

Computer Modeling of Positive Electrode Operation in Lithium–Ion Battery: Model of Equal–Sized Grains, Percolation Calculations

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Abstract—A computer simulation of the structure of the cathode active material in a lithium–ion battery is performed. The model of equal–sized grains of three types (active grains, grains of electrolyte, and carbon black grains) is studied. Acceptable bulk concentration of active grains g is estimated. It is in the range of zero to 0.3. Dependence of the key parameters of the electrode active material on its composition is determined: specific conductivity of electrolyte and specific surface area on which the electrochemical process occurs. It is shown that the average number of electrochemically active faces of active grains cannot be 100%, as usually assumed in the studies of diffusion processes occurring in an individual active grain. In the range of $0.0 \leq g \leq 0.3$, the average number of active faces \bar{n} is in the approximate range of $2 \leq \bar{n} \leq 3$. The final choice of the optimum composition of components for the active material of a lithium–ion battery cathode (and, primarily, choice of the value for parameter g) requires performing an additional complex of computer simulations.

Keywords: lithium–ion battery, positive electrode (cathode), galvanostatic discharge mode, computer simulation, model of equal–sized grains, percolation theory, intercalation

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PROBLEM STATEMENT

The most important elements of any chemical power source, whether a one–shot primary source, battery, or a fuel cell, are active layers of its electrodes [1]. The usual approach to theoretical description of operation of active layers in lithium–ion batteries may be called “mathematical simulation” [2–10]. It is stated in these studies that simulation of electrodes of lithium–ion batteries must be based on the general concepts of electrochemical systems with porous electrodes [11]. In reality, all is restricted to formation of a system of balance equations, after which the corresponding calculation is performed and all end with discussion of the obtained active layer characteristics. Of course, such an approach has a right to exist and yield certain results. But it is characterized by certain fundamental faults.

Firstly, the effective coefficients in the equations are defined insufficiently strictly. They are usually estimated using clearly objectionable formulas. Thus, e.g., effective ionic conductivity k^* with references to [12] is calculated according to the formula:

$$k^* = kg_i^{1.5}, \quad (1)$$

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in which k is specific conductivity of electrolyte, g_i is the bulk conductivity of the active layer component providing ionic conductivity.

However, as known from the percolation theory [13], no percolation cluster is formed yet in the concentration range of $0 \leq g_i \leq g_i^*$, where g_i^* is the percolation threshold. Therefore, effective ionic conductivity in this range must be identical to zero, which is in no way reflected in formula (1), as concentration g_i in it may be arbitrarily small.

Besides, not all structural elements of a percolation ionic cluster (its links or sites), but only their part contributes to development of effective ionic conductivity of the active layer. Therefore, in fact, not concentration g_i should be present in formula (1), but a lower value that must be found by means of percolation calculations. The choice of exponent 1.5 in formula (1) is also ambiguous.

The second and key fault of usual “mathematical simulation” is that it yields no answer to priority matters. For example, what should be the optimum loading of the electrode active material by active substance in which the process of intercalation of lithium atoms occurs (we will further designate such a substance as an “intercalating agent”)? What should be the volume fractions of other active layer components (electrolyte and the substance supplying electrons to the active

layer) for the cathode? What should be the optimum average size of the active substance grains?

Originators of the models pay no attention to the rather obvious fact that not all intercalating agent grains, but only their part can participate in the electrochemical process. Thus, the problem of determining the intercalating agent active grains and their separation for the passive grains appears. And this cannot be done without consideration of percolation problems under various models of the active layer structure.

Let us point out one more problem requiring percolation calculations. It is estimation of diffusion limitations appearing after removal (or supply) of lithium atoms from/into an active intercalating agent grain. It is usually assumed that an intercalating agent grain is spherical; it is herewith assumed that all of its spherical surface is electrochemically active. However, such a grain may be in reality adjacent to other intercalating agent grains and grains supplying electrons to the active layer. As a result, only a fraction of the external intercalating agent grain surface is open for the electrochemical process. And this circumstance must become a subject of analysis.

Thus, these examples (their number can be increased, if desired) point to the necessity of supplementing "mathematical simulation" in development of a full theoretical description of operation of lithium-ion batteries by another theoretical approach: "computer simulation" of operation of the active layers of the negative and positive electrodes in lithium-ion batteries, a method based on the achievements of the theory of porous electrodes.

A porous electrode is interpreted as a set of its structural elements (grains) randomly distributed in the active layer. Effective operation of a porous electrode requires formation of two particle clusters in the electrode active layer that provide for supply/removal of ions (ionic cluster) and electrons (electronic cluster). Therefore, of key importance in theoretical studies of the mechanism of action of porous electrodes should be investigation of connectivity of the sets of 3D structural elements of different nature participating in organization of the electrochemical process. Thus, the necessity of turning to a special branch of mathematics and theoretical physics, the percolation theory, comes to the foreground.

This very approach, computer simulation based on the theory of porous electrodes is followed by the authors of the present study. In [14], the methods of computer simulation (a two-component model of equal-sized grains was applied) were used to determine the optimum characteristics of the lithium-ion battery anode in the course of galvanostatic discharge mode. In the present work, determination of the optimum characteristics of a lithium-ion battery anode will be started.

The difference between the anode and cathode is that in the first case, we have a two-component system

(graphite grains + grains of electrolyte), while in the second case, the system is three-component. In the anode, graphite grains with high electronic conductivity provide both the lithium intercalation process and supply of electrons to loci where the electrochemical process occurs. Transport of electrons through the whole anode depth occurs unhindered if the concentration of graphite grains exceeds a certain threshold value (percolation threshold).

In the cathode, electronic conductivity of grains responsible for intercalation is very low. It is only sufficient to make possible occurrence of the electrochemical process. Therefore, to supply electron transport in the cathode active material that cannot be provided by intercalating agent grains, it is necessary to introduce into it grains of some carbon material (further, let us use for the sake of definiteness, carbon black grains). Thus, unlike the case of anode, the cathode represents a three-component system.

To determine characteristic (working) parameter of the cathode, as shown in [14] for the anode, it is necessary first to know two key parameters of the cathode active material: specific surface area S on which the electrochemical process occurs and the value of reduced specific conductivity of electrolyte k^* in the ionic percolation cluster (k^* is a dimensionless quantity).

The aim of this study was to perform all the required percolation calculations within the model of equal-sized grains of three types. As dependent on the composition of the cathode components (on the bulk concentrations of intercalating agent grains g , carbon black grains g_e , and grains of electrolyte g_i), they must determine the key parameters of the cathode: the fraction of active intercalation agent grains, conductivity by lithium ions and specific surface value on which the electrochemical process occurs. It is also important to establish which surface fraction of the active intercalating agent grains is accessible for the electrochemical process.

Only after this, one will be able to set about calculating the optimum working parameters of the lithium-ion battery cathode: its active layer thickness, discharge time, specific discharge capacitance of the cathode, and final cathode potential value.

COMPUTER MODEL

The model of equal-sized grains of three types is presented in Fig. 1. In it, intercalating agent grains are conventionally designated black, grains of electrolyte are gray, and carbon black grains are shaded.

The presence of cavities in the cathode material is obviously undesirable (cavities are nonfunctional: they do not contribute either to the electrochemical process, or to transport of electrons and lithium ions); therefore, let us assume that cavities are absent. If we

also neglect the presence of a binding agent, the following condition is satisfied:

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

Let us assume that the grains of carbon black, electrolyte, and intercalating agent have a similar shape and represent microcubes with edge length of L . Thus, from the standpoint of the percolation theory, one has to deal with a cubic lattice in the model of equal-sized grains [3].

If one continues description of the computer model, much will represent generalization of what was already assumed in consideration of a two-component model of equal-sized grains we used for studies of a fuel cell with solid polymer electrolyte [15]. Specifically, let us use a model cube with the arbitrary size of $N_s \times N_s \times N_s = N_s^3$ as a 3D model of the cathode active material.

A model cube must have microscopic dimensions. This means that the thickness of the cathode active material Δ must be, as in actual practice, much higher than the size of individual grains, much higher than edge length L of microcubes. As shown in [16], the character of percolation curves becomes stable and undergoes no more changes after reaching sufficiently high values of parameter N_s . This can be achieved by assuming $N_s = 100$. Further, the studied model cube will hold $100 \times 100 \times 100 = 10^6$: a million of grains of the three types.

In each cathode intercalating agent grain, active substance materials that receives or gives away lithium ions carry out the battery discharge (or charging) process. Lithium ions and electrons must be continuously supplied (discharge process) or removed (charging process) from the active substance molecules. The channels for supply or removal of lithium ions or electrons are the corresponding ionic (of grains of electrolyte) and electronic (of carbon black grains) percolation clusters formed in the cathode active material. Each of these clusters represents a set of directly interconnected grains of one kind or another. Percolation clusters penetrate the whole cathode active material depth.

Percolation clusters are formed after percolation threshold is reached if the bulk concentrations of corresponding grains reach the given value: g_i^* or g_e^* . In a cubic lattice we deal with, the percolation threshold, as shown in [17], is

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

Thus, it is required for good operation of the cathode active material that at least two conditions are satisfied:

$$g_i > 0.30, \quad g_e > 0.30. \quad (4)$$

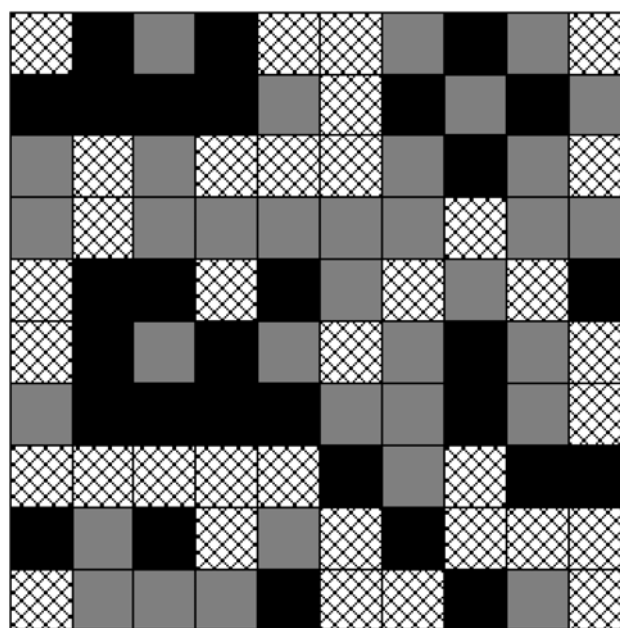


Fig. 1. Model of equal-sized grains of three types. Grains of the intercalating agent grains are black, grains of electrolyte are gray, carbon black grains are shaded.

The system of inequalities (4) together with condition (2) seems to point to the fact that the maximum value for the bulk concentration of intercalating agent grains in the cathode active material is $g_{\max} = 1 - 0.30 - 0.30 = 0.40$. That is, 40% of the cathode active material volume may be filled by intercalating agent grains. This conclusion is however not quite correct.

Fig. 2a shows an example of implementation of a percolation cluster in a $50 \times 50 \times 50$ model cube (a lattice). The concentration of conducting grains is 0.3099. Fig. 2a shows that the percolation cluster near the percolation threshold is yet underdeveloped, its main “bulk” does not wholly cover the model cube volume. Therefore, the greater part of intercalating agent grains remains unconnected with grains forming a part of the ionic and electronic percolation clusters. Therefore, it cannot receive or give lithium ions and electrons.

The second cause, why bulk concentration close to $g_i^* = g_e^* \approx 0.30$ cannot be used is that in this case, transport of lithium ions and electrons in the cathode active material is much hindered. The fact is that not all the grains within the percolation cluster but only their fraction take part in their transport. In a percolation cluster, one can identify its “trunk” (they also name it a “skeleton”) that is responsible for transport of lithium ions or electrons and the remaining part of percolation cluster elements: its “crown” [18].

The percolation cluster trunk may be obtained using a special procedure: the elements are eliminated (“dead-end” elements) that do not assist transport of

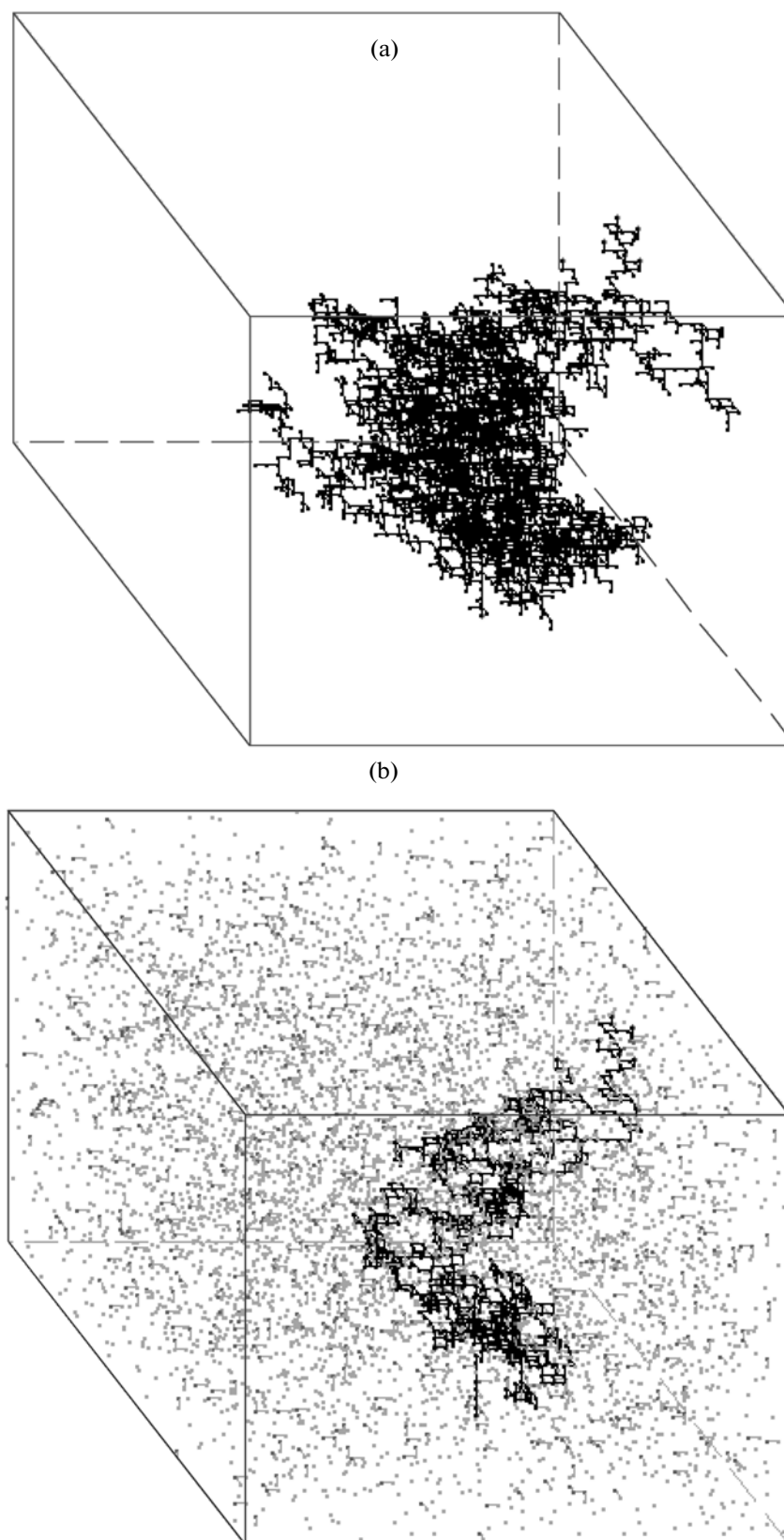


Fig. 2. Computer simulation of a conducting (electrons or ions) percolation cluster in a model cube with the volume of $50 \times 50 \times 50$ (lattice): (a) full percolation cluster, (b) percolation cluster trunk (skeleton). The concentration of conducting grains was 0.3099, the concentration of the intercalating agent grains in Fig. 2b (marked gray) was 0.05.

ions or electrons. The thus obtained trunk under percolation cluster depicted in Fig. 2a is presented in Fig. 2b. It also shows intercalating agent grains randomly distributed in the model cube volume. They are denoted by gray points, their bulk concentration $g = 0.05$.

Fig. 2b shows graphically that if the bulk concentration of grains forming the percolation cluster is close to the percolation threshold (in Fig. 2b, the concentration of the conducting component grains is 0.3099), then supply of lithium ions or accordingly electrons is very much hindered. In this case, only a negligible fraction of intercalating agent grains may be supplied by lithium ions or electrons.

Transport of lithium ions and electrons is considerably enhanced if the bulk concentration of grains of electrolyte and bulk concentration of carbon black grains is increased to the value of, e.g., $g_i = g_e = 0.35$. As follows from Fig. 3, in this case, both the full percolation cluster (Fig. 3a) and its trunk (Fig. 3b) already fill the model cube space sufficiently uniformly. Due to this, the further computer simulations involve the $g_{i\min} = g_{e\min} = 0.35$ values as the minimum values for the g_i and g_e concentrations.

The choice of bulk concentrations $g_i \geq 0.35$ and $g_e \geq 0.35$ means the presence of full percolation clusters and their trunks (skeletons) in the active material that provide supply of lithium ions and electrons through the whole depth of the active material. However, even in this case, not each intercalating agent grain can take part in the electrochemical process. For example, the intercalating agent cube may be adjacent to six (the number of faces) other intercalating agent cubes. Then it would probably be unable to receive (or give away) lithium ions.

An intercalating agent active grain may be called only a grain that at least on one of its 6 faces contacts the ionic percolation cluster and at least on one of its faces contacts the electronic percolation cluster. In the case of an intercalating agent grain, the maximum number of faces contacting the ionic percolation cluster is five. The sixth face is required for contact of this intercalating agent grain with the electronic percolation cluster.

The aim of computer percolation calculations consists, firstly, in determination of the fraction of intercalating agent active grains g^* ($g^* < g$), those grains that actually contribute to the electrochemical process. Secondly, one has to calculate the amount of active faces for intercalating agent active grains in a model cube with the size of $100 \times 100 \times 100$ and then use this value to calculate specific surface area S in the cathode active material (or reduced specific surface area SL , a dimensionless quantity), on which the electrochemical process occurs. And thirdly, one has to determine the value of reduced specific conductivity of electrolyte k^* in the ionic percolation cluster.

ALGORITHMS OF COMPUTER CALCULATIONS

The algorithm of generation of a 3D model cube structure with the cell size of $100 \times 100 \times 100$ with the arbitrary distribution of active material components was used in percolation calculations of the active material characteristics of a lithium-ion battery cathode. The cathode structure was determined by "phase" values of the 3D matrix elements $A(i, j, k)$, namely: if the cell is occupied by a carbon black grain, it is assigned, e.g., value "8"; if it is occupied by electrolyte, its value is "9", and if it contains an intercalating agent grain, it is assigned number "0". Matrix indices correspond to relative coordinates x, y, z of grains in the cube bulk.

For implementation of an arbitrary component distribution through the cells, a one-dimensional array of 10^6 numbers is first formed, in which the fraction of "8" is g_e , that of "9" is g_i , and the fraction of "0" is g . The classical "mixing" procedure described in [19] is used to obtain an array with arbitrary positions of the initial elements. Then, we consistently choose an element and its value from this array and assign its value to the subsequent cell of matrix $A(i, j, k)$. Matrix $A(i, j, k)$ represents a cathode model with arbitrary distribution of components; it serves as a basis for calculation of characteristics and parameters of the cathode active mass.

In the calculations of the key parameters of the cathode active mass, it is necessary in the first place to identify the presence of the electronic and ionic percolation clusters. The algorithm of identification and registration of each cluster is reduced to the following sequence of operations.

In the case of electronic percolation cluster conductivity, the sequence of operations is as follows. We find carbon black cells in phase "8" on the model cube surface ("front") (among matrix elements $A(i, j, k)$ with index $k = 1$) and transfer them to a new state designated, e.g., as phase "4". These cells are considered as "sources of perturbation" propagating through the model cube volume in the form of a wave. Environment is studied further for each source: if the neighboring cell has phase "8" (i.e., it is an unperturbed carbon black grain), its phase accordingly assumes a new value ("4") and its coordinates are entered into a numeric array determining the position of the new wave front. In their turn, carbon black cells forming the wave front become sources of secondary waves (similar to the Huygens-Fresnel principle in optics [20]). The wave front either reaches the opposite ("rear") cube surface ($k = 100$) in the case of end-to-end conductivity channels, or stops in the cells surrounded by foreign components if the channel is a dead-end.

To determine which carbon black grains form the percolation cluster, let us start an inverse wave from the cells with phase "4" in the direction from the "rear"

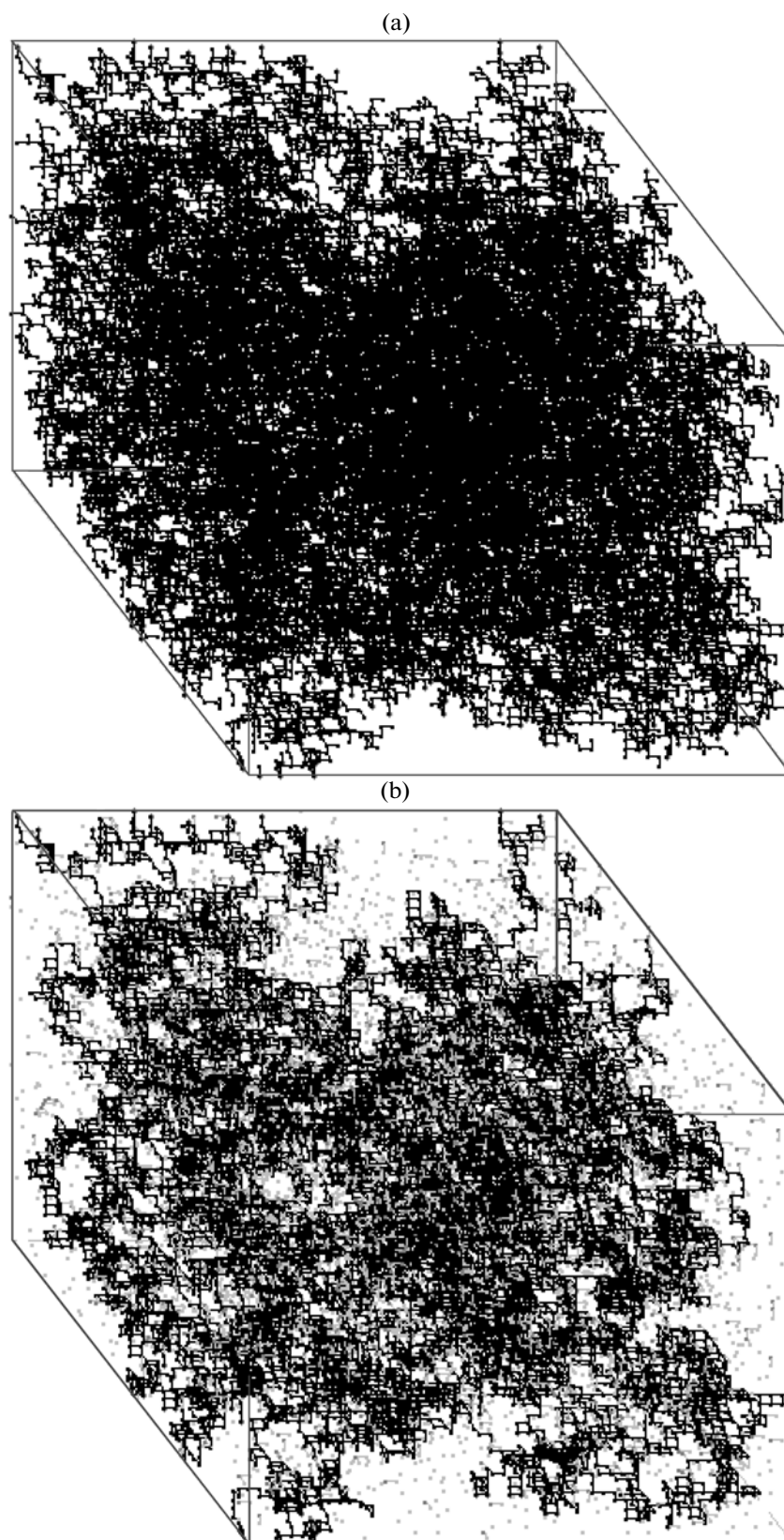


Fig. 3. Computer simulation of a conducting (electrons or ions) percolation cluster in a model cube with the volume of $50 \times 50 \times 50$ (lattice): (a) full percolation cluster, (b) percolation cluster trunk (skeleton). The concentration of conducting grains was 0.35, the concentration of the intercalating agent grains in Fig. 3b (marked gray) was 0.05.

model cube surface to its "front" surface. This inverse wave that changes phase "4" to new phase "1" allows identifying the cells from which one can reach both cathode active layer surfaces.

The ionic percolation cluster the cells of which are assigned values "2" is determined similarly.

Ultimately, the pattern of phase distribution through the cube volume is as follows. There are two branched clusters: electronic one uniting the cells with phase "1", ionic uniting the cells with phase "2", and the intercalating agent cells with phase "0" scattered through the cube volume.

Calculation of Fraction of Intercalating Agent Active Grains and Active Material Specific Surface

After the electronic and ionic percolation clusters are identified, let us consistently search through all cells occupied by intercalating agent grains, i.e. all matrix elements $A(i, j, k)$ with phase value "0". Choosing such a cell, let us identify the phases of all 6 neighboring cells and calculate how many of them have phase "1" and how many correspond to phase "2". If the intercalating agent grains contact each of these phases, the number of intercalating agent active grains increases by unity and the number of its faces bordering the ionic percolation cluster cells is included into the overall sum determining the cathode electrochemically active surface area.

Algorithm of Identifying the Percolation Cluster "Trunk"

The percolation cluster has a branched structure. However, transport of lithium ions or electrons is provided only by a part of grains forming the cluster "trunk". The grain chains branch off from the "trunk" in the form of dead-end channels ("branches") and provide no contribution either to ionic nor, accordingly, to electronic conductivity of the cathode active material. Therefore, it is necessary to eliminate these cluster branches in calculations of the cathode specific conductivity, for which the "plucking" procedure is used. It is also carried out with the help of the "wave" method.

Let us assume that the ionic cluster cells are initially designated as phase "2". It is clear that the cluster cells at one of the interfaces of the cathode active layer (e.g., the "front") are connected through the conductivity channels with the cells at the "rear" active layer interface. Therefore, we include these cells in its structure from the very start of the cluster "trunk" formation changing their phase, e.g., to phase "C" and consider these cells as the origins of conducting channels. Then we consistently choose one of these cells and start moving along the cluster checking each subsequent cell for its ability to participate in the through charge transportation. If confirmation is obtained that the cell belongs to the "trunk", then we assign it to the

new phase (the corresponding matrix element $A(i, j, k)$ is assigned the value of "C"). While the movement occurs along the cluster section without forks, there are no doubts as to the assignment of the cells under consideration to the "trunk" structure. When the fork is reached, we face the problem of identifying the status of cluster cells, namely: which of the branches is a dead-end and which is the transport extension that can be used to reach the final (rear) boundary.

The problem is solved as follows. The cells that were already passed and assigned to the "trunk" belong to phase "C", while the other ionic cells have nonperturbed phase "2". The cell corresponding to the cluster fork is temporarily transferred to the nonconducting type and assigned to phase "X". After that, we observe the phase wave that propagates from the given cell to all acceptable directions and changes phase "2" of the cluster cells to phase "T" (the so called "test wave").

When the wave process is over, we check the rear surface for the presence of cells with phase "T". If such are identified, this means that the cell under consideration is connected with the cathode surface by conducting channels and therefore is a part of the "trunk" structure. But before designating this cell as the "trunk" one, it is necessary to restore the initial state of conducting channels. This is achieved using an "inverse" wave propagating from the rear surface to cells with phase "T".

The "inverse" wave converges to phase "X" that hinders its further propagation to the dead-end branches. It is clear that the "inverse" wave at such an approach cannot appear in dead-end channels and in the loop-type chains, i.e., when the chain of interconnected cells starts and ends at the same fork. Thus, phase "T" in these channels does not change and therefore these cells must be excluded from the percolation cluster "trunk" structure.

The case is also possible when the "test wave" front propagating along the cells with phase "2" comes across the cell that has already been earlier counted as the trunk cell and therefore contains phase "C" differing from "2". This means that there are fork nodes interconnected by parallel channels (similar to parallel connection in electric circuits). In this case, when the "test wave" front stops, the phases of all the neighbors of the last cell from which the wave came are checked. If these include phase "C", then this cell is used as a source of the "inverse" wave that (same as the rear boundary wave) reduces the initial phases in the cells up to the checked cell with phase "X". The case under consideration also indicates that cell "X" may be considered a trunk cell and can be converted to the phase "C" state.

Assigning status "C" to cell "X", let us move further along each conductivity channel changing the cell phases to phase "C" until the next fork. At each fork, the procedure of determination of dead-end channels

Table 1. Dependence of reduced ionic conductivity of electrolyte in the cathode k^* on the bulk concentration of grains of electrolyte g_i in the cathode active material

g_i	k^*
0.35	6.1×10^{-3}
0.40	2.6×10^{-2}
0.45	6.1×10^{-2}
0.50	0.109
0.55	0.166
0.60	0.231
0.65	0.304
0.75	0.475
0.85	0.683
0.95	0.898
1.00	1.0

and conductivity channels is repeated. Thus, we move until we have studied all the cluster cells.

As a result, we obtain within the model cube volume a certain distribution of different phases, among which continuous cell chains designated by letter “C” determine the percolation cluster “trunk”.

RESULTS OF COMPUTER SIMULATION

Let us now pass to description of results of structure computer simulation and method of active material operation of a lithium–ion battery cathode. First of all, let us point to the relationship between conductivity k^* and the fraction of grains of electrolyte g_i . Similar calculations were already carried out in [15, 21]. The results of calculations are presented in Table 1. Ions in the cathode active material have to move through the ionic percolation cluster with a complex fractal structure, so that reduced ionic conductivity by lithium ions may decrease by one–two orders of magnitude at a decrease in g_i .

Let us now consider the data of Table 2. As follows from definition (2), fixation of any two values of the three parameters g , g_i , and g_e results in the constant value of the third parameter. With account for the fact that, as mentioned above, inequalities of $g_i \geq 0.35$ and $g_e \geq 0.35$ must be satisfied, the acceptable concentration of intercalating agent grains must be within the range of

$$0 \leq g \leq 0.30. \quad (5)$$

In Table 2, the main parameter is the bulk concentration of intercalating agent grains in the cathode active material g . Then variation of bulk concentrations of grains of electrolyte g_i (the first column in Table 2) is performed with the step of 0.05 under condition (2). Thus, the bulk concentration of carbon

black grains g_e is determined automatically (the second column in Table 2).

Table 2 as dependent on the set of concentrations (fractions) g , g_i , and g_e presents the following values obtained through computer simulation: fraction of intercalating agent active grains in the cathode active material g^* (the third column in Table 2) and percentage of intercalating agent active grains (quantity g^*/g , the fourth column in Table 2).

The fifth column of Table 2 presents the overall number of faces of intercalating agent active grains on which the electrochemical process may occur. The specific electrochemically active surface area is probably $S = L^2 n_s / 10^6 L^3$, so that reduced specific electrochemically active surface area $SL = n_s / 10^6$ (the sixth column of Table 2).

Finally, the last column in Table 2 presents the reduced specific ionic conductivity of electrolyte k^* in the ionic percolation cluster. Its value is determined only by the value of the fraction of grains of electrolyte in the cathode active material, as already shown in Table 1.

In the case of the practically maximum fraction of intercalating agent grains $g = 0.3$, only 50% of these grains are electrochemically active. At a decrease in concentration g (0.25; 0.20 etc), the percentage of intercalating agent active grains starts growing, which is hardly surprising, as a decrease in g_i results in the possibility of enhancing the values of other components of the cathode active mass: g_e and g^* . It is clear that the probability of a contact between the intercalating agent grain and the ionic and electronic percolation clusters herewith increases. At first, this results in a certain increase in g^* . But the further decrease in the fraction of intercalating agent grains in the cathode active material leads to a decrease in the absolute value of the concentration of active grains.

Similar behavior is also characteristic of reduced specific electrochemical surface area SL . At a decrease in g from $g = 0.30$, it first somewhat grows, reaches a certain extremum and then starts decreasing (curve 1 in Fig. 4).

Of special interest are the data of the last column of Table 2. At $g = 0.30$, the value of reduced specific ionic conductivity of electrolyte in the cathode k^* is very low, as the fraction of grains of electrolyte g_i is herewith low (it has the minimum possible value $g_i = 0.35$). A decrease in g allows working with high bulk concentrations of grains of electrolyte. Thence conductivity k^* starts increasing (curve 2 in Fig. 4). It reaches maximum, as seen from Table 2, at the minimum possible fraction of carbon black grains $g_e = 0.35$.

As shown in [14], the optimum active layer thickness of the lithium–ion battery electrode and therefore its electric capacitance depend on three parameters: on the concentration of intercalating agent active grains g^* , specific surface accessible for the electrochemical process S , and on reduced specific ionic

Table 2. Dependence of characteristics of the active material of the cathode in a lithium–ion battery on the bulk concentration of intercalating agent grains g and grains of electrolyte g_i (the model cube volume was $100 \times 100 \times 100$)

g	g_i	g_e	g^*	$g^*, \%$	n_s	SL	k^*
0.30	0.35	0.35	0.150	50	271273	0.271	0.0061
0.25	0.35	0.40	0.158	63.1	290531	0.290	0.0061
	0.40	0.35	0.157	62.6	329543	0.330	0.026
0.20	0.35	0.45	0.136	67.9	253860	0.254	0.0061
	0.40	0.40	0.157	78.5	338361	0.338	0.026
	0.45	0.35	0.135	67.5	323937	0.324	0.061
0.15	0.35	0.50	0.105	70	198250	0.198	0.0061
	0.40	0.45	0.126	84.2	276809	0.277	0.026
	0.45	0.40	0.126	84.2	311119	0.311	0.061
	0.50	0.35	0.104	69.5	281308	0.281	0.109
0.10	0.35	0.55	0.071	71.2	135245	0.135	0.0061
	0.40	0.50	0.087	86.7	192040	0.192	0.026
	0.45	0.45	0.090	90.2	226186	0.226	0.061
	0.50	0.40	0.087	86.6	239833	0.239	0.109
	0.55	0.35	0.071	70.5	210700	0.211	0.166
0.05	0.35	0.6	0.036	71.7	68463	0.068	0.0061
	0.40	0.55	0.044	87.9	98159	0.098	0.026
	0.45	0.50	0.046	92.8	117437	0.117	0.061
	0.50	0.45	0.046	92.7	130703	0.131	0.109
	0.55	0.40	0.044	87.7	134620	0.135	0.166
	0.60	0.35	0.036	71.1	116150	0.116	0.231

conductivity of electrolyte in the ionic percolation cluster k^* .

The theory involves (in the case of a galvanostatic discharge mode) three characteristic values [14]: the characteristic ohmic length

$$L_{\text{ohm}} = (2RTk^*k/FSi_0)^{1/2}, \quad (6)$$

where R is the gas constant, T is the absolute temperature, F is the Faraday constant, i_0 is the exchange current; characteristic ohmic current

$$I_{\text{ohm}} = (2RTk^*kSi_0/F)^{1/2} \quad (7)$$

characteristic discharge time

$$\tau = g^*Fc^*/Si_0, \quad (8)$$

where c^* is the maximum possible concentration of lithium in intercalating agent grains.

Analysis of the data presented in Table 2 shows that one must not work for the cathode active material with the maximum possible concentration of intercalating agent grains $g = 0.30$. This value should be decreased

to obtain higher values of reduced specific ionic conductivity of electrolyte in the cathode k^* .

It is necessary to work for possible highest value of specific ionic conductivity in the cathode kk^* (k is the specific conductivity of electrolyte) without excessive decrease in the bulk concentration of intercalating agent active grains g^* . This follows from the fact that the order of magnitude of quantity $k \approx 10^{-3} \text{ Ohm}^{-1} \text{ cm}^{-1}$ [22] and product kk^* , as shown by data in Table 1, may even decrease to $kk^* \sim 10^{-5} \text{ Ohm}^{-1} \text{ cm}^{-1}$. So, if no special measures are taken, the cathode active material thickness proportional to characteristic ohmic length- L_{ohm} will be very low (relationship (6)) and therefore the cathode electric capacitance will also be low. On the other hand, a significant decrease in g^* may cause a considerable decrease in the characteristic discharge time (relationship (8)), then the cathode discharge time will also be low.

In optimization of the g^* and k^* values, one must not forget the third important parameter: specific electrochemically active surface area of intercalating

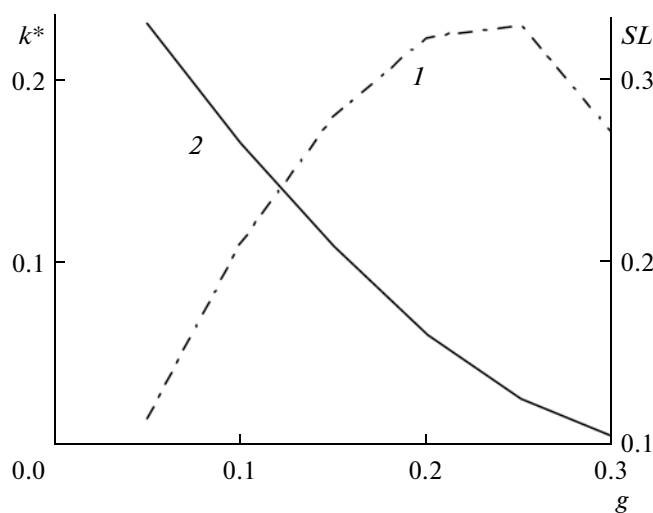


Fig. 4. (1) Dependence of the reduced specific surface area of intercalating agent active grains accessible for the electrochemical process SL and (2) reduced effective specific conductivity of electrolyte in the cathode active mass k^* on the fraction of the intercalating agent grains in the cathode active material. The curves were calculated under the condition that $g_e = g_{e\min} = 0.35$ (the model cube volume was $100 \times 100 \times 100$).

agent grains S . As already pointed out, Fig. 4 presents the dependence on g of conductivity k^* (curve 2) and electrochemically active reduced specific surface area of intercalating agent active grains SL (curve 1). Curves 1 and 2 in Fig. 4 are constructed under the condition that $g_e = \text{const} = g_{e\min} = 0.35$. Thus, as follows from the data of Table 2, conductivity k^* assumes the maximum possible values.

Fig. 4 (curve 1) shows that S somewhat increases at first at a decrease in g from 0.30 and then starts diminishing. Thus, the final choice of the optimum composition of components for a lithium-ion battery cathode is anything but simple. It requires an additional complex of calculations of cathode performance characteristics according to equations, the nature of which was discussed in detail for the case of the galvanostatic mode of the battery anode discharge [14].

It is necessary to discuss yet another important issue. It is usually implicitly assumed in theoretical studies of diffusion processes occurring in an individual intercalating agent grain [23, 24] that this grain is surrounded on all sides by electrolyte. However, the actual situation is much more complicated. In the “model of equal-sized grains of three types” under consideration, only a part of faces of the intercalating agent active grain (from 1 to 5) may be adjacent to grains of electrolyte. And this circumstance must also be taken into account in calculations of performance characteristics of a lithium-ion battery cathode.

It is necessary to find out how the numbers of electrochemically active grains n_i and average number of electrochemically active faces \bar{n} if intercalating agent

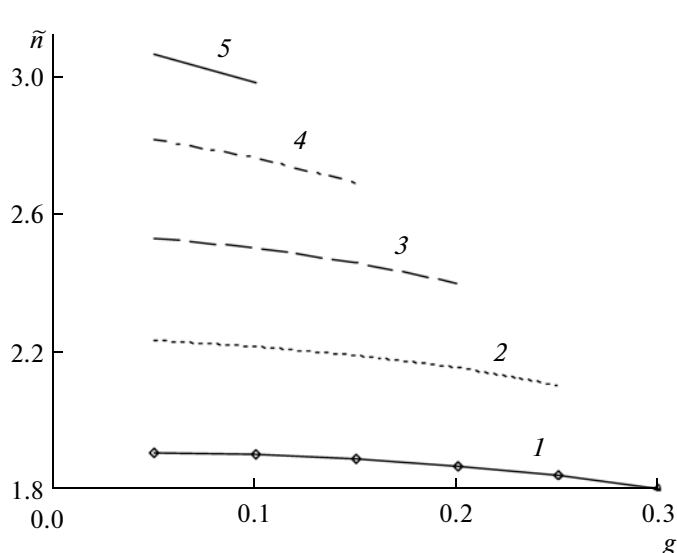


Fig. 5. Dependence of the average number of electrochemically active faces y of intercalating agent active grains \bar{n} on the concentration of its grains g at the given concentration of grains of electrolyte g_i : (1) 0.35, (2) 0.40, (3) 0.45, (4) 0.50, (5) 0.55 (the model cube volume is $100 \times 100 \times 100$).

grains vary under a change in the cathode active material composition (variation of the fraction of the three types of grains: g , g_i , and g_e).

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

$$\bar{n} = (1n_1 + 2n_2 + 3n_3 + 4n_4 + 5n_5) / \sum n_i, \quad (9)$$

in which summation in the denominator is performed from 1 to 5.

Correlation between g , g_i , g_e and n_i and \bar{n} is presented in Table 3. Same as in Table 2, we first fix the fraction of intercalating agent grains g and then go through the possible values of g_i and g_e with the step of 0.05 (limitations imposed by condition (2) and inequalities $g_i \geq 0.35$ and $g_e \geq 0.35$).

Now, if the fraction of grains of electrolyte g_i is fixed and the fraction of intercalating agent grains g is decreased, the dependence of \bar{n} on g will take the form presented in Fig. 5. Such shape of \bar{n} , g -curves is understandable. The higher the concentration of grains of solid polymer electrolyte g_i , the higher the probability of contact between the intercalating agent active grain and ionic percolation cluster. Therefore, the higher the \bar{n} value. The minimum of $\bar{n} = \bar{n}_{\min} = 1.804$ is reached at $g = 0.3$ and $g_i = 0.35$; and then it grows to $\bar{n} = \bar{n}_{\max} = 3.266$ at $g = 0.05$ and $g_i = 0.60$, as shown in Table 3.

A weak dependence of \bar{n} on g in Fig. 5 is explained by the fact that though the concentration of carbon black grains grows at an increase in g , but an intercalation agent grain is active if only there is a contact

Table 3. Dependence of the number of electrochemically active faces of intercalating agent active grains n_i and average number of electrochemically active grains of intercalating agent active grains \bar{n} on the fraction of intercalating agent grains g and fraction of grains of electrolyte g_i (the model cube volume was $100 \times 100 \times 100$)

g	g_i	g_e	n_1	n_2	n_3	n_4	n_5	\bar{n}
0.30	0.35	0.35	68152	51277	23917	6314	712	1.804
0.25	0.35	0.40	68944	53871	26528	7449	893	1.842
	0.40	0.35	49893	56370	36166	12323	1824	2.105
0.20	0.35	0.45	58025	46331	23535	7022	896	1.869
	0.40	0.40	47493	55709	37697	13816	2219	2.156
	0.45	0.35	29305	46134	38932	17337	3244	2.400
0.15	0.35	0.50	44063	35910	18507	5739	778	1.888
	0.40	0.45	37020	44321	30886	12026	2077	2.191
	0.45	0.40	25646	41786	37299	17851	3720	2.463
	0.50	0.35	14796	31124	34094	19568	4742	2.696
0.10	0.35	0.55	29679	24101	12698	4090	582	1.901
	0.40	0.50	24793	30195	21446	8581	1639	2.216
	0.45	0.45	17657	29091	26724	13635	3127	2.507
	0.50	0.40	11333	24428	28415	17591	4807	2.770
	0.55	0.35	6245	17138	23917	17807	5440	2.986
0.05	0.35	0.60	14887	12111	6430	2091	340	1.909
	0.40	0.55	12492	15046	10968	4514	923	2.234
	0.45	0.50	8936	14723	13698	7224	1813	2.531
	0.50	0.45	5786	12629	15101	9814	3020	2.820
	0.55	0.40	3559	9806	14574	11768	4131	3.071
	0.60	0.35	1907	6576	11665	11004	4416	3.266

between this grain and the electronic percolation cluster, but the number of contacts plays here no role.

CONCLUSIONS

A computer simulation of the structure of the cathode active material in a lithium-ion battery is performed. The model of equal-sized grains of three types was studied: of intercalating agent grains, their volume fraction (concentration) g , of grains of electrolyte, their volume fraction g_i , and of carbon black grains (electron carriers), their volume fraction g_e .

The performed percolation calculations yielded the following results.

(1) The acceptable concentration of intercalating agent grains varies in a sufficiently narrow range: $0.00 \leq g \leq 0.30$.

(2) Intercalating agent grains are divided into two types. These are active grains contacting both with the ionic and electronic percolation clusters, their fraction is g^* and inactive grains, their fraction is $g - g^*$. The fraction of intercalating agent inactive grains at $g = 0.30$ is high and reaches 50%. The fraction of inter-

calating agent inactive grains starts decreasing at a decrease in g ; herewith, the g^*/g ratio tends to unity.

(3) An important parameter in the cathode active material is its specific conductivity kk^* . It is very low at $g = 0.30$ ($\sim 10^{-5} \text{ Ohm}^{-1} \text{ cm}^{-1}$) and it may start increasing rapidly at a relevant choice of the cathode active material components at a decrease in g . Therefore, the sought-for optimum value of the fraction of intercalating agent grains in the cathode active material must be significantly lower than the value of the maximum bulk concentration of intercalating agent grains $g = 0.30$.

(4) Another important parameter of the cathode active material is the specific surface area of the intercalating agent active grains accessible for the electrochemical process S . At a decrease in g from 0.30, the specific surface area \bar{n} first somewhat increases and then starts diminishing, which naturally causes impaired operation of the cathode active material.

(5) It is usually implicitly assumed in theoretical studies of diffusion processes occurring in an individual intercalating agent grain that this grain is surrounded on every side by electrolyte and therefore the

whole outer surface may take part in the electrochemical process. However, the actual situation is much more complicated: an intercalating agent in the cathode active material contacts with grains of electrolyte in the ionic percolation cluster only through some of its faces. The value of the average number of electrochemically active faces of intercalating agent active grains \bar{n} is largely determined by the fraction of grains of electrolyte g_i . In the range of $0.00 \leq g \leq 0.30$, the average number of active faces is in the approximate range of $2 \leq \bar{n} \leq 3$.

(6) The final choice of the optimum composition of components for the active material of a lithium-ion battery cathode (and primarily, choice of the value for parameter g) requires performing an additional rather complex set of computer simulations.

DESIGNATIONS OF PARAMETERS CHARACTERIZING THE STRUCTURE OF A LITHIUM-ION BATTERY CATHODE

Structural Parameters

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

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

g_e is the bulk concentration (fraction) of grains supplying electrons (carbon black)

g_i^* is the intercalation cluster for the ionic cluster

g_e^* is the intercalation threshold for the electronic cluster

$g_{i \min}$ is the minimum possible value of the bulk concentration of grains of electrolyte

$g_{e \min}$ is the minimum possible value of the bulk concentration of carbon black grains

g_{\max} is the maximum possible bulk concentration of intercalating agent grains

g^* is the fraction of intercalating agent active grains

N_s is the size of model cube edges (in arbitrary units)

Δ is the cathode active material thickness

L is the size of grain edges of all three types

Amount of Faces of Intercalating Agent Active Grains Accessible for Electrochemical Process

n_{1-5} is the number of intercalating agent grains with one–five electrochemically active faces

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

n_s is the full amount of faces of intercalating agent active grains accessible for electrochemical process

Macro Characteristics of the Cathode

S is the specific surface area of the intercalating agent active grains accessible for the electrochemical process

SL is the reduced specific surface area of the intercalating agent active grains accessible for the electrochemical process

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

k is the specific conductivity of electrolyte

R is the gas constant

T is the absolute temperature

F is the Faraday constant

i_0 is the exchange current of the electrochemical process

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

REFERENCES

1. Bagotskii, V.S. and Skundin, A.M., *Khimicheskie Istochniki Toka* (Chemical Power Sources), Moscow: Energoizdat, 1981.
2. Doyle, M., Fuller, T.F., and Newman, J., *J. Electrochem. Soc.*, 1993, vol. 140, p. 1526.
3. Fuller, T.F., Doyle, M., and Newman, J., *J. Electrochem. Soc.*, 1994, vol. 141, p. 1.
4. Doyle, M., Newman, J., Gozdz, A.S., Schmutz, C.N., and Tarascon, J.-M., *J. Electrochem. Soc.*, 1996, vol. 143, p. 1890.
5. Arora, P., Doyle, M., and White, R.E., *J. Electrochem. Soc.*, 1999, vol. 146, p. 3543.
6. Song, L. and Evans, J.W., *J. Electrochem. Soc.*, 2000, vol. 147, p. 2086.
7. Gu, W.B. and Wang, C.Y., *J. Electrochem. Soc.*, 2000, vol. 147, p. 2910.
8. Srinivasan, V. and Wang, C.Y., *J. Electrochem. Soc.*, 2003, vol. 150, p. A98.
9. Doyle, M. and Fuentes, Y., *J. Electrochem. Soc.*, 2003, vol. 150, p. A706.
10. Sikha, G., Popov, B.N., and White, R.E., *J. Electrochem. Soc.*, 2004, vol. 151, p. A1104.
11. Chizmadzhev, Yu.A., Markin, V.S., Tarasevich, M.R., and Chirkov, Yu.T., *Makrokinetika protsessov v poristykh sredakh* (Macrokinetics of Processes in Porous Media), Moscow: Nauka, 1971.
12. Newman, J.S., *Electrochemical Systems*, New Jersey: Prentice Hall, Englewood Cliffs, 1991.
13. Tarasevich, Yu.Yu., *Perkolyatsiya: teoriya, prilozheniya, algoritmy* (Percolation: Theory, Applications, Algorithms), Moscow: Editorial URSS, 2001.
14. Chirkov, Yu.G., Rostokin, V.I., and Skundin, A.M., *Elektrokhimiya*, 2011, vol. 47, no. 1 [*Russ. J. Electrochem.* (Engl. Transl.)], vol. 47, no. 1].
15. Chirkov, Yu.G. and Rostokin, V.I., *Elektrokhimiya*, 2004, vol. 40, p. 1036 [*Russ. J. Electrochem.* (Engl. Transl.)], vol. 40, p. 898].

16. Chirkov, Yu.G. and Rostokin, V.I., *Elektrokhimiya*, 2003, vol. 39, p. 694 [*Russ. J. Electrochem. (Engl. Transl.)*, vol. 39, p. 622].
17. Chirkov, Yu.G., *Elektrokhimiya*, 1999, vol. 35, p. 1452 [*Russ. J. Electrochem. (Engl. Transl.)*, vol. 35, p.].
18. Chirkov, Yu.G. and Rostokin, V.I., *Elektrokhimiya*, 2002, vol. 38, p. 1437 [*Russ. J. Electrochem. (Engl. Transl.)*, vol. 38, p. 1299].
19. Korol', V.I., *Visual Basic 6.0 for Application*, Moscow: KUDITs-OBRAZ, 2000.
20. Landsberg, G.S., *Optika (Optics)*, Moscow: Fizmatlit, 2003.
21. Chirkov, Yu.G. and Rostokin, V.I., *Elektrokhimiya*, 2006, vol. 42, p. 799 [*Russ. J. Electrochem. (Engl. Transl.)*, vol. 42, p. 715].
22. Skundin, A.M., Efimov, O.N., and Yarmolenko, O.V., *Usp. Khim.*, 2002, vol. 71, no. 4, p. 378.
23. Zhang, Q. and White, R.E., *J. Power Sources*, 2007, vol. 165, p. 880.
24. Zhang, Q. and White, R.E., *J. Power Sources*, 2008, vol. 179, p. 793.

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