

Computer Simulation of Negative Electrode Operation in Lithium-Ion Battery: Optimization of Active Mass Composition

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Abstract—The work of the positive electrode (cathode) of a lithium-ion battery is simulated. The model of equally sized grains of three types: the intercalating agent grains with a volume fraction g , the electrolyte grains with a volume fraction g_i , and the carbon black grains with a volume fraction g_e is studied. The optimal composition of cathode active mass providing maximum specific electric capacitance of cathode is determined. It is shown that a fraction of carbon black grains should be as small as possible: $g_e = 0.35$. The variation in the fraction of intercalating agent grains within the allowable limits ($0 \leq g \leq 0.3$) changes the main parameters of cathode active mass: a fraction of electrochemically active intercalating agent grains g^* ($g^* < g$); a specific surface area S , on which the electrochemical process proceeds; and the conductivity k^* by lithium ions in the ionic percolation cluster, which forms in the cathode active mass. The parameters g^* and S decrease and parameter k^* steeply increases with decreasing g . Therefore, in the range of possible values of g , specific electric capacitance of cathode reaches the maximum value at $g = g_{\text{opt}}$. The value of g_{opt} is determined under the galvanostatic mode of cathode discharge. The cathode working parameters: the active layer thickness, discharge time, specific electric capacitance, and potential at the cathode active layer/interelectrode space interface at the instant of discharge completion are calculated in relation to a fraction of intercalating agent grains g .

Keywords: lithium-ion battery, positive electrode (cathode), optimal composition of cathode active mass, galvanostatic discharge mode, computer simulation, model of equally sized grains of three types, percolation theory, cluster conduction, intercalation

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STATEMENT OF PROBLEM

In the work, the procedure of determining the optimal working parameters of cathode of lithium-ion battery by the methods of computer simulation is demonstrated. Here, the composition of cathode active mass is optimized.

As well as in [1], we consider a model of equally sized grains of three types. The cathode active mass consists of the intercalating agent grains (with a volume fraction g), the grains of electron-donor material (carbon black) (with a volume fraction g_e), and the electrolyte grains (with a volume fraction g_i).

The presence of voids in the cathode material is undesirable, and it is assumed that the voids are absent. In addition, the presence of a binding agent in the cathode active mass is ignored. Under these assumptions, the following condition is true:

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

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All grains of carbon black, electrolyte, and intercalating agent are identical microcubes with edges L . Thus, within the percolation theory, in the model of equally sized grains, a cubic lattice is considered [2].

A model cube with conventional dimensions $N_s \times N_s \times N_s = N_s^3$ is taken as a three-dimensional model of cathode active mass. The model cube should have macroscopic dimensions. This means that the cathode active mass thickness Δ should be much larger than the dimensions of individual grains (the microcube edge L), which is actually true. Earlier [3], it was shown that the distribution of the components over the active mass becomes reproducible only at sufficiently high parameter N_s . One can obtain the reproducible curves by taking $N_s = 100$. Thus, we will consider a model cube containing $100 \times 100 \times 100 = 10^6$ grains of three types.

In each of cathode intercalating agent grain, the active substance molecules realize the battery charge or discharge process. Lithium ions and electrons should be permanently delivered to or removed from the active substance molecules. The ionic (of the elec-

trolyte grains) and electronic (of the carbon black grains) percolation clusters, which form in the cathode active mass, serve as the channels for delivery or removal of lithium ions or electrons, respectively. Each cluster consists of a set of immediately connected grains of one or another type. The percolation clusters extend any distance throughout the entire width of cathode active mass, and uniformly occupy the model cube volume.

The percolation clusters form, when the percolation threshold is reached, i.e. the volume fractions of the corresponding grains reach certain values: g_i^* and g_e^* . In the cubic lattice under consideration, as it was shown earlier [4], the percolation threshold is

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

Thus, the cathode active mass can operate provided that at least two conditions are fulfilled: $g_i > 0.3$ and $g_e > 0.3$. The variation in the structure of the corresponding percolation clusters after reaching the threshold values of g_i^* or g_e^* and with further increasing parameters g_i and g_e was analyzed in [5]. It was shown that, near the percolation threshold, the percolation cluster is weakly developed, and its main "mass" does not occupy completely the model cube volume. Therefore, most of intercalating agent grains are not connected with the grains involved in the ionic and electronic percolation clusters. These grains cannot accept or donate lithium ions and electrons, i.e. cannot take part in the electrochemical process.

The situation with the transport of lithium ions and electrons to the intercalating agent grains is improved [5], when the volume fractions of electrolyte grains and carbon black grains are raised to $g_i = g_e = 0.35$. In this case, the total percolation cluster and its core ("skeleton" providing transport of ions or electrons) sufficiently uniformly occupy the model cube volume. Therefore, the values $g_{i \min} = 0.35$ and $g_{e \min} = 0.35$ will be taken as the minimum values of concentrations g_i and g_e in the computer calculations. Thus, it is required that

$$g_i \geq 0.35, \quad (3)$$

$$g_e \geq 0.35. \quad (4)$$

Even in the presence of full-value ionic and electronic percolation clusters in the active mass, not every intercalating agent grain can take part in the electrochemical process. For example, an intercalating agent microcube can have 6 (in accordance with the number of faces) neighboring intercalating agent microcubes. In this case, it cannot accept (or donate) lithium ions.

Only a grain, which comes into contact with an ionic percolation cluster by at least one of its 6 faces and comes into contact with an electronic percolation cluster by at least one face, can be denoted active grain

of intercalating agent. Obviously, an intercalating agent grain can come into contact with an ionic percolation cluster by 5 faces at the most. The 6-th face is required for the contact of the intercalating agent grain with an electronic percolation cluster.

In [5], the following goals were accomplished by using the percolation computer calculations. First, a fraction of active grains of intercalating agent (the grains, which really contribute to the electrochemical process) g^* ($g^* < g$) was determined. Second, the number of electrochemically active faces of intercalating agent active grains in the model cube $100 \times 100 \times 100$ in size was calculated and, using this value, a specific surface area S (or a dimensionless reduced surface area SL) was calculated. Third, the dimensionless conductivity by lithium ions k^* in a percolation ionic cluster in the active cathode mass was determined.

As it was shown earlier [5], under the galvanostatic conditions of current generation in the electrodes of lithium-ion battery, three values g^* , SL , and k^* are sufficient for determining the working parameters of the battery. The theory involves three characteristic values:

the characteristic ohmic length:

$$L_{\text{ohm}} = (2RTkk^*/FSi_0)^{1/2}, \quad (5)$$

where R is the gas constant, T is the absolute temperature, F is the Faraday number, k is the electrolyte conductivity, and i_0 is the exchange current;

the characteristic ohmic current:

$$I_{\text{ohm}} = (2RTkk^*Si_0/F)^{1/2}; \quad (6)$$

and the characteristic time of cathode discharge:

$$\tau = g^*Fc^*/Si_0, \quad (7)$$

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

Table 1 gives the dependence of g^* , SL , and k^* on the active mass composition (g , g_i , and g_e). From Eq. (1) it follows that any two values of three parameters g , g_i , and g_e determine the third one. With regard for inequalities (3) and (4), the fraction of intercalating agent grains should fall in rather narrow range:

$$0 \leq g \leq 1 - 2 \times 0.35 = 0.3. \quad (8)$$

In Table 1, the volume fraction of intercalating agent grains in the cathode active mass g serves as the main parameter. The volume fraction of electrolyte grains g_i was varied in steps of 0.05 within the range allowed by conditions (1), (3), and (4) (Table 1, the first column). Then, the volume fraction of carbon black grains g_e appeared to be determined (Table 1, the second column).

Equations (5) and (6) show that the cathode specific electric capacitance (which is proportional to L_{ohm}) and the current generated in the cathode (which is proportional to I_{ohm}) increase with increasing ionic conductivity of cathode active mass as $(kk^*)^{1/2}$. The ionic conductivity by lithium in the cathode active

mass kk^* is very low. The value of k is approximately $10^{-3} \Omega^{-1} \text{cm}^{-1}$ [6], and the product kk^* , as it is seen from Table 2 [7], can decrease to approximately $10^{-5} \Omega^{-1} \text{cm}^{-1}$. Therefore, the value of kk^* should be maximized. This means that, at a given g , the lowest possible value of the fraction of carbon black grains g_e should be taken in order to obtain the highest k^* .

Figure 1 gives the dependences of g^* , SL , and k^* on g , which are plotted by the data of Table 1. The curves 2 and 3 (Fig. 1) are plotted provided that $g_e = \text{const} = g_{e \text{ min}} = 0.35$, and, as it is seen from Table 1, the conductivity k^* takes the highest possible values. With decreasing g , the conductivity k^* steeply increases; however, a fraction of active grains g^* and the surface area S , on which the electrochemical process proceeds, decrease. The specific electric capacitance of the cathode is

$$C \sim g^* L_{\text{ohm}} \sim g^* (k^*/S)^{1/2}. \quad (9)$$

Therefore, one should not try to reach the highest volume fraction of intercalating agent grains $g = 0.3$ in the cathode active mass. The value of g should be decreased to g_{opt} , at which the highest capacitance will be reached. The main goal of this study is to determine g_{opt} .

COMPUTATIONAL EQUATIONS

At the initial instant of time (at $t = 0$), the concentration of lithium atoms in all intercalating agent grains (for the sake of definiteness, hereafter, lithium nickelate Li_yNiO_2 will be considered) is c_0 . Then, in the course of cathode discharge, the concentration of lithium atoms in the intercalating agent grains will increase. The reduced concentration of lithium atoms in the intercalating agent grains is $\check{c} = c/c^*$, where c^* is the highest possible concentration.

The current density j , which is generated at the interface between the ionic percolation cluster and the surface of active intercalating agent grains, is as follows:

$$j = i_0 [(1 - \check{c}_s)^{1/2} \check{c}_s^{1/2}] \{e^\eta - e^{-\eta}\}, \quad (10)$$

where \check{c}_s is the reduced concentration of lithium atoms on the surface of active intercalating agent grains and i_0 is the exchange current. The dimensionless polarization is

$$\eta = F[E - U]/2RT, \quad (11)$$

where E is the cathode potential. The cathode open-circuit potential will as follows [8]:

$$U = 6.515 + 2.319\check{c} - 5.3342\check{c}^{1/2} + 0.41082 \times \exp[200(0.44 - \check{c})] - 0.24247 \exp[60(\check{c} - 0.99)]. \quad (12)$$

Figure 2 gives this dependence. The reduced concentration of lithium atoms in the intercalating agent grains ranges within the limits $0.45 < \check{c} < 1.0$ [8]; therefore, the highest possible potential is $(2RT/F) U = 50 \text{ mV} \times$

Table 1. The characteristics of cathode active mass of lithium-ion battery in relation to the volume fractions of intercalating agent grains g and solid polymeric electrolyte grains g_i (the volume of model cube is $100 \times 100 \times 100$)

g	g_i	g_e	g^*	SL	k^*
0.3	0.35	0.35	0.150	0.271	0.0061
0.25	0.35	0.4	0.158	0.290	0.0061
0.25	0.4	0.35	0.157	0.330	0.026
0.2	0.35	0.45	0.136	0.254	0.0061
0.2	0.4	0.4	0.157	0.338	0.026
0.2	0.45	0.35	0.135	0.324	0.061
0.15	0.35	0.5	0.105	0.198	0.0061
0.15	0.4	0.45	0.126	0.277	0.026
0.15	0.45	0.4	0.126	0.311	0.061
0.15	0.5	0.35	0.104	0.281	0.109
0.1	0.35	0.55	0.071	0.135	0.0061
0.1	0.4	0.5	0.087	0.192	0.026
0.1	0.45	0.45	0.090	0.226	0.061
0.1	0.5	0.4	0.087	0.239	0.109
0.1	0.55	0.35	0.071	0.211	0.166
0.05	0.35	0.6	0.036	0.068	0.0061
0.05	0.4	0.55	0.044	0.098	0.026
0.05	0.45	0.5	0.046	0.117	0.061
0.05	0.5	0.45	0.046	0.131	0.109
0.05	0.55	0.4	0.044	0.135	0.166
0.05	0.6	0.35	0.036	0.116	0.231

Table 2. The dependence of lithium conductivity in the ionic percolation cluster k^* on the volume fraction of electrolyte grains g_i

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
1.0	1.0

$$[6.515 + 2.3192 - 5.3342 + 0.41082 \times \exp(-112) - 0.24247 \exp(0.6)] = 4.036 \text{ V.}$$

From the conservation law of lithium ion fluxes in the electrolyte (in the grains of ionic percolation clus-

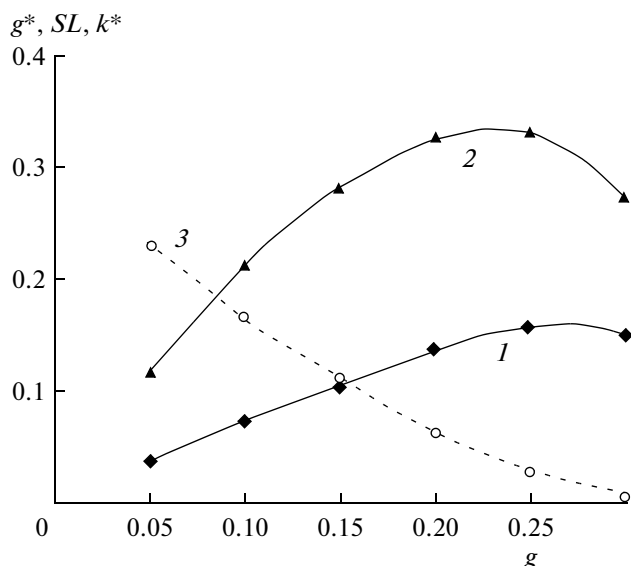


Fig. 1. Dependences of (1) a fraction of intercalating agent active grains g^* , (2) the reduced specific surface area of intercalating agent active grains, which is available for the electrochemical process SL , and (3) the conductivity of lithium ions in the ionic percolation cluster in the cathode active mass k^* on the fraction of intercalating agent grains g . The curves 2 and 3 were calculated provided that $g_e = g_{e \min} = 0.35$ (the model cube volume is $100 \times 100 \times 100$).

ter), the following equation for the polarization η in the cathode active layer can be obtained:

$$d^2\eta/d\hat{y}^2 = [(1 - \hat{c}_s)^{1/2} \hat{c}_s^{1/2}] \{e^\eta - e^{-\eta}\}, \quad (13)$$

where $\hat{y} = y/L_{\text{ohm}}$ is the reduced coordinate and L_{ohm} is the characteristic ohmic length (equation (5)). In the case of galvanostatic discharge mode, the boundary conditions for equation (13) are as follows:

$$-I_{\text{ohm}} d\eta/d\hat{y} = I = \text{const} \quad \text{at } y = 0, \quad (14)$$

$$d\eta/d\hat{y} = 0 \quad \text{at } y = \Delta \quad (\text{near the current collector}), \quad (15)$$

where I is the discharge current and I_{ohm} is the characteristic ohmic current (equation (6)).

The variation in the concentration of lithium atoms in the intercalating agent grains is described by the following equation:

$$d\check{c}/dr^* = [(1 - \hat{c}_s)^{1/2} \hat{c}_s^{1/2}] \{e^\eta - e^{-\eta}\}, \quad (16)$$

Here, $\check{c}(y, t)$ is the averaged concentration of lithium atoms in the intercalating agent grains at the instant of time t in the cross-section of cathode active layer with the coordinate y (the plane separating the cathode

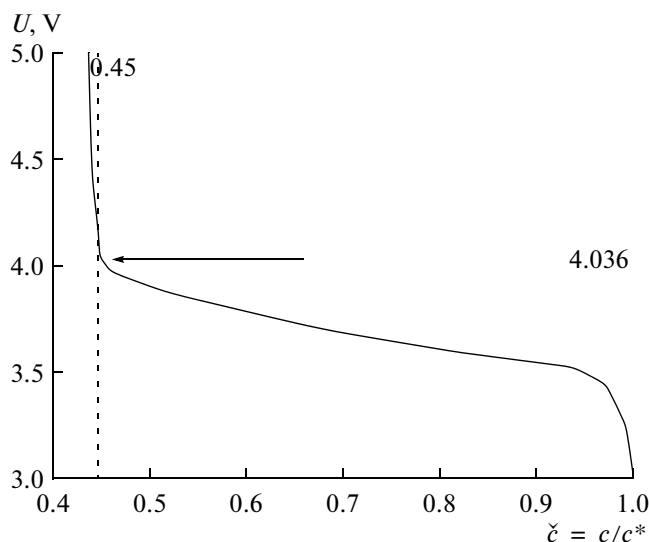


Fig. 2. The dependence of open-circuit potential of cathode with lithium nickelate (Li_xNiO_2) on the degree of lithium atom intercalation $\check{c} = c/c^*$ ($0.45 \leq \check{c} \leq 1.0$).

active layer from the interelectrode space has the coordinate $y = 0$). In equation (16), the reduced coordinate for instant of time t is as follows:

$$t^* = t/\tau, \quad (17)$$

where τ is the characteristic time defined by equation (7). The initial condition for equation (16) is as follows:

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

Table 3 lists the chosen parameters of cathode active mass. Then, using the data from Tables 1–3 and equations (5)–(7), the dependence of the characteristic parameters on the volume fraction of intercalating agent grains can be presented (Table 4).

The data presented in Table 4 enable us to estimate the working parameters of the cathode: the volume fraction of active intercalating agent grains, the active layer thickness, the current and the cathode discharge time. It is seen that the active layer is tens microns thick (Table 4, column 5), the characteristic current density is approximately 1 mA/cm^2 (Table 4, column 6), and the characteristic time of cathode discharge varies within an hour (Table 4, column 7).

Table 4 also allows us to estimate the cathode electric capacitance C by the following evident equation:

$$C = Fc^*g^*(1 - c_0) L_{\text{ohm}}. \quad (19)$$

Using the data of Tables 3 and 4 (and assuming that $c_0 = 0.45$), we can calculate the dependence of cathode specific capacitance C on the fraction of intercalating agent grains g in its active mass (Table 5).

As it was supposed, the data of Table 5 allow us to make an important conclusion that the optimal content of intercalating agent grains in the cathode active

Table 3. Initial parameters of cathode active mass

$k, \Omega^{-1} \text{ cm}^{-1}$	$D, \text{ cm}^2/\text{s}$	$i_0, \text{ A/cm}^2$	$L, \text{ cm}$	$c^*, \text{ g m/cm}^3$
10^{-3}	2×10^{-10}	2.1×10^{-4}	5×10^{-4}	3×10^{-2}

mass is not the highest possible value $g = 0.3$, but a smaller value $g = 0.15$. In this case, the cathode capacitance reaches the value $C = 1.131 \text{ C/cm}^2$.

Clearly, these are approximate estimates. In addition, it is desirable to know the variation in the distribution of concentration of lithium atoms across the active layer width and the variation of potential at the cathode active layer/interelectrode space interface with the time of cathode discharge. Other peculiarities of cathode discharge process can also be of interest. All the above can be determined by calculating precisely the working parameters of cathode active layer.

RESULTS OF CALCULATION OF CATHODE WORKING PARAMETERS

System of equations (13) and (16) incompletely describes the processes proceeding in the cathode active mass. The right-hand side of equation (13) involves \hat{c}_s , the concentration of lithium atoms at the intercalating agent active grains/electrolyte grains interface, and the left-hand side of equation (16) involves \check{c} , the averaged concentration of lithium atoms in the intercalating agent grains. The interrelation between these concentrations was discussed in details in [5]. Hereafter, it is assumed that the effect of diffusion of lithium atoms in the intercalating agent grains on the cathode parameters may be ignored. In this case, we can assume that

$$\check{c} = \hat{c}_s. \quad (20)$$

Rather rigid criterion of fulfillment of equation (20) will be determined. Assuming that an intercalating agent grain is approximately spherical with radius $R = L/2$, the condition of equal fluxes of lithium atoms (the diffusion transfer in the intercalating agent grains) and ions (in the active layer) at the interface between the intercalating agent active grains and the electrolyte grains incorporated in the ionic percolation cluster is as follows:

$$-\chi d\hat{c}/d\hat{r} = [(1 - \hat{c}_s)^{1/2} \hat{c}_s^{1/2}] \{e^\eta - e^{-\eta}\}, \quad (21)$$

where $d\hat{c}/d\hat{r}$ is the reduced flux of lithium atoms at the surface of intercalating agent grain [5], and

$$\chi = F D c^* / R i_0. \quad (22)$$

Obviously, condition (20) is fulfilled provided that the flux of lithium atoms near the surface of intercalating agent grain is $d\hat{c}/d\hat{r} \approx 0$. This is true provided that

$$\chi \gg 1. \quad (23)$$

From the data presented in Table 3, the value of parameter χ is estimated at 11.

The point of the effect of diffusion of lithium atoms in the intercalating agent grains on the processes proceeding in the active mass of battery electrodes requires further thorough analysis. However, it is clear that inequality (23) will be fulfilled well for the cathodes with nano-sized grains.

Table 4. The dependence of characteristic parameters on the volume fraction of intercalating agent grains g ($k = 10^{-3} \text{ W}^{-1} \text{ cm}^{-1}$, $g_e = 0.35$)

g	g^*	$S, \text{ cm}^{-1}$	k^*	$L_{\text{ohm}}, \mu\text{m}$	$I_{\text{ohm}}, \text{ mA/cm}^2$	$\tau, \text{ s}$
0.30	0.150	542	0.0061	16.5	0.187	3815
0.25	0.157	660	0.026	30.8	0.427	3279
0.20	0.135	648	0.061	47.6	0.647	2872
0.15	0.104	562	0.109	68.3	0.806	2551
0.10	0.071	422	0.166	97.3	0.862	2319
0.05	0.036	232	0.231	155	0.754	2139

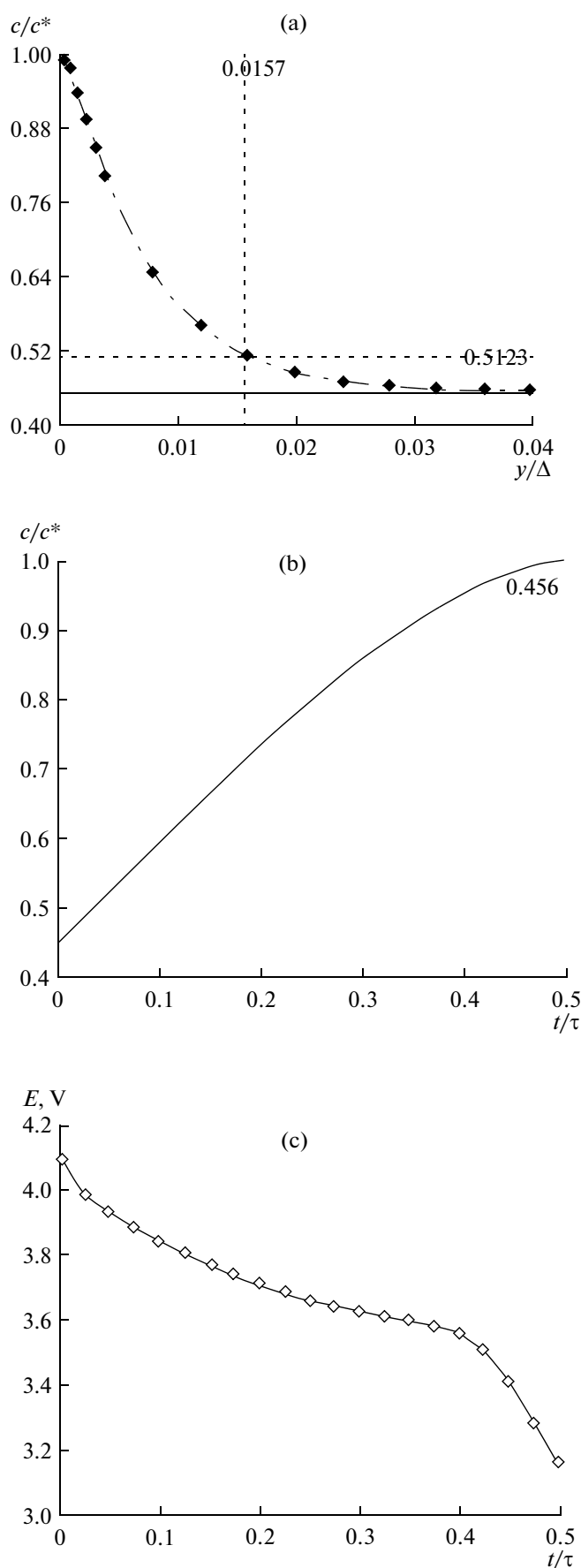
Table 5. The dependence of the fraction of active intercalating agent grains g^* and specific capacitance C on the volume fraction of intercalating agent grains g

g	g^*	$C, \text{ C/cm}^2$
0.30	0.150	0.394
0.25	0.157	0.770
0.20	0.135	1.023
0.15	0.104	1.131
0.10	0.071	1.010
0.05	0.036	0.888

Here, it is sufficient to assume that, to the first approximation, the cathode with the parameters listed in Table 3 can be approximately characterized by the condition (20). Then, the working parameters of lithium-ion battery cathode under consideration can be calculated by equations (13) and (16) assuming that $\hat{c}_s = \check{c}$.

Obviously, the discharge in the cathode active layer should be terminated, when the intercalating agent grains, which are located on the plane separating the cathode active layer from the interelectrode space, become filled with lithium atoms almost to the limiting value. Assume that the concentration of lithium atoms in an intercalating agent grain can increase only to $c = 0.99c^*$. This is also the point of cathode discharge termination.

Now, the working parameters of lithium-ion cathode will be estimated. The computational procedure will be demonstrated by the example of the cathode with $g = 0.15$; initially, a discharge current I of 1 mA/cm^2 is taken. First, the intercalating agent grains, which are located at the cathode active layer/interelectrode space interface, are considered. Here, in the course of cathode discharge, the concentration of lithium atoms in the intercalating agent grains will increase (equation (16)) from $c/c^* = 0.45$ to $c/c^* = 0.99$ (see Fig. 3a). (In other layers of cathode active layer, the final concentration of lithium atoms will be lower.)



In Fig. 3a, the entire store of lithium atoms accumulated during discharge is located between the horizontal line $c/c^* = 0.45$ (the initial content of lithium atoms in the intercalating agent grains) and the final discharge curve. The optimal thickness of cathode active layer Δ^* is determined as follows. The entire lithium accumulated in the discharge period is collected (integrated); then, a cross-section of active layer Δ^* , to which (from the cross-section $y = 0$ to the cross-section $y = \Delta^*$) the amount of collected lithium is 90% of the total lithium amount, which can be collected ideally. This value Δ^* (it is indicated in Fig. 3a) is a reasonable optimal thickness of the cathode active layer.

The next step is to determine the anode discharge time t . We are again interested only in the intercalating agent grains at the cathode active layer/interelectrode space interface. The reduced concentration at this interface increases with the time (Fig. 3b). The time, when the reduced concentration reaches 0.99, will be the discharge time $t = t^{**}$.

Potential E at this interface decreases with the time (Fig. 3c) and its value $E = E^*$ is recorded at the instant of discharge termination. The anode capacitance is estimated by the following simple equation:

$$C = It^{**}, \quad (24)$$

where I is the cathode discharge current.

The computational procedure was repeated for various values of volume fraction of intercalating agent g in the cathode active layer and for various discharge currents I . The results are shown on Fig. 4 and listed in Tables 6–8.

For each of possible values of g at the minimum fraction of grains of electron-donor substance (carbon black) $g_e = \min = 0.35$, the optimal working parameters of cathode active layer are calculated: its thickness Δ^* , the cathode discharge time t^{**} , specific capacitance of active mass C , and potential at the cathode active layer/interelectrode space interface at the instant of cathode discharge termination E^* .

It is shown that the optimal volume fraction of intercalating agent grains is $g_{\text{opt}} = 0.15$. With a decrease in the discharge current from $I = 10 \text{ mA/cm}^2$ (Table 6) to $I = 0.1 \text{ mA/cm}^2$ (Table 8), the specific capacitance of cathode active mass C increases from 0.236 (Table 6) to 1.515 C/cm^2 (Table 8). Further decrease in the discharge current density has almost no effect on C .

The cathode discharge time t^{**} varies from several minutes to several hours; the optimal thickness of

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Fig. 3. (a) Concentration profile of lithium atoms in the cathode active layer at the instant of time, when lithium concentration on the surface of intercalating agent active grain is $c/c^* = 0.99$. (b) The time dependence of concentration of lithium atoms in the intercalating agent grains at the active layer/interelectrode space interface. (c) The time dependence of potential on the cathode active layer/interelectrode space interface. $g = 0.15$, $I = 1 \text{ mA/cm}^2$.

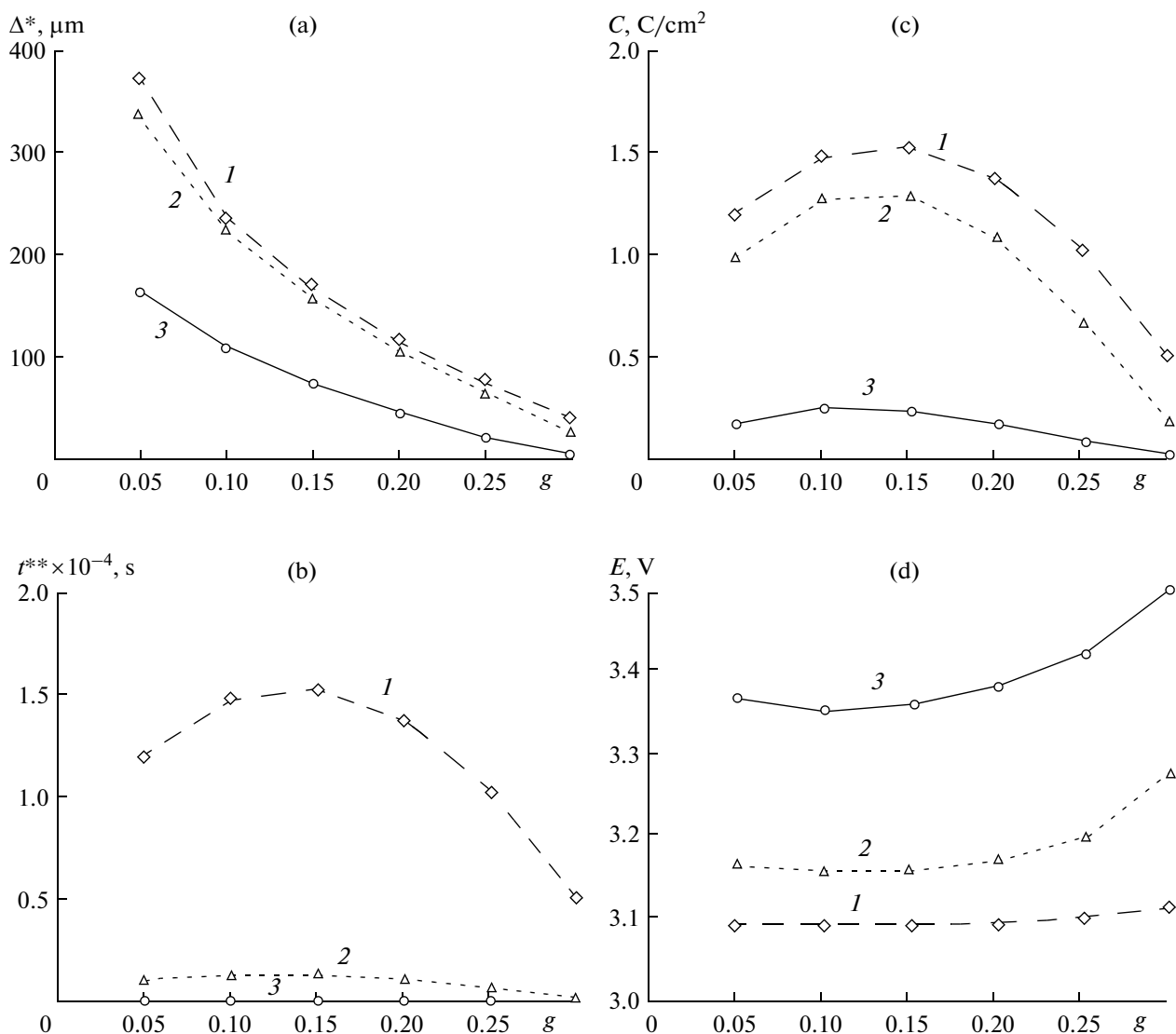


Fig. 4. The dependences of the main cathode working parameters: (a) the optimal active layer thickness Δ^* , (b) the discharge time t^{**} , (c) specific electric capacitance C , and (d) the final potential at the cathode active layer/interelectrode space interface E^* on the volume fraction of intercalating agent grains in the cathode active mass. I , mA/cm^2 : (1) 10^{-1} , (2) 1, and (3) 10.

cathode active layer Δ^* varies from tens to hundreds μm ; at the instant of discharge termination, the potential E^* at the cathode active layer/interelectrode space interface varies insignificantly: from 3.5 to 3.1 V.

It should be emphasized that precise values of Δ^* , t^{**} , and C (Tables 6–8) correlate well the values obtained in section Computational Equations, where the cathode working parameters were estimated by using Tables 4 and 5. Table 5 enabled us to estimate sufficiently accurately the optimal composition of cathode active mass $g = 0.15$ and $g_e = 0.35$ ($g_i = 0.5$) and cathode capacitance $C = 1.13 \text{ C/cm}^2$; approximate values of cathode active layer thickness and discharge time were also obtained.

Equation (6) is also important for estimating the cathode parameters. The characteristic ohmic current I_{ohm} is

an approximate optimal value for the discharge current density I . In Table 4, at $g = 0.15$ and $g_e = 0.35$ ($g_i = 0.5$), the characteristic current is $I_{\text{ohm}} = 0.806 \text{ mA/cm}^2$. The data of Tables 6–8 and Fig. 4 indicate that the value $I = 1 \text{ mA/cm}^2$ should be chosen as an approximate upper limit for the discharge current density.

If we deal with the cathodes for powerful batteries with a discharge current density of 100 mA/cm^2 , in accordance with equations (5)–(7), the size of grains in the active mass should be decreased to nanometers. For example, instead of $L = 5 \times 10^{-4} \text{ cm}$ (Table 3), $L = 50 \text{ nm}$ should be taken. In this case, if the ionic conductivity of electrolyte k can be increased by two orders of magnitude ($k = 0.1 \text{ } \Omega^{-1} \text{ cm}^{-1}$ instead of $k = 10^{-3} \text{ } \Omega^{-1} \text{ cm}^{-1}$, Table 3), (it should be noted that optimally moistened proton-conducting solid polymeric

Table 6. Dependence of cathode optimal working parameters on the volume fraction of intercalating agent (Li_yNiO_2) grains g . The discharge current $I = 10 \text{ mA/cm}^2$, $g_e = 0.35$

G	g_i	Δ^* , μm	t^{**} , s	C , C/cm^2	E^* , V
0.30	0.35	5.4	1.95	0.019	3.50
0.25	0.40	21.3	8.6	0.086	3.42
0.20	0.45	45.0	17.2	0.172	3.38
0.15	0.50	74.4	23.6	0.236	3.36
0.10	0.55	111	24.5	0.245	3.35
0.05	0.60	165	17.4	0.173	3.37

Table 7. Dependence of cathode optimal working parameters on the volume concentration of intercalating agent (Li_yNiO_2) grains g . The discharge current $I = 1 \text{ mA/cm}^2$, $g_e = 0.35$

g	g_i	Δ^* , μm	t^{**} , s	C , C/cm^2	E^* , V
0.30	0.35	27.8	181	0.181	3.28
0.25	0.40	61.3	328	0.328	3.17
0.20	0.45	106	1071	1.071	3.17
0.15	0.50	157	1275	1.275	3.16
0.10	0.55	225	1262	1.262	3.16
0.05	0.60	335	975	0.975	3.16

Table 8. Dependence of cathode optimal working parameters on the volume concentration of intercalating agent (Li_yNiO_2) grains g . The discharge current $I = 0.1 \text{ mA/cm}^2$, $g_e = 0.35$

g	g_i	Δ^* , μm	t^{**} , s	C , C/cm^2	E^* , V
0.30	0.35	39.4	5112	0.51	3.11
0.25	0.40	74.4	10260	1.026	3.10
0.20	0.45	115	13700	1.37	3.09
0.15	0.50	165	15150	1.515	3.09
0.10	0.55	235	14750	1.475	3.09
0.05	0.60	374	11890	1.189	3.09

Table 9. Dependence of characteristic parameters of active layers of high-power cathodes on the volume fraction of intercalating agent (Li_yNiO_2) grains g ($L = 50 \text{ nm}$, $k = 0.1 \text{ } \Omega^{-1} \text{ cm}^{-1}$)

G	g^*	S , cm^{-1}	$k k^*$	L_{ohm} , μm	I_{ohm} , mA/cm^2	τ , s
0.30	0.150	5.42×10^4	0.00061	16.5	18.7	38.15
0.25	0.157	6.60×10^4	0.0026	30.8	42.7	32.79
0.20	0.135	6.48×10^4	0.0061	47.6	64.7	28.72
0.15	0.104	5.62×10^4	0.0109	68.3	80.6	25.51
0.10	0.071	4.22×10^4	0.0166	97.3	86.2	23.19
0.05	0.036	2.32×10^4	0.0231	155	75.4	21.39

electrolyte Nafion exhibits this protonic conductivity), the discharge current density can be raised immediately by two orders of magnitude.

Similarly to the data presented in Table 4, Table 9 lists the characteristic parameters of active layers of powerful cathodes. It should be noted that, according to equations (19) and (5)–(7), the specific capacitance of powerful cathodes remains the same $C \sim 1.5 \text{ C/cm}^2$; only the discharge current density changes by a hundred times (Table 9, column 6) and, correspondingly, the discharge time decreases by hundreds times (Table 9, column 7).

If the cathode capacitance should be raised by an order of magnitude (to $C \sim 15 \text{ C/cm}^2$) and the working value of current in it should be raised by an order of magnitude (to $I \sim 10 \text{ mA/cm}^2$), it is necessary to keep constant the size of intercalating agent grains ($L = 5 \times 10^{-4} \text{ cm}$) and raise significantly the ionic conductivity of electrolyte (up to $k = 0.1 \text{ } \Omega^{-1} \text{ cm}^{-1}$).

Figure 5 gives the dependences of optimal active layer thickness Δ^* and specific capacitance C on the volume fraction of intercalating agent grains in the cathode active mass of lithium-ion battery for three ionic conductivities of electrolyte (k , $\Omega^{-1} \text{ cm}^{-1}$: 10^{-3} , 10^{-2} , and 10^{-1}). The battery discharge current density is $I = 1 \text{ mA/cm}^2$.

CONCLUSIONS

In the work, the computer simulation of the work of positive electrode (cathode) of lithium-ion battery, which was begun in [5], is continued. The model of equally sized grains of three types: the intercalating agent grains with a volume fraction g , the electrolyte grains with a volume fraction g_i , and the carbon black grains (electron conductors) with a volume fraction g_e (it is assumed that $g + g_i + g_e = 1$) is studied.

The allowable volume fraction of intercalating agent grains was estimated earlier [1]. It was shown that the volume fraction of intercalating agent grains falls within rather narrow limits ($0 \leq g \leq 0.3$), and the volume fractions of electrolyte grains and carbon black grains should obey the following inequalities: $g_i \geq 0.35$ and $g_e \geq 0.35$. It was also shown that not all of intercalating agent grains can be involved in the electrochemical process. A fraction of electrochemically active grains of intercalating agent was calculated by using special algorithms of computer calculations.

The variation of a fraction of intercalating agent grains within the allowable limits leads to a change of important parameter of cathode active mass: a fraction of active intercalating agent grains g^* , the specific surface area S , on which the electrochemical process proceeds, and the conductivity k^* by lithium ions in the percolation ionic cluster, which forms in the cathode active mass. The first and second parameters (g^* and S) decrease, whereas k^* steeply increases with decreasing g . Therefore, in the range of allowable values of g , the

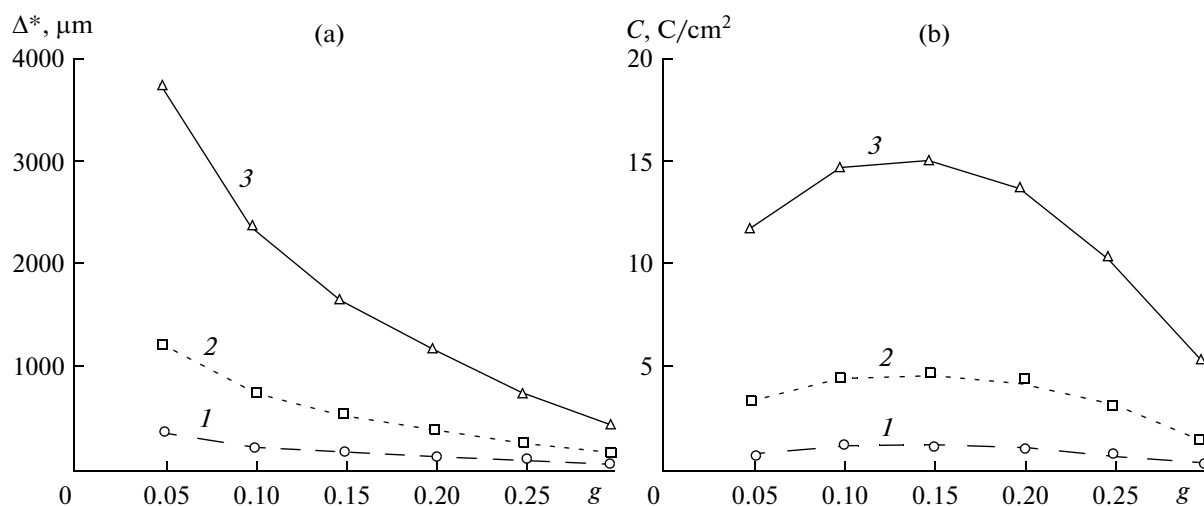


Fig. 5. The dependences of (a) active layer optimal thickness Δ^* and (b) specific capacitance C of the cathode of lithium-ion battery on the volume fraction of intercalating agent grains in the cathode active mass; $k, \Omega^{-1} \text{ cm}^{-1}$: (1) 10^{-3} , (2) 10^{-2} , and (3) 10^{-1} ; $I = 1 \text{ mA/cm}^2$.

specific capacitance of cathode reaches the maximum value at a certain value $g = g_{\text{opt}}$.

This work is devoted predominantly to choosing the optimal composition of cathode active mass of lithium-ion battery and, primarily, the optimal value of parameter g . The procedure of selecting the optimal composition of cathode active mass is demonstrated. It is shown that a fraction of carbon black grains should be the smallest possible: $g_e = 0.35$.

The value of g_{opt} was determined by the example of galvanostatic mode of cathode discharge. All cathode working parameters: the active layer thickness, the discharge time, specific electric capacitance, and potential at the cathode active layer/interelectrode space interface at the instant of discharge termination were calculated in relation to a fraction of intercalating agent grains g .

These calculations confirmed the existence of the optimal composition of cathode active layer. The value $g = g_{\text{opt}}$ was determined. For instance, at the following chosen parameters of cathode active mass: the electrolyte conductivity $k = 10^{-3} \Omega^{-1} \text{ cm}^{-1}$, the exchange current $i_0 = 2.1 \times 10^{-4} \text{ A/cm}^2$, the intercalating agent grain dimension $L = 5 \times 10^{-4} \text{ cm}$, and the highest concentration of lithium atoms in an intercalating agent grain $c^* = 3 \times 10^{-2} \text{ g m/cm}^3$, the optimal value of g was $g_{\text{opt}} = 0.15$ and the specific electric capacitance reached $C = 1.52 \text{ C/cm}^2$.

Other optimal cathode working parameters were also calculated: the active layer thickness, the discharge time, and the variation of potential at the cathode active layer/interelectrode space interface with the time were also calculated.

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

External Parameters

- t is the cathode discharge time
- $t^* = t/\tau$ is the reduced time of cathode discharge
- t^{**} is the optimal time of cathode discharge
- τ is the characteristic time of cathode discharge
- $C, \text{ C/cm}^2$ is the specific electric capacitance of cathode
- $T = 293 \text{ K}$ is the working temperature of the cathode
- Δ is the thickness of cathode active layer
- Δ^* is the optimal thickness of cathode active layer

Parameters of Electrochemical Kinetics

- $F = 9.65 \times 10^4 \text{ C/mol}$ is the Faraday's number
- $I, \text{ A/cm}^2$ is the cathode discharge current
- $j, \text{ A/cm}^2$ is the current density at the intercalating agent grain/electrolyte interface
- i_0 is the exchange current
- η is the dimensionless polarization
- E is the cathode potential
- E^* is the cathode potential at the active layer/interelectrode space interface at the instant of discharge termination
- U is the open-circuit potential of cathode
- $L_{\text{ohm}}, \text{ cm}$ is the characteristic ohmic length
- $I_{\text{ohm}}, \text{ A/cm}^2$ is the characteristic ohmic current
- y is the coordinate
- $\hat{y} = y/L_{\text{ohm}}$ is the reduced coordinate

Parameters of Active Layer Structure

g is the volume fraction of intercalating agent grains

g^* is the volume fraction of intercalating agent active grains

g_{opt} is the optimal volume fraction of intercalating agent grains

g_i is the volume fraction of electrolyte grains

g_e is the volume fraction of electron-donor material (carbon black)

g_i^* is the percolation threshold for the ionic percolation cluster

g_e^* is the percolation threshold for the electronic percolation cluster

$g_{i \text{ min}} = 0.35$ is the minimum allowable volume fraction of electrolyte grains

$g_{e \text{ min}} = 0.35$ is the minimum allowable volume fraction of black carbon grains

L is the grain edge length of intercalating agent, carbon black, and electrolyte

S , cm^{-1} is the specific surface area of interface between active intercalating agent grains and ionic percolation clusters

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

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

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

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

χ is the parameter determining the mode of lithium atom recovery from the intercalating agent grains

Parameters Determining Mass and Electric Transfer

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

k is the ionic conductivity of electrolyte

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

kk^* is the ionic conductivity of cathode active mass

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