that in the case of battery anodes with a porous active layer, its main parameter, the specific elec-

tric capacitance decreases at an increase in S . A decrease in C in the anodes under growing S is very significant, as conductivity of lithium ions in their active mass is two orders of magnitude lower ($k \sim 10^{-3}$ Ohm⁻¹ cm⁻¹) than in the case of cathodes of fuel cells with polymer electrolyte (here, conductivity of protons $k \sim 10^{-1}$ Ohm⁻¹ cm⁻¹) and the exchange current in the active material of a lithium–ion battery anode A is four orders of magnitude higher ($i_0 \sim 10^{-4}$ A/cm²) than that of the fuel cell cathode.

As a result, while in the case of fuel cell cathodes, the specific surface area of the electrochemical reaction zone must be developed in every possible way, in the case of lithium–ion battery anodes, it is necessary to act in the opposite direction: one must where possible try to decrease the S , value which according to condition (6) would promote an increase in the anode specific electric capacitance. Thus, a question appears as to the extent to which it is at all justified to use porous active layer in electrodes of a lithium–ion battery.

It may be shown that specific surface area S on which the electrochemical process occurs is related to the average size of anode grains L (in the model of equal–sized grains [1]) through an obvious relationship:

$$S = \zeta/L, \quad (7)$$

where the value of numerator ζ in (7) is approximately unity [2]. Therefore, the requirement of decreasing surface area S in anodes of lithium–ion batteries with a porous active layer leads to the necessity of forming the active anode material wherever possible with intercalating agent grains of large size.

Let us perform specific estimations. Table 1 presents a rather characteristic set of parameters for the active material of a lithium–ion battery anode. Let us estimate how its specific electric capacitance C changes at an increase in grain size L in the active anode material as based on formulas (2), (6), and (7). Let us choose for the concentration of intercalating agent grains the optimum value of $g = g_{\text{opt}} = 0.4$ (then, as shown in [3], $g^* = 0.348$, $\zeta = 1.2$). As to the quantities of k , i_0 , c^* , they feature at the room temperature the values presented in Table 1. Let us assume $k^* = 0.231$ [2], $c_0 = 0.7$.

Now, let us construct for these parameters the curves of dependence of L_{ohm} on L (Fig. 1). At an increase in L , the characteristic ohmic length increases, and therefore specific electric capacitance of the anode grows according to formula (6), as shown by the data presented in Table 2.

The data of Table 2 allowing making several important conclusions. They explain why the usual average size of the active material (intercalating agent) grains is in the range of $10^{-4} < L < 10^{-3}$ cm (cf. the data of Table 1, where $L = 5 \times 10^{-4}$ cm). Only in an active material with such an intercalating agent grain size, one may reach the specific electric capacitance of the

anode of several C/cm^2 . At lower L values, the anode capacitance becomes very low.

The usual choice of values of $10^{-4} < L < 10^{-3}$ cm also points to the fact that according to formulas (2) and (7), the active layer thickness Δ of an anode with a porous active layer (more precisely, the characteristic ohmic length value) must be in the range of $31 < \Delta < 98$ μm (Fig. 1). But let us stipulate it again, this is an approximate estimate, the lower estimate. The actual thickness of porous active layers of anodes in lithium-ion batteries, as shown further in calculations of working parameters of anodes and supported by the practice of organization of active layers in such anodes, is several hundreds of μm .

Let us turn again to the data of Table 2. The next natural question arises: why do they not work in practice with active anode materials, in which average size of intercalating agent grains would reach $L = 10^{-2}$ cm (hundreds of μm) and higher? Indeed, in that case it would seem possible to increase the electric capacitance of the anode by an order of magnitude (data of Table 2)? We will try to answer this question below.

2. ESTIMATION OF REASONABLE DISCHARGE CURRENT DENSITY

In [3], we suggested a simplified model of the structure of the active intercalating agent grain and the character of the diffusion process in it. It was shown that the actually occurring process of diffusion of lithium atoms is not three-dimensional, but quasiunidimensional.

It was shown that how one can calculate the anode working parameters not approximately, but quite exactly. Namely, the quantitative ratio of concentration \check{c} of lithium atoms in an active intercalation agent grain averaged by its volume and the value of concentration a_s of lithium atoms in an active intercalation agent grain on the surface on which it contacts a grain of electrolyte. However, revealing such a relationship between concentrations \check{c} and a_s was obtained under limitations imposed on the mutual values of two key parameters of an intercalating agent grain: its size L and diffusion coefficient D of lithium atoms in it.

Reasonable discharge current density I^* was also evaluated; it was the maximum current density at which full recovery of lithium atoms from an active intercalating agent grain is still possible. Discharge current I must not exceed a certain reasonable value of I^* . It is also necessary to organize the discharge process so that the values of averaged concentration of lithium atoms in it \check{c} and concentration of lithium atoms on the surface of an active intercalating agent grain a_s practically coincided in the course of recovery of lithium atoms from an active intercalating agent grain. Let the difference $\check{c} - a_s$ be, e.g., about 0.1.

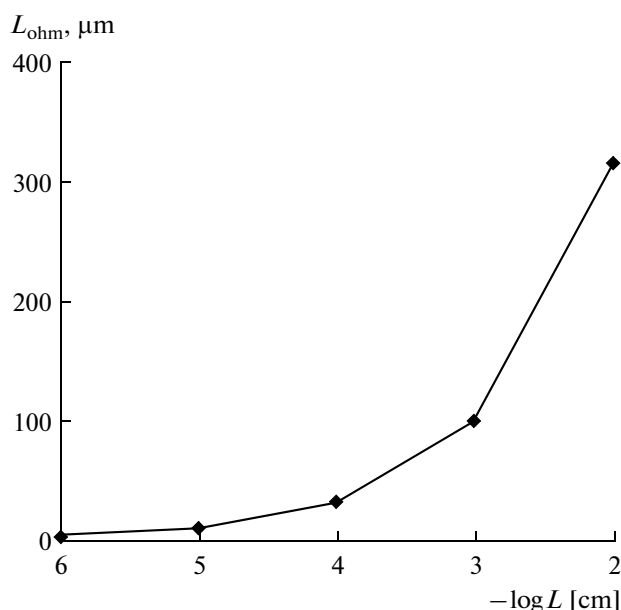


Fig. 1. Dependence of characteristic ohmic length L_{ohm} on the anode grain size L (porous active layer, model of equal-sized grains).

The condition was obtained that provided practically full recovery of lithium atoms from intercalating agent grains; it takes the form of

$$L/D \leq 0.1(g^*Fc^*/\zeta i_0). \quad (8)$$

Condition (8) allows making an important conclusion. Let us assume that the concentration of intercalating agent grains is optimum and equal to $g = 0.4$. Then $g^* = 0.348$ and $\zeta = 1.2$. Besides, let us assume (data of Table 1) that $c^* = 3 \times 10^{-2}$ g-m/cm³, $i_0 = 10^{-4}$ A/cm² and $F = 9.65 \times 10^4$ C/g-m. When these values are substituted into (8), we obtain the following inequality:

$$L/D \leq 10^6. \quad (9)$$

As the size of intercalating agent grains may apparently vary in the range of 10^{-6} cm (10 nm) $\leq L \leq 10^{-2}$ cm (100 μm), according to condition (9), this means that diffusion coefficient D must not be higher than $D = 10^{-12}$ cm²/s (at the minimum value of $L = 10^{-6}$ cm, $L/D = 10^{-6}/10^{-12} = 10^6$). Now, it is impossible to fully recover lithium atoms from intercalating agent grains with diffusion coefficient $D \leq 10^{-13}$ cm²/s.

One should also note that the diffusion coefficient value must have not only the minimum possible value $D = 10^{-12}$ cm²/s, but also the maximum possible value of $D = 10^{-8}$ cm²/s (due to the very nature of the process of recovery of lithium atoms from intercalating agent grains). Thus, setting a particular value of diffusion coefficient D implies setting the values of permissible limits for size L of intercalating agent grains. At $D = 10^{-12}$ cm²/s, according to criterion (9), an intercalating agent grain must have the precise size of $L = 10^{-6}$ cm. At $D = 10^{-11}$ cm²/s, an intercalating agent grain may already

Table 3. Dependence of reasonable current density I^* on the value of admissible values of the diffusion coefficient of lithium atoms in intercalating agent grains D and admissible values of size L of intercalating agent grains. Bulk concentration of intercalating agent grains $g = 0.4$

$L, \text{ cm}$	D/L	$I^*, \text{ A/cm}^2$
	$D = 10^{-12} \text{ cm}^2/\text{s}$	
10^{-6}	10^{-6}	2.9×10^{-4}
	$D = 10^{-11} \text{ cm}^2/\text{s}$	
10^{-6}	10^{-5}	2.9×10^{-3}
10^{-5}	10^{-6}	2.9×10^{-4}
	$D = 10^{-10} \text{ cm}^2/\text{s}$	
10^{-6}	10^{-4}	2.9×10^{-2}
10^{-5}	10^{-5}	2.9×10^{-3}
10^{-4}	10^{-6}	2.9×10^{-4}
	$D = 10^{-9} \text{ cm}^2/\text{s}$	
10^{-6}	10^{-3}	2.9×10^{-1}
10^{-5}	10^{-4}	2.9×10^{-2}
10^{-4}	10^{-5}	2.9×10^{-3}
10^{-3}	10^{-6}	2.9×10^{-4}
	$D = 10^{-8} \text{ cm}^2/\text{s}$	
10^{-6}	10^{-2}	2.9
10^{-5}	10^{-3}	2.9×10^{-1}
10^{-4}	10^{-4}	2.9×10^{-2}
10^{-3}	10^{-5}	2.9×10^{-3}
10^{-2}	10^{-6}	2.9×10^{-4}

have size L within the range of $10^{-6} \leq L \leq 10^{-5}$ cm. At $D = 10^{-10} \text{ cm}^2/\text{s}$, it is within the range of $10^{-6} \leq L \leq 10^{-4}$ cm. At $D = 10^{-9} \text{ cm}^2/\text{s}$, it is in the range of $10^{-6} \leq L \leq 10^{-3}$ cm and at $D = 10^{-8} \text{ cm}^2/\text{s}$, it is in the range of $10^{-6} \leq L \leq 10^{-2}$ cm.

It was also shown that the condition of practically full recovery of lithium atoms from intercalating agent grains requires yet another limitation. The current density of anode discharge (A/cm^2) must not exceed the critical (reasonable) value of I^* equal to

$$I^* = 0.1 Fc^*(D/L) \text{ A/cm}^2. \quad (10)$$

Assuming that $F = 9.65 \times 10^4 \text{ C/g-m}$, $c^* = 3 \times 10^{-2} \text{ g-m/cm}^3$, we have instead of (10):

$$I^* = 2.9 \times 10^2 (D/L) \text{ A/cm}^2. \quad (11)$$

Therefore, for the pair of values of $D = 10^{-12} \text{ cm}^2/\text{s}$ and $L = 10^{-6}$ cm, current $I^* = 0.29 \text{ mA/cm}^2$. Now, for the pair of parameters of $D = 10^{-8} \text{ cm}^2/\text{s}$ and $L = 10^{-6}$ cm, discharge current could apparently rise to a very significant value: $I^* = 2.9 \text{ A/cm}^2$. Dependence of the reasonable discharge current density I^* for the practically possible set of D and L parameters is presented in Table 3.

The data of Table 2 (estimate of specific electric capacitance C of the anode with a porous active layer) corresponded to an ideal case: it was tacitly assumed that diffusion limitations related to the process of recovery of lithium atoms from active intercalating agent grains under battery discharge are practically absent. This could be achieved in principle by consistent decreasing or increasing according to the data of Table 3 the value of reasonable discharge current density I^* . For diffusion coefficient $D = 10^{-10} \text{ cm}^2/\text{s}$ given in Table 1 and usually assumed value of the average grain size in the active material $10^{-4} < L < 10^{-3}$ cm (in Table 1, $L = 5 \times 10^{-4}$ cm), the value of the reasonable discharge current density must be approximately $I^* = 1 \text{ mA/cm}^2$. This is indeed the case.

Let us set ourselves a goal to perform a stricter estimation of specific electric capacitance than follows from the data of Table 2. On the whole, let us also calculate precise values of other anode working parameters. With account for the fact, that not only average grain size L may vary in practice, but also the value of diffusion coefficient D of lithium atoms in intercalating agent grains. To achieve this goal, we have to formulate a full system of equations describing all processes occurring in the porous active layer of a lithium-ion battery anode.

3. SYSTEM OF EQUATIONS FOR ACTIVE ANODE LAYER

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

Current density j generated at the interface of the ionic (the set of interconnected grains of electrolyte) and electronic (the set of interconnected intercalating agent grains) percolation cluster takes the form of:

$$j = i_0 [(1 - a_s)^{1/2} a_s^{1/2}] \{e^{\eta} - e^{-\eta}\}, \quad (12)$$

where a_s is the reduced value of the lithium concentration in active intercalating agent grains on the surface of their contact with grains of electrolyte and reduced polarization

$$\eta = F[E - U]/2RT, \quad (13)$$

where E is the potentials of the intercalating agent and electrolyte, accordingly, and potential U is [4]

$$U = -0.16 + 1.32 \exp(-3\check{c}). \quad (14)$$

Let us assume that the concentration of lithium atoms in active intercalating agent grains is in the range of $0.0 < \check{c} < c_0 = 0.7$.

The process of ohmic limitations in the anode active layer describes the set of the ohmic equations and boundary equations (1)–(5) and the process of decrease in the concentration of lithium atoms in active intercalating agent grains (in the electronic percolation cluster) is described by the following equation:

$$d\check{c}/dt^{**} = -[(1 - a_s)^{1/2} a_s^{1/2}] \{e^\eta - e^{-\eta}\}, \quad (15)$$

here, $\check{c}(y, t)$ is the concentration of lithium atoms averaged by the volume of an active intercalating agent grain at time moment t in the cross-section of the anode active section with coordinate y . The meaning of the rightmost part of equation (15) is a decrease in the concentration of lithium atoms in the intercalating agent grains, as they are oxidized to lithium ions and pass into the ionic percolation cluster. Reduced time takes the form of

$$t^{**} = t/\tau, \quad (16)$$

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

$$\tau = g^* F c^* / S i_0. \quad (17)$$

The initial condition for equation (15) is:

$$\check{c} = c_0 \quad \text{at } t = 0. \quad (18)$$

Thus, the set of equations (1) and (15) would seem to allow tracing changes in reduced polarization in time and in each point of the anode active layer:

$$\psi = FE/2RT \quad (19)$$

and concentration of lithium atoms \check{c} averaged by the volume of active intercalating agent grains. But this can be done only in the case when the value of concentration a_s of lithium atoms on the surface of an active intercalating agent grain in the rightmost parts of equations (1) and (15) is known. Thus, the system of equations (1) and (15) appears incomplete. One has to elucidate the relationship between quantities a_s and \check{c} . This problem was solved in [4]. It was found that

$$\check{c} = a_s + (\lambda/3)[(1 - a_s)^{1/2} a_s^{1/2}] \{e^\eta - e^{-\eta}\}, \quad (20)$$

where parameter

$$\lambda = L \bar{n} i_0 / F D c^*, \quad (21)$$

and \bar{n} is the average number of electrochemically active faces on intercalating agent active grains.

4. CALCULATION OF WORKING PARAMETERS OF ANODE WITH POROUS ACTIVE LAYER

The results of calculation of the anode working parameters as dependent on the admissible values of diffusion coefficient D of lithium atom in intercalating

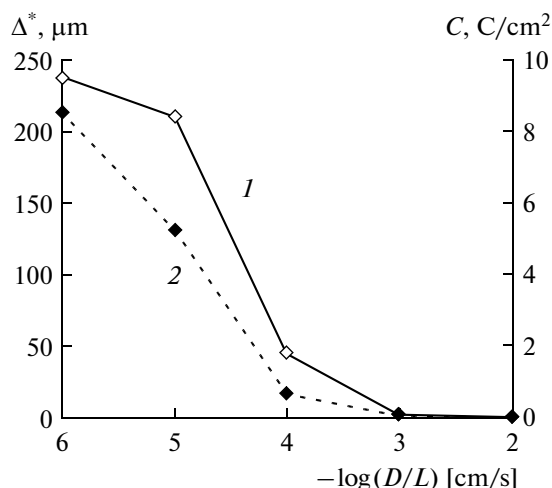


Fig. 2. Dependence of main optimum working parameters of an anode with a porous active layer on parameter D/L (the ratio of the diffusion coefficient to the intercalating agent grain size): (1) active layer thickness, (2) specific electric capacitance.

agent grains and admissible values of size L of intercalating agent grains are presented in Table 4 and in Fig. 2.

At a given value of diffusion coefficient D in the range of admissible values for the grain size L in the active layer, the highest specific electric capacitance $C = 8.51 \text{ C}/\text{cm}^2$ is characteristic of the anode, for which L is maximum and the D/L ratio is minimum. Herewith, the active layer thickness is also maximum, $\Delta^* = 237 \mu\text{m}$. These conclusions agree qualitative with the results of approximate estimations performed in section 1 of this paper (Table 2).

At a decrease in grain size L (at an increase in the D/L ratio), the active layer thickness and accordingly specific capacitance C of the anode start decreasing rapidly. For the pair of parameters $D = 10^{-8} \text{ cm}^2/\text{s}$ and $L = 10^{-6}$ (the maximum possible diffusion coefficient and minimum possible grain size), the value of the anode working parameters becomes already practically indefinite.

The data of Table 4 and Fig. 2 show again that using a porous active layer in the anodes is reasonable only in the case of low values of specific surface area S on which the electrochemical process occurs. Or, which is the same, this is true for active layers that according to condition (7) have the maximum possible grain size.

Besides, the data of Table 4 allow answering the question formulated at the end of section 1 of this paper: why do they not use active anode materials with the intercalating agent grain size $L = 10^{-2} \text{ cm}$. The fact is that one can work with grains of such a large size ($L = 10^{-2} \text{ cm}$) only in one case: if diffusion coefficient $D = 10^{-8} \text{ cm}^2/\text{s}$ (Table 4). But this case is practically impracticable. And at $D < 10^{-8} \text{ cm}^2/\text{s}$, one can obtain practically full recovery of lithium atoms from active

Table 4. Dependence of the optimum working parameters of the anode with a porous active layer on the admissible values of diffusion coefficient D of lithium atoms in intercalating agent grains and admissible values of size L of intercalating agent grains. Bulk concentration of intercalating agent grains $g = 0.4$

$D, \text{cm}^2/\text{s}$	L, cm	D/L	$\Delta^*, \mu\text{m}$	$t^{***}\tau, \text{s}$	$C, \text{C}/\text{cm}^2$	E^*, V
10^{-12}	10^{-6}	10^{-6}	237	2.93×10^4	8.51	1.14
10^{-11}	10^{-6}	10^{-5}	210	1.81×10^3	5.25	1.24
10^{-11}	10^{-5}	10^{-6}	237	2.93×10^4	8.51	1.14
10^{-10}	10^{-6}	10^{-4}	45	22.4	0.65	1.35
10^{-10}	10^{-5}	10^{-5}	210	1.81×10^3	5.25	1.24
10^{-10}	10^{-4}	10^{-6}	237	2.93×10^4	8.51	1.14
10^{-9}	10^{-6}	10^{-3}	2	0.21	0.06	1.36
10^{-9}	10^{-5}	10^{-4}	45	22.4	0.65	1.35
10^{-9}	10^{-4}	10^{-5}	210	1.81×10^3	5.25	1.24
10^{-9}	10^{-3}	10^{-6}	237	2.93×10^4	8.51	1.14
10^{-8}	10^{-6}	10^{-2}	—	—	—	—
10^{-8}	10^{-5}	10^{-3}	2	0.21	0.06	1.36
10^{-8}	10^{-4}	10^{-4}	45	22.4	0.65	1.35
10^{-8}	10^{-3}	10^{-5}	210	1.81×10^3	5.25	1.24
10^{-8}	10^{-2}	10^{-6}	237	2.93×10^4	8.51	1.14

intercalating agent grains under discharge only under the condition that $L \ll 10^{-2} \text{ cm}$ (Table 4).

So, it would seem that we cannot indefinitely increase the size of intercalating agent grains in the active layer. However, fortunately, it is still possible to eliminate the limitations imposed on the grain size. Let us consider the limiting case: let us formally assume $L = \infty$ (then $S = 0$). In other words, let us wholly abandon manufacturing a porous active layer, replacing it by a film of constant thickness of 100% intercalating agent, without admixture of grains of electrolyte. Herewith, the electrochemical process will occur on the minimum possible surface: only in the plane separating the intercalating agent film from the interelectrode space filled with electrolyte.

Two qualitatively different models of the anode active layer structure are presented in Table 3. Fig. 3a shows the model with a porous active layer, while Fig. 3b corresponds to the model with a pure intercalating agent film. Advantages and faults of the model with a porous active layer we discussed in detail above. Now, we will show the advantages and limitations of the film model.

5. FILM MODEL

Let us start studying the anode film model. Distribution of reduced concentration $a = c/c^*$ of lithium atoms in the film follows satisfies the equation:

$$da/dt^* = d^2a/dz^2, \quad (22)$$

where reduced coordinate z in the film with thickness δ is

$$z = x/\delta, \quad (23)$$

and reduced time

$$t^* = t/\tau, \quad (24)$$

where τ is the characteristic time determined by the following expression:

$$\tau = \delta^2/D, \quad (25)$$

D is the diffusion coefficient of lithium atoms in the film (in intercalating agent grains).

Let us write down the initial and boundary conditions for equation (22). We have:

$$a \equiv c_0 \quad \text{at } t = 0, \quad (26)$$

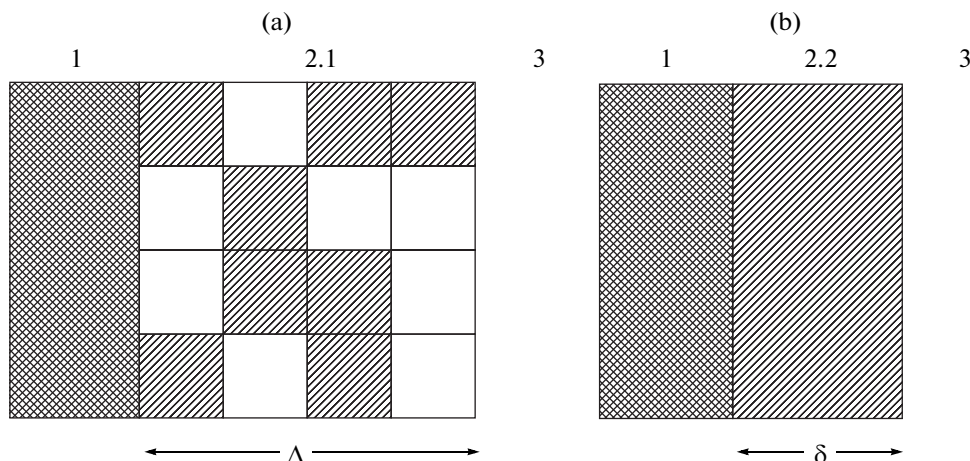


Fig. 3. Scheme of two types of the anode of a lithium-ion battery: (a) with a porous active layer, (b) with an intercalating agent film. (1) current tap, (2.1) active layer, the model of equal-sized cubic intercalating agent grains (shaded) and grains of electrolyte (white), Δ is the active layer thickness, (2.2) intercalating agent film, δ is the film thickness, (3) electrolyte in the interelectrode space.

on the film surface closed for exchange of lithium atoms,

$$da/dz = 0 \quad \text{at } z = 0, \tag{27}$$

on the film surface contacting electrolyte (condition of equality of fluxes of lithium atoms and ions in the plane separating the anode from the interelectrode space)

$$-\chi da/dz = \left[(1 - a_s)^{1/2} a_s^{1/2} \right] \{ e^\eta - e^{-\eta} \} = I/i_0 = \text{const} \quad \text{at } z = 1, \tag{28}$$

where parameter

$$\chi = F D c^* / \delta i_0. \tag{29}$$

Finally, we have instead of (28)

$$da/dz = -I\delta / F D c^* = B = \text{const} \quad \text{at } z = 1. \tag{30}$$

The analytical solution for equation (22) with boundary and initial conditions (26), (27), (30) takes the form of:

$$a(z, t^*) = c_0 + B \left(t^* + \frac{3z^2 - 1}{6} + \frac{2}{\pi^2} \times \sum_{k=1}^{\infty} (-1)^{k+1} \frac{\cos(k\pi z)}{k^2} \exp(-k^2 \pi^2 t^*) \right). \tag{31}$$

Integration of the rightmost part of formula (31) through the film depth allows finding how volume-averaged concentration a_t of lithium atoms in an active intercalating agent grain changes in time. It appears that this value may be evaluated using the formula:

$$a_t = c_0 - a_1 = c_0 + B t^* = c_0 - (I\delta / F D c^*) t^*, \tag{32}$$

where a_1 is the amount of lithium atoms recovered from the intercalating agent film up to the time moment t^* .

If one assumes $z = 1$ in formula (31), one can determine how the concentration of lithium atoms on the film face surface a_s changes in time. Namely,

$$a_s = c_0 + B \left(t^* + \frac{1}{3} - \frac{2}{\pi^2} \sum_{k=1}^{\infty} \frac{\exp(-k^2 \pi^2 t^*)}{k^2} \right). \tag{33}$$

We will assume further for definiteness that the process of recovery of lithium atoms from the intercalating agent film stops if the a_s value decreases to $a_s = 0.01$. Thus, the conditional moment of the end of discharge of an anode with a film $t^* = t^{**}$ will be determined by relationship (33), if one assumes $a_s = 0.01$.

Recovery of lithium atoms from an intercalating agent film may be performed to various degrees. This value must be specified in advance. Let us assume, e.g., that the amount of lithium atoms in the film decreased by 10 times and dropped down to $a_t = 0.07$ (assuming that the initial value was $c_0 = 0.7$). Then it follows from (32) that $-B t^* = c_0 - a_t = a_1 = 0.63$. This condition together with condition (33), in which $a_s = 0.01$, allows determining the pair of the sought-for values: parameter $-B t^*$ and the moment of the end of discharge t^{**} .

There is another possible way of solving the same problem. Through simple transformations of conditions (32) and (33), after excluding time t^* , one can show that

$$a_t = 0.01 - B \left\{ 1/3 - (2/\pi^2) \sum \exp[-k^2 \pi^2 (a_t - c_0)/B] \right\}. \tag{34}$$

In condition (34), the a_t quantity is a function of a single variable B . Fig. 4 presents the graphic solution of

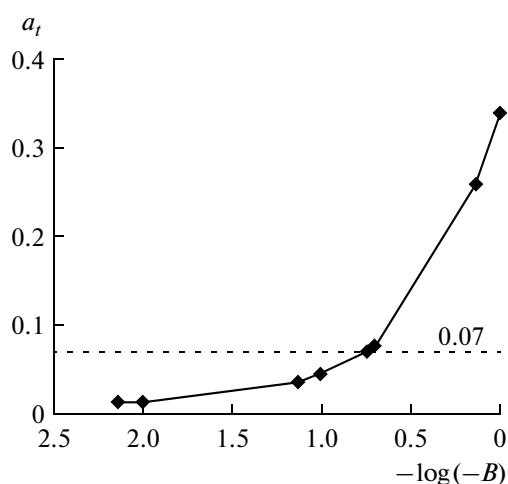


Fig. 4. Dependence of the concentration of lithium atoms a_t averaged by the volume of the active intercalating agent grains in the film on the value of parameter B .

equation (34) for the B value. The growing curve constructed in Fig. 4 (the rightmost part of equality (34) at $a_t = 0.07$) is the function of $\log(-B)$, its intersection with the dashed horizontal ($a_t = 0.07 = \text{const}$) and yields the sought-for value of $-B^* = 0.18$. Herewith, $t^{**} = 3.5$.

Table 5. Dependence of parameter $-B^*$, amount (fraction) of lithium atoms recovered from the intercalating agent film a_1 , and reduced discharge time t^{**} on the final amount (fraction) of lithium atoms in the intercalating agent film a_t

a_t	$-B^*$	a_1	t^{**}
0.038	1	0.362	0.362
0.258	0.744	0.442	0.595
0.077	0.200	0.623	3.117
0.070	0.180	0.630	3.500
0.043	0.100	0.657	6.567
0.035	0.074	0.665	8.941
0.013	0.010	0.687	68.670
0.012	0.007	0.688	92.410

The same operations may also be performed for a number of other a_t values differing from $a_t = 0.07$. The results of calculations of triads a_1 , t^{**} , and $-B^*$ as functions of the chosen a_t value (at $c_0 = 0.7$) are presented in Table 5. As the amount of lithium atoms recovered from the film increases (the third column in Table 5), the discharge time grows (the fourth column in Table 5) and the value of parameter $-B^*$ decreases (the second column in Table 5).

6. CALCULATION OF WORKING PARAMETERS OF FILM-TYPE ANODE

Having determined B^* (the value of parameter B at which a certain amount of lithium atoms remains in the grain after the end of discharge, e.g., $a_t = 0.07$), one may also find the threshold value of discharge current I^* corresponding to the value of B^* . According to definition (30),

$$I^* = -B^* F D c^* / \delta. \quad (35)$$

Specific capacitance C of the film appears to be as follows (let us stress that the whole film and not its fraction takes part in the process of diffusion recovery of lithium atoms from the film):

$$C = F c^* a_1 \delta. \quad (36)$$

Herewith, the film-type anode discharge time expressed in seconds is determined by the following formula:

$$t^{***} = t^{**} \tau = t^{**} \delta^2 / D. \quad (37)$$

Let us perform numeric evaluation of quantities I^* , C , and t^{***} . The parameter will be film thickness δ . Let us assume $D = 10^{-10}$ cm²/s, $F = 9.65 \times 10^4$ C/g-m, $c^* = 3 \times 10^{-2}$ g-m/cm³. Besides, let us assume that $a_t = 0.07$, then $a_1 = 0.63$, $-B^* = 0.18$, $t^{**} = 3.5$. The results of variation of δ are presented in Table 6. The thicker the film (the higher δ), the lower discharge current density I^* and the higher specific electric capacitance C and discharge time t^{***} .

The data of Table 6 point to a very importance circumstance. Let us compare the data of Table 4 and Table 6. In the presence of a porous active layer (Fig. 3a), the value of specific electric capacitance C cannot rise above 8.51 C/cm². While in the case of a film active layer structure (Fig. 3b), specific capacitance may assume the values that are an order of magnitude higher. On the whole, according to formula (3b), specific capacitance would appear to grow indefinitely at an increase in the film thickness. Unfortunately, in this case, the value of physically reasonable discharge current density I^* (formula (35)) also decreases indefinitely.

According to the data of Tables 3, 4, specific capacitance $C = 8.51$ C/cm² (for the anode with $D = 10^{-10}$ cm²/s and grain size $L = 1$ μ m) corresponds to physically reasonable current density $I^* = 0.29$ mA/cm². While in the case of an intercalating agent film with thickness

$\delta = 10^{-2}$ cm, specific capacitance $C = 18.2$ C/cm² (data of Table 6) corresponds to physically reasonable current density that is by two orders of magnitude lower: $I^* = 5.21 \times 10^{-3}$ mA/cm². Thus, the film model of an active anode layer allows increasing significantly specific capacitance of the anode, but this is reached at the cost of high losses in the physically reasonable discharge current density value.

The value of the latter value in the film model may be increased considerably, if one does not require practically full ($a_t = 0.07$) recovery of lithium atoms from intercalating agent grains in the film. Let us require that not $a_t = 0.63$ were recovered from the film (data of Table 5, parameter $-B^* = 0.18$), but a lower amount of lithium atoms, e.g., $a_t = 0.442$. The latter value in Table 5 corresponds to parameter $-B^* = 0.744$ and discharge time $t^{***} = 0.595$.

The dynamics of the process of lithium atom recovery from the film for these two cases is shown in Fig. 5. If practically full recovery of lithium atoms from the film is required (a decrease in the concentration from $c_0 = 0.7$ to $a_t = 0.07$, Fig. 5a), then according to (35), the discharge current density $I^* = 5.21 \times 10^{-3}$ mA/cm² at the intercalating agent film thickness of $\delta = 10^{-2}$ cm. Whereas if the atom recovery from the film is partial (from $c_0 = 0.7$ to $a_t = 0.442$, Fig. 5b), then the discharge current density at the same film thickness of $\delta = 10^{-2}$ cm would increase by $0.744/0.18$ times and would reach the value of $I^* = 2.15 \times 10^{-2}$ mA/cm². However, in this case, the specific capacitance of the anode (formula (36)) and its discharge time (formula (37)) would decrease. All these values changing as a result of variation of parameter $-B^*$ are presented in Table 7. It demonstrates how at $-B^* = 0.744$ ($a_t = 0.442$) the main working parameters of the anode vary at an increase in the film thickness: the physically rea-

Table 6. Film anode model. Dependence of reasonable anode discharge current density I^* , its specific capacitance C , and discharge time t^{***} on the intercalating agent film thickness d . Parameter $-B^* = 0.18$ ($a_t = 0.07$)

δ , cm	I^* , mA/cm ²	C , C/cm ²	t^{***} , s
10^{-5}	5.21	1.82×10^{-2}	3.5
10^{-4}	5.21×10^{-1}	0.182	350
10^{-3}	5.21×10^{-2}	1.82	3.5×10^4
10^{-2}	5.21×10^{-3}	18.2	3.5×10^6
10^{-1}	5.21×10^{-4}	182	3.5×10^8

Table 7. Film anode model. Dependence of the anode discharge current density I^* , its specific working capacitance C , and discharge time t^{***} on the intercalating agent film thickness δ . Parameter $-B^* = 0.744$ ($a_t = 0.442$)

δ , cm	I^* , mA/cm ²	C , C/cm ²	t^{***} , s
10^{-5}	21.5	1.28×10^{-2}	0.595
10^{-4}	2.15	0.128	59.5
10^{-3}	0.215	1.28	5.95×10^3
10^{-2}	2.15×10^{-2}	12.8	5.95×10^5
10^{-1}	2.15×10^{-3}	128	5.95×10^7

sonable anode discharge current density I^* , its specific capacitance C , and discharge time t^{***} .

The latter value decreases at an increase in parameter $-B^*$, as shown in Fig. 6, where the dependences of the reduced concentration a_s of lithium atoms on the intercalating agent film/interelectrode space

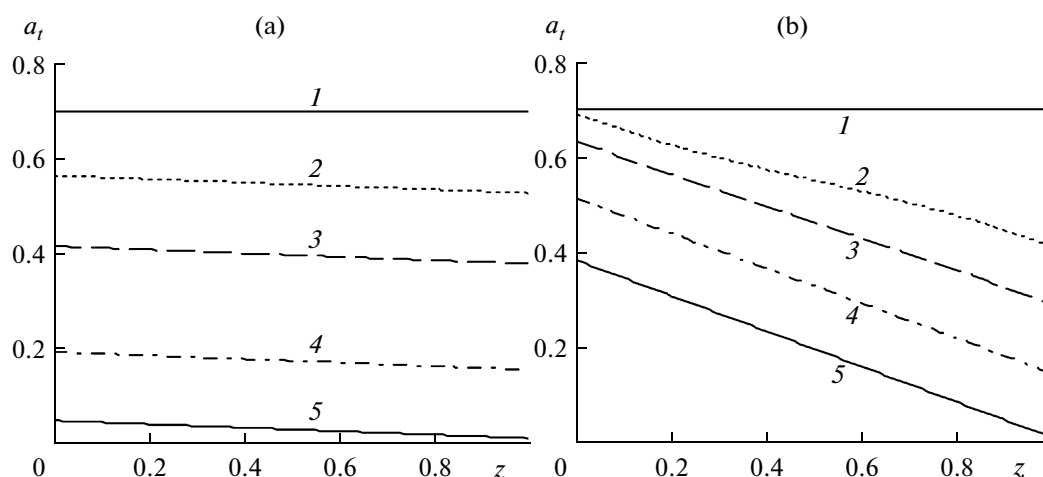


Fig. 5. Distribution of concentration of lithium ions in an intercalating agent film at different moments of anode discharge for two values of parameter $-B^*$: $-B^* = 0.18$ (Fig. 5a, $a_t = 0.07$), t^{***} : (1) 0, (2) 2, (3) 4, (4) 7, (5) 8.941 and $-B^* = 0.744$ (Fig. 5b, $a_t = 0.442$), t^{***} : (1) 0, (2) 0.2, (3) 0.4, (4) 0.7, (5) 1.0.

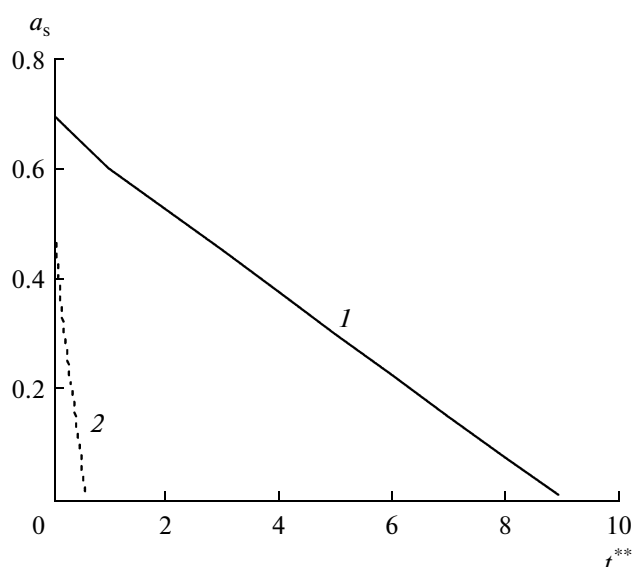


Fig. 6. Dependence of concentration a_s of lithium atoms on the intercalating agent film/interelectrode space interface on reduced time t^{**} for two values of parameter $-B^*$: (1) 0.18 and (2) 0.744.

interface on time are constructed for two values of parameter $-B^*$: 0.18 (curve 1) and 0.744 (curve 2).

7. CONCLUSIONS

Developed (with a high specific surface area S on which the electrochemical process occurs) porous electrode layer is absolutely necessary, e.g., for cathodes of fuel cells with polymer electrolyte and gas reagents. However, as shown by calculations, in the case of anodes of lithium-ion batteries with a porous active layer, it is desirable not to increase the S value, but to decrease it, as the lower the S value and the higher the size of the active material (intercalating agent) grains, the higher the specific electric capacitance of lithium-ion electrodes.

But a decrease in the surface area S of the reaction region has its limits, as the higher the intercalating agent grain size, the more difficult it becomes to recover lithium atoms from active intercalating agent grains in the course of the discharge process. Therefore, two problems appear in the theory of the electrodes of lithium-ion batteries:

(1) What should be the maximum size of intercalating agent grains in the case of using porous electrode active layers?

(2) To what extent is using porous active layers in electrodes of lithium-ion batteries at all justified? Should they be replaced by an intercalating agent film, which would limit the surface area on which the electrochemical reaction occurs to the planar active electrode layer/interelectrode space interface?

In connection with the concepts above in this paper, two models of active anode layers in a lithium-ion battery are consistently compared: the model of a porous active layer and a film model of pure intercalating agent. It is found that each of these two models has its advantages and faults.

Specific electric capacitance C cannot exceed 10 C/cm^2 when a porous active layer is used. Whereas in the film model, much higher values of C may be obtained: tens and even hundreds of C/cm^2 . On the other hand, in the case of the galvanostatic discharge mode, the physically reasonable discharge current density values, its maximum values, at which practically full recovery of lithium atoms from active intercalating agent grains is still possible, prove to be by orders of magnitude higher in the case of an anode with a porous active layer, as compared with a film-type anode.

Thus, in the case of development of electrode active layers of lithium-ion batteries, there is a possibility of choosing from two variants. There is the variant of an active film-type layer providing high capacitance values, but low values of physically reasonable discharge current density. Or there is another variant: a porous active layer with limited capacitance but then much higher values of physically reasonable discharge current density.

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

External Parameters

t is the current discharge time of the anode

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

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

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

τ is the characteristic discharge time of the anode

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

$C, \text{ C/cm}^2$, is the specific electric capacitance of the anode

R is the gas constant

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

Δ is the thickness of the anode active layer

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

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

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

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

I is the anode discharge current

j is the electrochemical reaction current density
 i_0 is the exchange current
 η is the reduced polarization
 ψ is the reduced difference of potentials at the intercalating agent/electrolyte interface
 E is the potential of an intercalating agent grain near the intercalating agent/electrolyte interface
 E^* is the difference of potentials at the intercalating agent/electrolyte interface at the active layer/inter-electrode space interface
 U is the intercalating agent grain potential
 L_{ohm} is the characteristic ohmic length
 I_{ohm} is the characteristic ohmic current
 y is the coordinate of the anode active layer
 $\hat{y} = y/L_{\text{ohm}}$ is the reduced coordinate in the active layer

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

g is the bulk concentration (fraction) of intercalating agent grains
 g^* ($g^* < g$) is the fraction of intercalating agent active grains
 g_i is the bulk concentration of grains of electrolyte
 L is the average diameter of grains of intercalating agent and electrolyte
 S , cm^{-1} , is the specific contact surface area between electron and ion percolation clusters
 c^* is the maximum possible concentration of lithium atoms in an intercalating agent grain
 $\check{c} = c/c^*$ is the reduced concentration of lithium atoms averaged by the intercalating agent grain volume
 $\check{c} = c_0$ is the initial degree of filling of intercalating agent by lithium atoms

*Parameters Determining the Diffusion Processes
in an Active Intercalating Agent Grain*

a is the constant determining the anode operation mode

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

*Parameters Determining the Processes
of Mass and Electric Transfer*

D is the diffusion coefficient of lithium atoms in intercalating agent grains
 k is the specific conductivity of electrolyte
 k^* is the conductivity of lithium atoms in the percolation ionic cluster

Parameter of the Intercalating Agent Film

δ is the intercalating agent film thickness
 a is the reduced concentration of lithium atoms in the film
 a_s is the reduced concentration of lithium on an electrochemically active film surface
 a_t is the concentration of lithium atoms averaged by the film volume at the given time moment
 a_1 is the amount (fraction) of lithium atoms recovered from the film
 $z = x/L$ is the reduced coordinate in the film

REFERENCES

1. Chirkov, Yu.G., Rostokin, V.I., and Skundin, A.M., 1 *Elektrokhimiya*, 2011, vol. 47, no. 1 [*Russ. J. Electrochem.* (Engl. Transl.), vol. 47, no. 1].
2. Chirkov, Yu.G., Rostokin, V.I., and Skundin, A.M., 1 *Elektrokhimiya*, 2011, vol. 47, no. 1 [*Russ. J. Electrochem.* (Engl. Transl.), vol. 47, no. 1].
3. Chirkov, Yu.G., Rostokin, V.I., and Skundin, A.M., 1 *Elektrokhimiya*, 2011, vol. 47, no. 3 [*Russ. J. Electrochem.* (Engl. Transl.), vol. 47, no. 3].
4. Doyle, M., Newman, J., Gozdz, A.S., Schmutz, C.N., and Tarascon, J.-M., *J. Electrochem. Soc.*, 1996, vol. 143, p. 1890.

SPELL: 1. ok