

# Computer Modeling of Negative Electrode Operation in Lithium–Ion Battery: Model of Equal–Sized Grains, Galvanostatic Discharge Mode, Calculation of Characteristic Parameters

Yu. G. Chirkov<sup>a, z</sup>, V. I. Rostokin<sup>b</sup>, and A. M. Skundin<sup>a</sup>

<sup>a</sup>*Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences, Moscow, Russia*

<sup>b</sup>*National Research Nuclear University “Moscow Engineer Technical Institute”, Moscow, Russia*

Received December 23, 2009

**Abstract**—A computer simulation of the negative electrode (anode) operation in a lithium–ion battery is performed. A complete research program is carried out in accordance with the recommendations of the theory of porous electrodes: the “model of equal–sized grains of two types” was studied, percolation properties of the anode active layer were researched, values of effective coefficients were calculated for charge transfer and mass transport, a complete system of equations describing operation of the anode is presented. Two specific cases of galvanostatic mode of anode discharge are considered in detail: an “ideal” anode and anode with nanosize particles. Working anode parameters are calculated: optimum bulk concentration of graphite in the active layer, active layer thickness, time of complete anode discharge, its specific electric capacitance and polarization of the graphite/electrolyte interface on the active/layer interelectrode space interface. Advisability of working with anodes with nanosize grains and electrolyte with enhanced specific conductivity is shown.

**Keywords:** lithium–ionic battery, negative electrode (anode), “ideal anode”, anode with nanosize grains, galvanostatic discharge mode, theory of porous electrodes, computer simulation, model of equal–sized grains, percolation theory, cluster conductivity, intercalation

**DOI:** 10.1134/S1023193511010058

## PROBLEM STATEMENT

The main difficulty in studying the mechanism of operation of any chemical power source, whether a primary cell, a battery, or a fuel cell [1], is related to the necessity of understanding how the active material (active layers) of its electrode function. Here, assistance is rendered by the concepts developed in a special discipline: the theory of porous electrodes. This theory owes its rapid development to achievements in creation of hydrogen–oxygen fuel cells, when special efforts had to be made to organize the so called three–phase interface in the electrode active layers (primarily, cathodes): a region where all participants of the electrochemical process meet: gas, liquid electrolyte and metal (catalyst) [2].

Porous electrodes represent the most important element of many types of industrial electrochemical devices: fuel cells, electrolyzers, setups for electrosynthesis etc. In order to obtain high overall currents or accumulate a sufficient amount of the target product in the porous electrode, it is necessary to organize channels for continuous supply of all its required compo-

nents (reagents, ions, and electrons) to the zone where the electrochemical process occurs for the most part.

As a rule, the porous electrode represents a number of components that are randomly distributed in the active layer. Effective operation of a porous electrode requires formation in the active material of at least two particle clusters providing supply/removal of ions and electrons. Therefore, the main issue in theoretical studies of the mechanism of action of porous electrodes must be research of connectivity of structural elements of various nature participating in organization of the electrochemical process. Thus, the necessity of turning to such a branch of mathematics and theoretical physics as the percolation theory comes to the fore [3].

Computer modeling of a porous electrode of one kind or another consists of a number of successive steps:

(1) Necessity of accounting for the characteristic features of the method of porous electrode active material preparation; clear idea of the structure of the channels supplying all the electrochemical process participants into the active material.

(2) Development of a computer model of the porous electrode structure.

<sup>z</sup> Corresponding author: olga.nedelina@gmail.com (Yu.G. Chirkov).

(3) Studies of percolation properties of such a computer model.

(4) Determination of the values of effective coefficients (electronic and ionic conductivity, diffusion coefficient etc) of the active layer.

(5) Derivation of a system of equations adequately describing the whole set of processes occurring in the active layer.

(6) Calculation of the main overall parameters of the porous electrode.

(7) Optimization of the work of the studied electrode.

This will be our basis in this and further studies for computer simulation of operation of the negative electrode (further designated as the anode) of a lithium–ion battery.

The final aim of the studies is to determine the optimum performance characteristics of the lithium–ion battery anode on the basis of the available parameters of the main anode components of the lithium–ion battery and the given discharge current value.

The performance characteristics are: the optimum bulk concentration of graphite in the active layer, active layer thickness, time of full anode discharge, its specific electric capacitance, and polarization. The parameters are: the average size of graphite grains, maximum lithium concentration in graphite, exchange current of the Li/Li<sup>+</sup> system, diffusion coefficient of lithium atoms in graphite, and specific conductivity of electrolyte on the active material.

### MODEL OF EQUAL-SIZED GRAINS

The history of lithium–ion batteries starts in the early nineties of the last century and studies of mathematical modeling of its operation have been continued practically all these years. Modeling of lithium–ion batteries in all cases was based on the general concepts of electrochemical systems with porous electrodes (see, e.g., [4]).

The overwhelming majority of works represent a lithium–ionic battery as an assembly consisting of two porous electrodes with electrolyte (usually, a matrix) in-between. As a rule, electrochemically active anode components are modeled by a system of equal-sized spheres. The models most often take into account the slow diffusion of lithium atoms in the active material solid phase, slow ion discharge reaction (the electrochemical stage of the electrode process), ohmic resistance of electrolyte (both in the electrolyte matrix and in the electrode pores).

In the present paper, for the sake of simplicity, the variant of a two–phase electrode containing only active material grains and electrolyte is considered (i.e., the presence of the binding agent is not taken into account). It is assumed for definiteness that the active material of the negative electrode is graphite. The essential issue of the present model is also consider-

ation of percolation as the necessary factor contributing to anode operation.

Let us use for the anode active material the model of the structure of the chemical power source active material suggested in the works on computer simulation of cathodes of hydrogen–oxygen fuel cells with solid polymer electrolyte: the model of equal-sized grains (Fig. 1) [5, 6].

In Fig. 1, grains of graphite with lithium atoms are dark gray and grains of electrolyte are light gray. Let us assume further that

$$g + g_1 = 1, \quad (1)$$

where  $g$  is the fraction of the active layer volume corresponding to graphite grains,  $g_1$  is the fraction of the active layer volume corresponding to electrolyte.

Let us consider a 3D model. Let us assume that the plane separating the current collector from the active layer has the coordinate of  $y = \Delta$  ( $\Delta$  is the anode active layer thickness), while the plane separating the active layer from the interelectrode space has the coordinate of  $y = 0$ .

All graphite grains and electrolyte grains are similar. They represent microcubes with edges with the length of  $L$ . Thus, in terms of the percolation theory [3], one must deal in the model of equal-sized grains with the cubic lattice of sites.

### DETERMINATION OF STRUCTURAL PARAMETERS

Percolation properties of the studied computer model of equal-sized grains (the third item in the program of studies of the porous electrode listed in the problem statement) were analyzed in detail in [5, 6]. Electronic (the set of interconnected graphite grains) and ionic (the set of interconnected electrolyte grains) percolation clusters must be organized in the anode for its normal operation.

Let us derive formulas for calculation of all effective coefficients in the equation in the anode active layer (the fourth item in the program of the porous electrode studies). The point in question is the reduced specific surface of contact between electronic and ionic percolation clusters  $SL$  (where the electrochemical process occurs), reduced effective conductivity  $k^*$  of the ionic percolation cluster (grains of electrolyte) and reduced effective diffusion coefficient of lithium atoms  $D^*$  in the electronic percolation cluster (graphite grains).

It is obvious that before reaching the percolation threshold ( $g_1^*$ ) in the cubic lattice, up to the critical value of the concentration of electrolyte grains [7]

$$g_1 = g_1^* = [(1 + 2^{1/2})^{1/3} + (1 - 2^{1/2})^{1/3}] / 2 = 0.298 \quad (2)$$

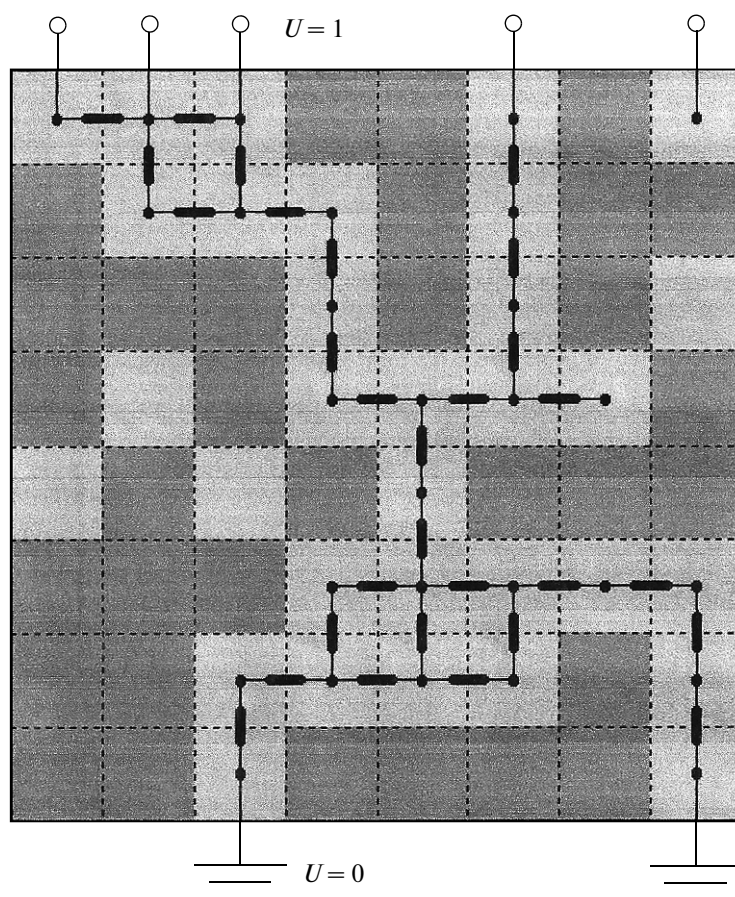


Fig. 1. Model of equal-sized grains. Grains of electrolyte are light gray, grains of graphite with lithium atoms are dark gray.

the ionic percolation cluster is not yet formed, so that parameters  $k^*$  and  $S$  in the region of  $0 \leq g_1 \leq 0.3$  and also current  $I$  generated in the anode are practically zero; the current is also zero in the range of  $0.7 \leq g_1 \leq 1.0$ , as no electronic percolation cluster is formed yet ( $g \leq 0.3$ ).

Specially performed studies [5, 6] showed that the percolation cluster is yet weakly developed near the percolation threshold. It cannot cover the whole volume of the anode active layer and therefore cannot provide complete supply of electrons or ions to graphite grains.

The fact is that not all grains of the corresponding percolation cluster, but only their fraction actually take part in transport of electrons or ions. It is known that a percolation cluster can be divided into its “trunk” (also named “skeleton”) that is responsible for transport of lithium ions or electrons and the rest part of percolation cluster elements: “crown”.

Taking into account the nature of the percolation cluster, the range of reasonable values for parameter  $g$ , at which the anode current becomes different from

zero, must be not  $0.3 < g < 0.7$ , but can be arbitrarily chosen in a narrower range:

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

Let us emphasize once more this important issue: the electronic and ionic percolation clusters must be formed not at the value of  $g = 0.3$  (for the electronic cluster) and not at  $g_1 = 0.3$  (for the ionic cluster), but accordingly, at  $g = 0.35$  and at  $g_1 = (1 - 0.65) = 0.35$ .

Let us now use the results of computer percolation calculations in the model of equal-sized grains in [5, 6]. In it, structure simulation and studies of percolation properties of the porous electrode active layer of two grain types were performed. Herewith, the  $SL$ ,  $k^*$ ,  $D^*$  values were determined. Their dependence on the volume fraction of graphite grains in the anode active layer is presented in Table 1.

It can be seen that the specific surface of contact between the electronic and ionic percolation clusters  $S$  reaches its maximum at  $g = 0.5$ . Naturally, reduced effective conductivity in the ionic percolation cluster  $k^*$  may grow to the maximum possible value of  $k^* = 1$  (at  $g = 0$ ) at a decrease in parameter  $g$  and the reduced

**Table 1.** Dependence of effective coefficients of electron and ion percolation clusters on the volume fraction of graphite grains  $g$

$g$	$SL$	$k^*$	$D^*$
0.65	0.907	$6.1 \times 10^{-3}$	0.304
0.60	1.197	$2.6 \times 10^{-2}$	0.231
0.55	1.325	$6.1 \times 10^{-2}$	0.166
0.50	1.362	0.109	0.109
0.45	1.325	0.166	$6.1 \times 10^{-2}$
0.40	1.197	0.231	$2.6 \times 10^{-2}$
0.35	0.907	0.304	$6.1 \times 10^{-3}$

effective diffusion coefficient  $D^*$  in the electronic percolation cluster becomes practically zero at  $g = 0.3$ .

### SYSTEM OF EQUATIONS

Let us now set about the fifth item in the program of studies of the porous electrode: derivation of equations describing the processes in the active layer in space and time.

At the initial time moment (at  $t = 0$ ), all grains have the concentration of lithium ions  $c_0$ . Then, in the course of anode discharge, the concentration of lithium atoms starts decreasing. The reduced value of lithium concentration in graphite grains  $\check{c} = c/c^*$ , where  $c^*$  is the maximum possible lithium concentration.

Let us assume that current density  $j$  generated at the interface of the ionic (the whole set of interconnected grains of electrolyte) and electronic (the whole set of interconnected graphite grains) percolation cluster, takes the form of:

$$j = i_0[(1 - \check{c}_s)^{1/2} \check{c}_s^{1/2}] \{e^\eta - e^{-\eta}\}, \quad (4)$$

where  $\check{c}_s$  is the reduced value of the lithium concentration on the contact surface between graphite grains and grains of electrolyte,  $i_0$  is the exchange current and

$$\eta = F[E - U]/2RT, \quad (5)$$

where  $E$  is the anode potential under current  $j$  and  $U$  is the equilibrium (currentless) potential depending in the concentration of lithium ions in a graphite grain  $\check{c}$  according to the following empirical relationship [8]:

$$U = -0.16 + 1.32 \exp(-3\check{c}). \quad (6)$$

It is usually assumed that the concentration of lithium atoms in graphite grains is within the range of  $0.0 \leq \check{c} \leq c_0 = 0.7$ .

An equation for polarization  $\eta$  distribution 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):

$$d^2\eta/d\hat{y}^2 = [(1 - \check{c}_s)^{1/2} \check{c}_s^{1/2}] \{e^\eta - e^{-\eta}\}, \quad (7)$$

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

$$L_{\text{ohm}} = (2RTk^*k/FSi_0)^{1/2}, \quad (8)$$

$k$  is the specific conductivity of electrolyte ( $k^*k$  is the effective specific conductivity of the active layer),  $S$  is the specific contact surface between the electronic and ionic percolation clusters. The boundary conditions for equation (7) in the case of galvanostatic discharge mode take the form of:

$$-I_{\text{ohm}}d\eta/d\hat{y} = I = \text{const at } y = 0, \quad (9)$$

$$d\eta/d\hat{y} = 0 \text{ at } y = \Delta, \quad (10)$$

$I$  is the discharge current and the characteristic ohmic current

$$I_{\text{ohm}} = (2RTk^*kSi_0/F)^{1/2}. \quad (11)$$

Mass transport of lithium atoms in graphite grains (in the electronic percolation cluster) is described by the following equation:

$$d\check{c}/dt^* = \Omega d^2\check{c}/d\hat{y}^2 - [(1 - \check{c}_s)^{1/2} \check{c}_s^{1/2}] \{e^\eta - e^{-\eta}\}, \quad (12)$$

in which  $\check{c}(y, t)$  is the average concentration of lithium ions in a graphite grain at time  $t$  for the anode active layer cross-section with coordinate  $y$ . In equation (12), the first addend on the right is responsible for diffusion leveling of the concentration of lithium atoms (exchange of lithium atoms between the neighboring graphite grains); the second addend characterizes a decrease in the active layer of the content of lithium atoms converted to lithium ions and passing into the ionic percolation cluster. In equation (12), parameter

$$\Omega = (L_d/L_{\text{ohm}})^2 = gFD^*c^*/2RTk^*, \quad (13)$$

where  $\hat{y} = y/L_d$  is the reduced coordinate and  $L_d$  is the characteristic diffusion length determined by the following expression:

$$L_d = (gFD^*c^*/Si_0)^{1/2}, \quad (14)$$

$D^*$  is the effective diffusion coefficient of lithium atoms in the electronic percolation cluster, the reduced time takes the form of

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

where  $t$  is the time and  $\tau$  is the characteristic time determined by the following expression:

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

Let us now write down the initial and boundary conditions for equation (12). We have:

$$\check{c} = c_0 \text{ at } t = 0, \quad (17)$$

$$d\check{c}/d\check{y} = 0 \text{ at } y = 0, \quad (18)$$

$$d\check{c}/d\check{y} = 0 \text{ at } y = \Delta. \quad (19)$$

Conditions (18) and (19) mean that lithium atoms may leave graphite grains only by being transformed into lithium ions in the course of an electrochemical reaction.

### DISTRIBUTION OF LITHIUM CONCENTRATION IN A SEPARATE GRAPHITE GRAIN

In equation (12), two reduced concentration of lithium atoms in graphite grains are present: concentration averaged by the graphite grain volume  $\check{c}$  and concentration on the graphite grain surface  $\check{c}_s$ . To determine the ratio of the  $\check{c}$  and  $\check{c}_s$  values, it is necessary to consider the diffusion mass transport of lithium atoms in a separate graphite grain. In order not to complicate calculations unduly, let us assume that a graphite grain may also be presented in the form of the radius of a sphere:

$$R = L/2. \quad (20)$$

The distribution of reduced concentration  $\check{c}$  in a graphite grain satisfies the equation of

$$d\check{c}/d\check{r}^{**} = \{d^2\check{c}/d\check{r}^2 + (2/\check{r})d\check{c}/d\check{r}\}, \quad (21)$$

where the reduced spherical radius of the grain is

$$\check{r} = r/R, \quad (22)$$

and the reduced time now takes the form of

$$t^{**} = t/\tau^*, \quad (23)$$

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

$$\tau^* = R^2/D, \quad (24)$$

$D$  is the diffusion coefficient of lithium atoms in a graphite grain.

Let us write down the initial and boundary conditions for equation (21). We have:

$$\check{c} = c_0 \text{ при } t = 0, \quad (25)$$

in the graphite grain center;

$$d\check{c}/d\check{r} = 0 \text{ при } \check{r} = 0, \quad (26)$$

on the surface of a spherical graphite grain at  $\check{r} = 1$  (condition of equality of fluxes of lithium atoms and ions)

$$-\chi d\check{c}/d\check{r} = [(1 - \check{c}_s)^{1/2} \check{c}_s^{1/2}] \{e^\eta - e^{-\eta}\}, \quad (27)$$

where

$$\chi = FDc^*/\gamma Ri_0, \quad (28)$$

and parameter

$$\gamma = SL/3. \quad (29)$$

Introduction of such a factor is related to an attempt to reflect the fact that each graphite grain is actually only in part surrounded grains of electrolyte contacting it. Parameter  $\gamma$  represents the fraction of the surface corresponding to contacts between the electronic and ionic percolation clusters of the overall specific contact surface of all grains per active layer volume unit equal to  $3/L$ .

There are extensive literature references where attempts are made to develop the method of approximate solution of equation (21). Review of such works is presented in [9]. In the present paper, we will apply the "diffusion length method" developed in [10, 11]. According to it, the relationship between concentrations  $\check{c}$  and  $\check{c}_s$  is provided by the following system of differential and algebraic equations, that is:

$$d\check{c}/d\check{r}^{**} = -3\alpha[(1 - \check{c}_s)^{1/2} \check{c}_s^{1/2}] \{e^\eta - e^{-\eta}\}, \quad (30)$$

$$\check{c} - \check{c}_s = (\beta/5) \{1 - \exp[-(20/3)(\alpha/\beta)^{1/2}(t^{**})^{1/2}]\} \times [(1 - \check{c}_s)^{1/2} \check{c}_s^{1/2}] \{e^\eta - e^{-\eta}\}, \quad (31)$$

where constants  $\alpha$  and  $\beta$  were determined as follows:

$$\alpha = g/SR, \quad (32)$$

$$\beta = Ri_0/DFc^*. \quad (33)$$

Thus, the set of equations (7), (12), and formulas (30)–(33) establishing the relationship between concentrations  $\check{c}$  and  $\check{c}_s$ , including condition (6), with initial and boundary conditions (9), (10), (17)–(19) allows tracing variations of the reduced anode potentials:

$$\psi = FE/2RT, \quad (34)$$

and averaged concentration  $\check{c}$  of lithium atoms in graphite grains in the anode active layer.

### SPECIFIC MODES OF ANODE OPERATION

Tables of parameters assumed for characteristics of the anode active layer ( $\text{Li}_x\text{C}_6$ ) can be found in many papers [8, 10, 12–16]. Large dispersion is observed in the values presented therein. Thus, the diffusion coefficient of lithium in graphite  $D$ , e.g., has the following values,  $\text{cm}^2/\text{s}$ :  $3.9 \times 10^{-10}$  [10],  $5 \times 10^{-9}$  [12],  $1.6 \times 10^{-10}$  (at  $T = 298 \text{ K}$ ) [13],  $2 \times 10^{-10}$  [14],  $1 \times 10^{-11}$  [15].

With account for the data of Table 1 and the rather arbitrary values we chose for other key parameters:  $k = 10^{-3} \text{ S/cm}$  [16],  $D = 2 \times 10^{-10} \text{ cm}^2/\text{c}$  [14],  $i_0 = 2.1 \times 10^{-4} \text{ A/cm}^2$  [14, 15],  $L = 5 \times 10^{-4} \text{ cm}$  [15],  $c^* = 3 \times 10^{-2} \text{ g-mol/cm}^3$  [15], one can estimate the values involved in calculations: characteristic ohmic length  $L_{\text{ohm}}$  (8), characteristic diffusion length  $L_d$  (14), characteristic ohmic current  $I_{\text{ohm}}$  (11), and parameter  $\Omega$  (13). All these data are presented in Table 2.

**Table 2.** Dependence of characteristic parameters of the anode active mass on the volume fraction of graphite grains  $g$ 

$g$	$L_{\text{thm}}, \text{cm}$	$L_d, \text{cm}$	$I_{\text{ohm}}, \text{A/cm}^2$	$\Omega$	$\tau, \text{s}$
0.65	$8.94 \times 10^{-4}$	$1.76 \times 10^{-6}$	$3.41 \times 10^{-4}$	$3.88 \times 10^{-6}$	$4.94 \times 10^3$
0.50	$3.11 \times 10^{-3}$	$7.56 \times 10^{-7}$	$1.78 \times 10^{-3}$	$5.91 \times 10^{-8}$	$2.53 \times 10^3$
0.35	$6.32 \times 10^{-3}$	$5.64 \times 10^{-7}$	$2.40 \times 10^{-3}$	$7.96 \times 10^{-9}$	$2.66 \times 10^3$

The data of Table 2 evidence that due to the low value of the diffusion coefficient of lithium atoms in graphite grains  $D$ , characteristic diffusion value  $L_d$  proves to be much lower than characteristic ohmic length  $L_{\text{ohm}}$  at any reasonable values of bulk concentration of graphite grains in the anode active layer  $g$ . The values of parameter  $\Omega$  are negligible, so that the contribution of the first addend in the rightmost part of equation (12) can always be neglected. From the physical standpoint, this means that there is practically no exchange by lithium atoms between the contacting graphite grains in the electronic percolation cluster.

The data of Table 2 evidence that one should probably assume the optimum bulk concentration of graphite grains in the anode active layer to be  $g = 0.5$ . At  $g = 0.65$ , problems appear regarding removal of lithium atoms from the anode (characteristic ohmic length  $L_{\text{ohm}}$  becomes low), while at  $g = 0.35$ , the amount of lithium atoms in the anode will decrease significantly. This rather arbitrary conclusion will be further refined in the course of exact calculations.

One can point out three special cases of galvanostatic discharge mode, when there is no necessity to perform calculations of anode characteristics using all three equations: (7), (12), and (21).

**Discharge Mode 1 (“Ideal” Anode).** Let us introduce the concept of an “ideal” anode. The word ideal means the following. For such an anode, one can obtain analytical expressions for the dependence of its main characteristics (degree of filling by graphite grains by lithium atoms  $\check{c}$  and  $\psi = FE/2RT$ ) on time. Herewith, the values of quantities  $\check{c}$  and  $\psi$  will be independent of coordinate  $y$ .

The active layer of an “ideal” anode has its particular features. Firstly, it must be sufficiently thin. This means that its thickness  $\Delta$  must be much lower than the characteristic ohmic length; in other words, the following condition must be fulfilled:

$$\Delta \ll L_{\text{ohm}} = (2RTkk^*/FSi_0)^{1/2}. \quad (35)$$

This inequality is the higher the more significant the value of effective conductivity of electrolyte  $k^*$  and the lower the product of specific surface area  $S$  by exchange current  $I_0$ .

Secondly, the size of graphite grains in an “ideal” anode must be so small that the diffusion limitations for lithium ions would become negligible. This mean

technically that parameter  $\chi$  in relationship (27) must satisfy the following inequality:

$$\chi = FDC^*/\gamma Ri_0 \gg 1. \quad (36)$$

In the case when conditions (35), (36) are fulfilled, the procedure for calculation of the anode active layer characteristics becomes much simpler. In an “ideal” anode, one can assume reduced polarizations  $\eta$  (5) and  $\psi$  (34) constant through the active layer depth. The prove to depend only on the discharge time. Besides, due to fulfillment of condition (36), there is no difference between concentrations  $\check{c}$  and  $\check{c}_s$  in the grains of an “ideal” anode. Therefore, it is no more necessary to perform calculations according to equation (21). The following equality is true:

$$\check{c} = \check{c}_s. \quad (37)$$

As shown by estimations, inequality (36) and equality (37) remain quite true at a transition to anodes with nanosized grains.

#### Discharge Mode 2 (Anode with Nanosize Grains).

At a transition to anodes with nanosize grains, as already pointed out, the difference between lithium concentrations in graphite grains  $\check{c}$  and  $\check{c}_s$  becomes low, and condition (37) is fulfilled. Thence, to find the values of  $\check{c}$  and  $\psi$  one is only to use the system of equations (7) and (12). The difference between cases 2 and 1 is that  $\check{c}$  and  $\psi$  are now functions of coordinate  $y$ .

**Discharge Mode 3 (Anodes with a Thin Active Layer).** Finally, one can also consider the case of anodes with very thin active layers, when only criterion (35) is fulfilled. It can also be assumed now that quantities  $\check{c}$  and  $\psi$  are constant through the active layer depth. But the dependence of these values on time should be determined using equations (12) and (21). Let us note that anode capacitance in the case of mode 3 will probably be very low.

#### CALCULATION OF CHARACTERISTICS OF “IDEAL” ANODE

Let us assume  $g = 0.5$ . Then, as follows from Table 2, characteristic ohmic length  $L_{\text{ohm}} = 31 \mu\text{m}$ . Thus, the anode may be assumed “ideal” if the active layer thickness does not exceed approximately  $3 \mu\text{m}$ .

Let us note further that parameter  $\chi = FDC^*/\gamma Ri_0 = 24.3$  in boundary condition (27) for equation (21) at  $g = 0.5$  (the data of Table 2). From the physical standpoint, this means prevalence (in the case of not very

high discharge currents) of the process of diffusion of lithium atoms in a graphite grain over the slow discharge process on the surface of graphite grains. Due to this, one may assume that the concentration of lithium atoms is constant through the graphite grain depth. Thus, one may assume that  $\check{c} = \check{c}_s$ . This leads to the necessity of substitution of equation (12) by a practically equivalent equation:

$$-gFc^*d\check{c}/dt = Si_0[(0.7 - \check{c})^{1/2}\check{c}^{1/2}]\{e^\eta - e^{-\eta}\}. \quad (38)$$

The physical meaning of the rightmost part of equation (38) is the value of discharge current  $I$  divided by the anode active layer thickness  $\Delta$ . Current  $I$  is constant, as the galvanostatic mode is considered. By integrating (38) and assuming that the initial concentration of lithium atoms in a graphite grain  $\check{c} = 0.7$ , we obtain:

$$\check{c} = 0.7 - t/\tau^{**}, \quad (39)$$

where

$$\tau^{**} = g\Delta Fc^*/I \quad (40)$$

corresponds to the characteristic discharge time. Estimations show that in the case of the active layer with the thickness of 3  $\mu\text{m}$  and discharge current  $I = 1 \text{ mA/cm}^2$ , time  $\tau^{**} = 434 \text{ s}$ .

As follows from formula (40), specific capacitance of the anode we studied  $C = c_0\tau^{**} = 0.7c^*g\Delta F = 0.7 \times 3 \times 10^{-2} \times 0.5 \times 3 \times 10^{-4} \times 9.65 \times 10^4 = 0.1 \text{ C/cm}^2$ .

Expression (38) also allows obtaining the formula for calculation of the dependence of anode polarization on time. Namely, the following equation is observed:

$$I^* = [(t/\tau^{**})^{1/2}(0.7 - t/\tau^{**})^{1/2}]\{e^\eta - e^{-\eta}\}, \quad (41)$$

where characteristic current

$$I^* = I/\Delta Si_0. \quad (42)$$

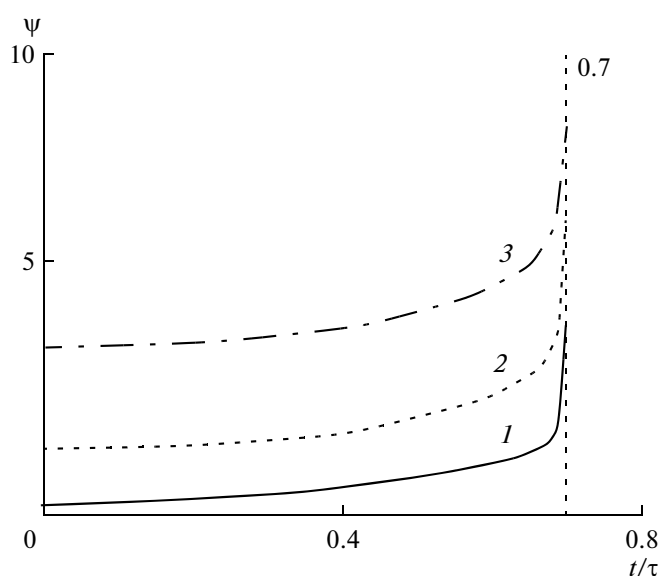
Its value in the case of the "ideal" anode active layer thickness  $\Delta = 3 \mu\text{m}$  and discharge current of  $I = 1 \text{ mA/cm}^2$  is  $I^* = 5.83$ .

Relationship (41) allows obtaining the dependence of the "ideal" value of  $\psi = FE/2RT$  on reduced time  $t/\tau$  under the conditions when there are no ohmic limitations for movement of lithium ions in electrolyte and no diffusion limitations for intercalation of lithium ions in graphite grains. In the calculations, it is necessary to take into account the presence of another obvious formula:

$$\eta = \psi + 0.16 - 1.32 \exp[-3(0.7 - t/\tau^{**})]. \quad (43)$$

Equation (41) allows obtaining an analytical equation for the dependence of  $\psi$  on time. It takes the form of

$$\psi = 1.32 \exp[-3(0.7 - t/\tau^{**})] - 0.16 + \ln\{A/2 + [A^2/4 + 1]^{1/2}\}, \quad (44)$$



**Fig. 2.** Dependence of reduced potential of an "ideal" anode  $\psi$  on reduced time  $t/\tau^{**}$  for three values of discharge current  $I$ ,  $\text{mA/cm}^2$ : (1) 0.1, (2) 1, (3) 10.  $g = 0.5$ ,  $\Delta = 10 \mu\text{m}$ .

where

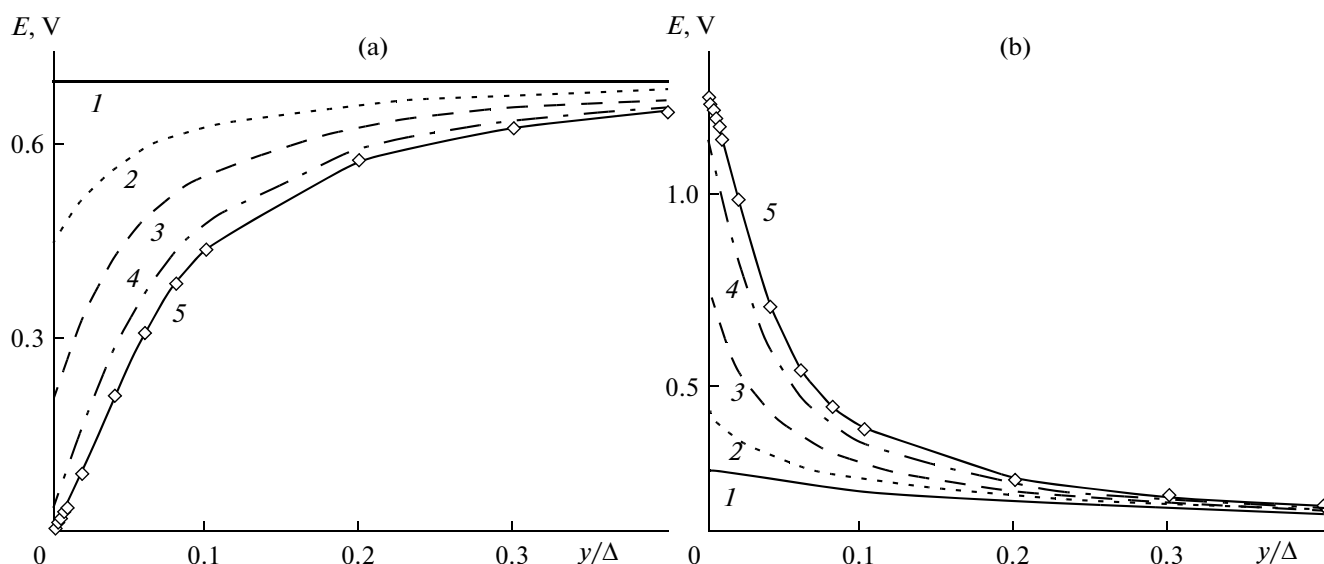
$$A = I^*/[(t/\tau^{**})^{1/2}(0.7 - t/\tau^{**})^{1/2}]. \quad (45)$$

The dependence of  $\psi$  on reduced time  $t/\tau$  calculated according to formulas (44), (45) for a number of values of discharge current  $I$  (0.1, 1, and 10  $\text{mA/cm}^2$ ) is presented in Fig. 2. Table 3 shows the values of parameters of an "ideal" anode (characteristic current  $I^*$ , characteristic time  $\tau^{**}$  and initial anode potential  $(2RT/F)\psi_0$ ) as a function of the anode discharge current value  $I$ .

Let us point out an important fact. If the average size of graphite grains and grains of electrolyte in the anode is decreased to  $L = 5 \times 10^{-4} \text{ cm}$  to nanometers, say, to the value of  $L = 5 \times 10^{-6} \text{ cm}$  (50 nm), characteristic current values  $I^*$  in Table 3 decrease by two orders of magnitude. Now, even for discharge current  $I = 10 \text{ mA/cm}^2$ , the initial anode potential will be not 3354 mV, but, as follows from formulas (44) and (45) and from the data of the same Table 3, will be much lower: 192 mV. Therefore, the size of grains in the anode active layer must be decreased for significant

**Table 3.** Dependence of parameters of an "ideal" anode on discharge current  $I$

$I$ , $\text{A/cm}^2$	$I^*$	$\tau^{**}$ , s	$(2RT/F)\psi_0$ , mV
0	—	—	1.9
0.1	0.58	4340	192
1.0	5.83	434	1189
10	58.3	4.3	3354



**Fig. 3.** Variation of distribution through the anode active layer depth of (a) reduced concentration of lithium atoms in graphite grains and (b) potential with time  $t/\tau$ : (1) 0, (2) 0.015, (3) 0.030, (4) 0.045, (5) 0.052.  $g = 0.5$ ,  $I = 10 \text{ mA/cm}^2$ .

improvement of performance of the lithium–polymer battery with an “ideal” anode.

#### CHARACTERISTICS OF ANODE WITH NANOSIZE PARTICLES

Let us study the second specific case of anode discharge, discharge mode 2, that is of great practical interest. Let us assume as before that the bulk concentration of graphite grains in the active layer  $g = 0.5$  and let us for definiteness assume discharge current  $I = 10 \text{ mA/cm}^2$ .

Now, the  $\check{c}$  and  $\psi$  values depend not only on time, but also on the coordinate. The results of calculations performed on the basis of equations (7) and (12) are presented in Fig. 3 (parameter  $\Delta$  in the figure is arbitrary; it must be high enough so that the chosen active layer thickness may be assumed practically infinite). Fig. 3 presents the distribution through the active layer depth of the reduced concentration of lithium atoms in graphite grains  $c/c^*$  (Fig. 3a) and anode potential  $E$  (Fig. 3b) at the contact interface of the ionic and electronic clusters at various time moments. Herewith, characteristic time  $\tau$  (16) was 2530 s. The full discharge time is thus  $2530 \times 0.052 = 131.6 \text{ s}$ .

The discharge process in the active layer of arbitrary thickness must obviously be terminated when the graphite grains located in the active layer/interelectrode space plane become practically devoid of lithium atoms. Let us further assume that the concentration of lithium atoms in graphite may increase only to the value of  $c = 0.01c^*$ . This is also the moment of termination of the anode discharge process.

Let us proceed to systematic estimation of performance characteristics of a lithium–ion anode with

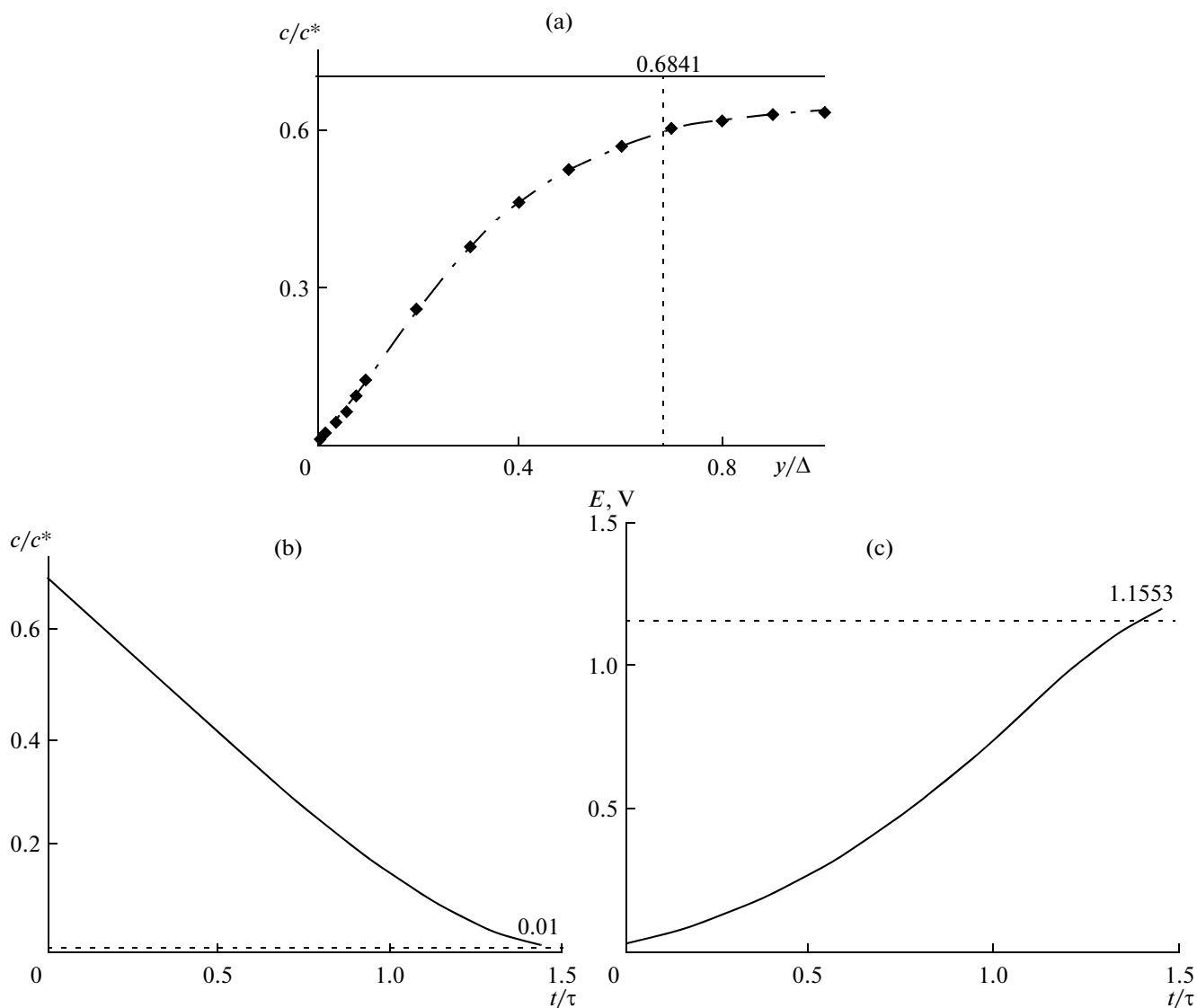
nanosize grains. Let us present an example of such a calculation (let us again assume  $g = 0.5$  and the discharge current of  $I = 1 \text{ mA/cm}^2$ ). We are interested only in the behavior of graphite grains located on the active layer/interelectrode space interface (this plane has the coordinate of  $y = 0$ ). In the course of anode discharge, the concentration of lithium atoms in graphite decreases to the level of  $c/c^* = 0.01$ , as shown in Fig. 4a (the concentration of lithium atoms in other layer of the active layer is always higher).

In Fig. 4a, the whole stock of lithium atoms to be discharged is located between the horizontal of  $c/c^* = 0.7$  (this is the initial concentration of lithium atoms in the graphite grains) and the final discharge curve. The optimum anode active layer thickness  $\Delta^*$  is determined as follows. Integration is used to calculate the whole amount of lithium to be discharged and then the active layer section  $\Delta^*$  is determined that corresponds to 90% of the calculated value (from the section at  $y = 0$  to the section at  $y = \Delta^*$ ). This  $\Delta^*$  value corresponds to the reasonable optimum thickness of the active layer.

The following step is determination of anode discharge time  $t$ . Again, we are only interested in what occurs with lithium at the active layer/interelectrode space interface. Fig. 4b shows how the reduced concentration decreases at this interface. The discharge time determines the moment it reaches the value of 0.01. Potential  $E$  also increases in time, as shown in Fig. 4c; the  $E^*$  value is recorded at the moment when the discharge is over. The anode capacitance is estimated according to a simple formula:  $C = It^{***}$ .

All this calculation procedure was repeated many times for a number of values of graphite bulk concentration in the active layer  $g$  and for various values of





**Fig. 4.** (a) Concentration profile of lithium atoms in the anode active layer at the time moment when concentration on the active layer/interelectrode space surface is  $c/c^* = 0.01$ . (b) Decrease in time of the concentration of lithium atoms in graphite on the active layer/interelectrode space surface. (c) Increase in the anode potential with time.  $g = 0.5$ ,  $I = 1 \text{ mA/cm}^2$ .

discharge current  $I$ . The results of this work are in part reflected in Table 4.

Finally, it is necessary to make the following significant observation. Formula (11) determining characteristic ohmic current  $I_{\text{ohm}}$  actually determines the upper limit of discharge currents. Indeed, estimates show that the values of characteristic ohmic current are several  $\text{mA/cm}^2$ . Therefore, it is natural that capacitance in Tables 4–6 start rapidly decreasing at discharge currents exceeding  $10 \text{ mA/cm}^2$ . The discharge current can be significantly enhanced by decreasing the grain size. The characteristic ohmic current in the case of grains with the size of  $L = 50 \text{ nm}$  increases by an order of magnitude, up to tens of  $\text{mA/cm}^2$ . One can reach the discharge currents of several A if one can additionally enhance drastically the

specific conductivity of electrolyte, e.g., to  $k = 0.1 \text{ S/cm}$ .

Let us now determine the value of the optimum bulk concentration of graphite  $g^*$  in the active layer. For this purpose, let us construct the dependence on  $g$  for all optimum working parameters of the anode of a lithium-ion battery. Such curves are presented in Fig. 5.

At an increase in  $g$ , the optimum active layer thickness  $\Delta^*$  of about tens of  $\mu\text{m}$  decreases monotonously (curves 1'–3' in Fig. 5a); the dependence of discharge time  $t^{***}$  on  $g$  features approximately the same behavior (curves 1–3 in Fig. 5a). Anode capacitance is maximum in the range of  $0.35 < g < 0.4$ , after which it starts decreasing (curves 1–2 in Fig. 5b). It also decreases at an increase in the discharge current value (curve 3 in

**Table 4.** Optimum anode working parameters at various  $g$ 

$g$	$I, \text{A/cm}^2$	$\Delta^*, \mu\text{m}$	$t^{***}, \text{s}$	$C, \text{C/cm}^2$	$E^*, \text{V}$
0.65	0.1	21.3	$1.41 \times 10^4$	1.41	1.14
	1	18.3	798	0.8	1.25
	10	5.1	9.6	$9.6 \times 10^{-2}$	1.48
0.50	0.1	68.7	$3.78 \times 10^4$	3.78	1.13
	1	68.4	3612	3.61	1.16
	10	50.0	123.6	1.24	1.31
	100	9.4	1.3	0.13	1.54
0.35	0.1	86.5	$4.93 \times 10^4$	4.93	1.12
	1	86.3	$4.82 \times 10^3$	4.82	1.15
	10	77.0	220.4	2.2	1.29

Fig. 5b). At first, potential  $E^*$  changes relatively slightly at an increase in  $g$  (curves 1'–3' in Fig. 5a), after which it starts growing rapidly. On the whole, the value of  $E^*$  remains in the range of 1.1–1.5 V.

## CONCLUSIONS

A computer simulation of the operation of the negative electrode (anode) in a lithium–ion battery is performed. The model of equal size grains (active substance (graphite) and electrolyte) is studied. The grains represented microcubes with similar edge lengths.

Percolation properties of the anode active layer are studied in accordance with the theory of porous electrodes: percolations thresholds are established; these correspond to the critical bulk concentrations of graphite grains and grains of electrolyte starting from which two percolation clusters, electron (from graphite grains) and ion (from grains of electrolyte) are formed. Such clusters provide the supply of electrons and lithium ions participating in the electrochemical reaction into the active layer.

The values are calculated for effective coefficients characterizing the anode active mass: effective conductivity by lithium ions (their supply into the active layer occurs through the ion percolation cluster) and effective diffusion coefficient of lithium atoms (their redistribution in graphite grains in the anode active layer occurs through an electron percolation cluster). It is shown that the value of the effective diffusion coefficient of lithium atoms is negligible. The specific surface on which the electrochemical process occurs in the active layer is also calculated.

A complete system of equations describing the operation of the anode active layer is presented. Both the general case and special modes of anode discharge

are considered. Special attention is paid to two discharge modes: on an “ideal” anode and on an anode with nanosize grains.

The working parameters are calculated for all the above types of anodes: the optimum bulk concentration of graphite in the active layer, the active layer thickness, time of full anode discharge, its specific electric capacitance, and the anode potential.

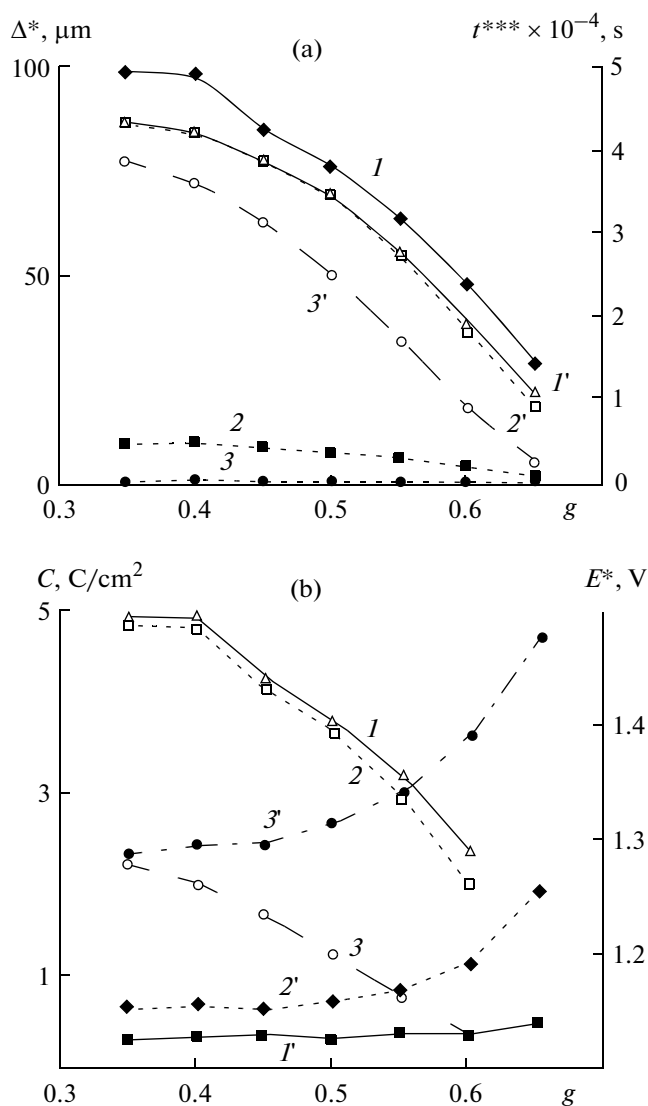
The characteristics of the anode active mass are: average size of graphite grains and grains of electrolyte, maximum concentration of lithium in graphite, exchange current of the Li/Li<sup>+</sup> system, diffusion coefficient of lithium atoms in graphite and specific conductivity of electrolyte.

Advisability of working with anodes with nanosize grains and electrolyte with enhanced specific conductivity is shown.

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

### *External Parameters*

- $t$  is the discharge time of the anode
- $t^*$  is the reduced discharge time of the anode
- $t^{**}$  is the reduced characteristic time of the process of recovery of lithium atoms from a graphite grain
- $t^{***}$  is the discharge time of the anode with nanosize particles
- $\tau$  is the characteristic discharge time of the anode
- $\tau^*$  is the characteristic time of the process of recovery of lithium atoms from a graphite grain
- $\tau^{**}$  is the characteristic discharge time of an “ideal” anode
- $C, \text{C/cm}^2$  is the specific capacitance of the anode
- $T = 293 \text{ K}$  is the working temperature of the anode



**Fig. 5.** Dependence of the key working parameters of the anode on the graphite bulk concentration in the active layer. (a) ( $I$ – $3'$ ) optimum active layer thickness and ( $I$ – $3$ ) discharge time, (b) ( $I$ – $3$ ) electric capacitance and ( $I$ – $3'$ ) final anode potential at  $I$ , mA: ( $I$ ,  $I'$ ) 0.1, ( $2$ ,  $2'$ ) 1, ( $3$ ,  $3'$ ) 10.

$\Delta$  is the thickness of the anode active layer

$\Delta^*$  is the optimum active layer thickness

#### Parameters of Electrochemical Kinetics

$n = 1$  is the amount of electrons participating in the electrochemical process

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

$I$ , A/cm<sup>2</sup> is the discharge current

$I^*$  is the reduced characteristic current of an "ideal" anode

$j$ , A/cm<sup>2</sup> is the current density at the interface of electron percolation cluster and ion percolation cluster

$i_0$  is the exchange current

$\eta$  is the polarization

$\psi$  is the reduced potential

$E$  is the anode potential

$E^*$  is the final anode potential

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

$L_d$ , cm is the characteristic diffusion length

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

$y$  is the coordinate

#### Parameters of the Active Layer Structure

$g$  is the bulk concentration of graphite grains

$g_1$  is the bulk concentration of grains of electrolyte

$L$  is the average size of grains of graphite and electrolyte

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

$c^*$  is the maximum concentration of lithium ions in graphite

$\check{c} = c/c^*$  is the reduced average concentration of lithium atoms in graphite grains

$c_0$  is the initial concentration of lithium atoms in graphite grains

$\check{c}_s$  is the reduced concentration of lithium on the graphite grain surface

$\check{c}(r)$  is the reduced concentration of lithium in a graphite grain

$\check{r}$  is the reduced spherical radius of a graphite grain

$R$  is the average radius of spherical graphite grains

$\gamma$  is the fraction of the contact surface area between graphite grains and grains of electrolyte given that they all are a part of electron or ion percolation clusters

$\chi$  is the parameter determining the mode of recovery of lithium atoms from graphite grains

#### Parameters Determining the Processes of Mass and Electric Transfer

$D$  is the diffusion coefficient of lithium atoms in graphite grains

$k$  is the specific conductivity of electrolyte

$k^*$  is the reduced effective specific conductivity of electrolyte in the anode active layer

#### REFERENCES

1. Bagotskii, V.S. and Skundin, A.M., *Khimicheskie istochniki toka* (Chemical Power Sources), Moscow: Energoizdat, 1981.
2. Chizmadzhev, Yu.A., Markin, V.S., Tarasevich, M.R., 1 and Chirkov, Yu.T., *Makrokinetika protsessov v poristykh sredakh* (Macrokinetics of Processes in Porous Media), Moscow: Nauka, 1971.
3. Tarasevich, Yu.Yu., *Perkolyatsiya: teoriya, prilozheniya, 1 algoritmy* (Percolation: Theory, Applications, Algorithms), Moscow: Editorial URSS, 2001.
4. Newman, J.S., *Electrochemical Systems*, New Jersey: Prentice Hall, Englewood Cliffs, 1991.

5. Chirkov, Yu.G. and Rostokin, V.I., *Elektrokhimiya*, 2004, vol. 40, p. 1036 [*Russ. J. Electrochem.* (Engl. Transl.), vol. 40, p. 898].
6. Chirkov, Yu.G. and Rostokin, V.I., *Elektrokhimiya*, 2006, vol. 42, p. 799 [*Russ. J. Electrochem.* (Engl. Transl.), vol. 42, p. 715].
7. Chirkov, Yu.G., *Elektrokhimiya*, 1999, vol. 35, p. 1449 [*Russ. J. Electrochem.* (Engl. Transl.), vol. 35, p. 1281].
8. Doyle, M., Newman, J., Gozdz, A.S., Schmutz, C.N., and Tarascon, J.-M., *J. Electrochem. Soc.*, 1996, vol. 143, p. 1890.
9. Zhang, Q. and White, R.E., *J. Power Sources*, 2007, vol. 165, p. 880.
10. Wang, C.Y., Gu, W.B., and Liaw, B.Y., *J. Electrochem. Soc.*, 1998, vol. 145, p. 3407.
11. Wang, C.Y. and Srinivasan, V., *J. Power Sources*, 2002, vol. 110, p. 364.
12. Fuller, T.F., Doyle, M., and Newman, J., *J. Electrochem. Soc.*, 1994, vol. 141, p. 1.
13. Botte, G.G., Johnson, B.A., and White, R.E., *J. Electrochem. Soc.*, 1999, vol. 146, p. 914.
14. Arora, P., Doyle, M., and White, R.E., *J. Electrochem. Soc.*, 1999, vol. 146, p. 3543.
15. Zhang, Q. and White, R.E., *J. Power Sources*, 2008, vol. 179, p. 793.
16. Skundin, A.M., Efimov, O.N., and Yarmolenko, O.V., *Usp. Khim.*, 2002, vol. 71, no. 4, p. 378.

SPELL: 1. ok