

# Porous Electrodes with Immobilized Enzymes: The Fractal–Percolation Properties of Supports Manufactured from Particles of Finely Divided Colloidal Graphite

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**Abstract**—The development of a porous active layer with an immobilized enzyme of a sufficiently large thickness is one of the problems that unavoidably emerge when constructing biofuel cells with high characteristics. Mounting up the thickness can be obstructed not only by the ohmic and diffusion limitations, which have been studied well enough. One more possibility of limitations (supports manufactured from finely divided colloidal graphite, FDCG), namely a “fractal–percolation effect,” which has recently been discovered experimentally, is discussed in the paper. The essence of the effect consists of that the particles that are constituting a porous support may gather in random fractal clusters, which are connected with one another (the percolation part of the problem) with a probability that is other than unity. As a result, the electrons that are required for performing bioelectrocatalysis are capable of penetrating into a porous support only to a limited depth. Computer simulation of the fractal and percolation processes is performed in this work. As a result, quantitative relationship of the bulk concentration of FDCG in solution with the size of random fractal clusters, with the probability of their contact with one another, and with the degree of providedness of the material of the support by electrons is established. It may happen that all this information can become useful for the development of porous electrodes with an immobilized enzyme of high activity.

*Key words:* computer simulation, biofuel cell, porous electrode, support, finely divided colloidal graphite, immobilized enzyme, fractals, random fractal cluster, percolation

## AN INTRODUCTION TO THE PROBLEM

To estimate the electrochemical activity  $I$ , A cm<sup>−2</sup> of active layers (AL) of porous electrodes in biofuel cells (of particular interest here are hydrogen–oxygen systems [1–5], for the electrocatalysts here are used laccase and cytochrome *c* oxidase on the oxygen electrode and hydrogenase and glucose oxidase, if there is proceeding the process of oxidation of glucose, on the hydrogen electrode) one can employ the simple formula

$$I = JN_A\Delta, \quad (1)$$

where  $J$ , A is the current, which is generated by an individual molecule of the enzyme;  $N_A$ , cm<sup>−3</sup> is the number of active molecules of the enzyme in a unit volume, those molecules to which access is provided for all the required participants of the electrochemical process (substrate, electrons, and ions); and  $\Delta$ , cm is the thickness of AL. The magnitude of  $J$  is defined by the nature of the selected enzyme and the magnitude of polarization, more complicated is the question of the magnitude

of  $N_A$ . We attempted to determine this quantity by a method of computer simulation [6] in [7–11], where we investigated AL of very diverse architecture, specifically, stochastic (all particles are distributed in space in a random fashion) and with partially (insertion of regular gas pores [9]) and completely regular structure [10, 11]. We have demonstrated how important it is to create an effective porous support in AL for placing as large a number of active molecules of the enzyme on its surface as possible. Obviously, the larger the specific surface area of a porous support  $S$ , the larger  $N_A$ . The former is inversely proportional to the radius of individual particles of the support  $r$

$$S \sim 1/r. \quad (2)$$

Various carbonaceous components—carbon blacks, activated carbons, pyrographite [12–16]—are used for the material of porous supports. The highest specific surface area of a porous support (formula (2)) can, probably, be obtained by using finely divided colloidal graphite (FDCG) [17–19]. The average diameter of particles of the FDCG has nanometer dimensions. We will yet come back to a discussion of the fractal–percolation properties of porous supports manufactured from parti-

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cles of FDCG, but at this juncture we will address ourselves to the third cofactor in the right-hand part of relationship (1).

Should we start raising the thickness of AL  $\Delta$  from zero, the current  $I$  at first would start linearly rise (region of equiaccessibility). However, this rise would continue only to a certain limit. The presence of unavoidable ohmic and diffusion limitations [20–23] would lead to that the current little by little would reach a maximum and then it would either reach a limiting value or it would start to drop. Really the working thickness of AL  $\Delta^*$  is defined by the smaller out of two characteristic lengths—ohmic  $L_{\text{ohm}}$  and diffusion  $L_d$ . Actually, one of the problems that stand before a theory of porous electrodes in biofuel cells consists precisely of the calculation of the magnitude of  $\Delta^*$  on the basis of data concerning the structure of AL, the distribution of active molecules of the enzyme in it, and the numerical values of parameters that are characterizing ohmic and diffusion limitations. However, all of a sudden it became clear [24] that not only ohmic and diffusion limitations can restrict the growth of current following an increase in thickness.

#### EXPERIMENTAL EVIDENCE

The authors of [24] were studying AL of the oxygen electrode of a biofuel cell on the basis of a nanocomposite material that had been manufactured from finely divided carbonaceous supports with molecules of an enzyme—laccase—immobilized on them. Earlier it had been demonstrated in [25–27] that, when immobilized on carbonaceous materials by means of adsorption, laccase is capable of realizing mediatorless electrochemical reduction (direct bioelectrocatalysis) of oxygen in weakly acid solutions of electrolytes. It is precisely in these conditions that the authors of [24] investigated the effect the thickness of an active layer exerted on the magnitude of dimensional current  $I$  in a broad range of potentials (from 0.7 V, which is a stationary potential, to 0.3 V). In particular, when utilizing FDCG in the role of a support, the authors of [24] observed independence of specific current ( $I/\Delta$ ) of the reduction of oxygen by laccase at amounts of composite (FDCG + laccase) from 0.3 to 0.5 mg cm<sup>-2</sup> (which corresponds to thicknesses equal to approximately 3–5  $\mu\text{m}$ ), while the specific current of reduction of oxygen dropped by more than three times following an increase in the amount of the active mass on the electrode to 1.5 mg cm<sup>-2</sup> (to  $\Delta = 15 \mu\text{m}$ ). This experimental fact demanded an explanation.

At first it was assumed that ohmic and diffusion limitations were to blame for the decrease in the current. The relevant estimates showed as follows. The ratio  $L_d/L_{\text{ohm}} = 0.043$ . Consequently, one could have restricted oneself to taking into account only the diffusion limitations. On the other hand, an estimate of a characteristic diffusion length gave, however,  $L_d = 11.7 \mu\text{m}$ . Even a simple comparison of this value to the

range of thicknesses of AL (from 5 to 15  $\mu\text{m}$ ), which were investigated in [24], was pointing to the insignificance of the diffusion limitations. The ultimate outcome of the estimates was as follows. An experimental curve  $I/\Delta, \Delta$  was lying considerably lower than a corresponding calculated curve that was describing the diffusion limitations. The implication of this fact was that taking into account only the possible diffusion limitations does not give a possibility to make theory agree with experiment. There probably were some other factors that reduced currents following the mounting of the thickness of AL.

It was assumed that the decrease in the specific currents, which was observed experimentally, was caused by the steadily worsening, with the thickening of AL, supply of particles of the carbonaceous support (FDCG) by electrons. Naturally, the carbonaceous particles that were directly abutting to a current lead were receiving electrons. But, if the process of a relay passing of electrons to carbonaceous particles that were situated farther away from a current lead was complicated, if it occurred with a probability other than 100%, then, on average, the farther away from the current lead were situated particles of the carbonaceous support, the greater was the probability that they would not be furnished with electrons. Consequently, laccase molecules that are “sitting” on these particles would not enter the composition of active molecules of the enzyme and would not make any contribution to the process of generation of current.

Thus, it was hypothesized that, in this particular case, probably, there manifested itself a process, which is known in science under the name of percolation. Theory of percolation, which was started by the pioneering work [28], strongly expanded at present [29–35]. The theory speaks of the possibility or the absence of topological connectedness of a certain aggregate of elements, which are connected with one another in a random fashion with a certain probability  $\gamma$ . In such a system of elements, once parameter  $\gamma$  reached critical value  $\gamma = \gamma^*$  (“threshold of percolation”), there emerges an infinitely large (macroscopic) cluster of elements connected with one another (“percolation cluster”). In so doing, the penetrating agent (in the percolation theory they usually speak of the “flowing” of a certain “fluid,” while in our case we speak of the penetration of electrons from the surface of a current lead into the depth of the active layer) is capable of spreading in the structure under investigation to any distance. As to the situation existing before the instant of the formation of a percolation cluster, the fluid (electrons) is capable of penetrating AL only to a finite depth. In these conditions the providedness of particles of the support with electrons rapidly drops upon moving away from the current lead and, consequently, there must be observed a rapid drop of an  $I/\Delta, \Delta$  curve.

At this juncture it is pertinent to again revert to the details of experiments that were performed by the

authors of [24]. At present, for an AL of an electrode in a biofuel cell to have a large specific surface area (formula (2)), it is manufactured with the aid of methods borrowed from colloid chemistry [36–42]. The authors of [24] manufactured a nanocomposite on the basis of laccase and FDCG as follows. Two milligrams of the carbonaceous component were deployed in 100  $\mu\text{l}$  of a citrate–phosphate buffer solution of laccase that contained 16  $\mu\text{g}$  of laccase, thoroughly mixed, and left for two hours. Then an aliquot of the mixture was deployed on a porous support (“floating” electrode providing for the supply of gas) and dried up at room temperature.

Afterwards there were created AL of various thickness. To verify a percolation hypothesis, also created were porous layers of FDCG containing no laccase. And there was determined their specific capacitance ( $C/\Delta$ ). In so doing, observed was independence of the specific capacitance of thickness up to 0.3  $\text{mg cm}^{-2}$  (up to a thickness of approximately 3  $\mu\text{m}$ ), following a further increase in the layer thickness, the specific capacitance dramatically dropped. Another version of capacitance measurements—the creation of AL containing laccase, here the specific capacitance dropped with increasing layer thickness even more significantly. In so doing, the absolute value of the specific capacitance of the FDCG + laccase composite was smaller than the value of the specific capacitance that was measured on the support containing no laccase. Apparently, the additionally inserted molecules of laccase, which are not conductors of electrons, disengage agglomerates of FDCG particles even greater, the conducting electrons, thus increasing the drop of the capacitance.

### THE FRACTAL–PERCOLATION EFFECT

The assumption about a percolation effect is plausible enough. However, we do not understand why the FDCG particles, which conduct electric current (their average diameter amounts to 3–4 nm, the specific surface area of FDCG is equal to 2000  $\text{m}^2 \text{g}^{-1}$ ), when having gathered in a liquid solution into agglomerates and entered the composition of AL, do not provide for a relay passing of electrons in layers of large thickness. Probably there exists a mechanism, which may be obstructing the passing of electrons from one agglomerate of FDCG particles to another. We deem it possible to assume that the reason for the decrease in the specific activity of reduction of oxygen by laccase that is immobilized on FDCG is the frustration of electron contact between agglomerates of carbonaceous particles in the composite material.

When utilizing a composite material on the basis of FDCG, a possible reason for the percolation effects may be the existence of vanishingly thin hydration layers between particles of the carbonaceous material in the agglomerates. As had been pointed out by M. Smolukhovskii (together with A. Einstein he developed theory of Brownian movement of colloidal particles [43]), for the free energy of a system to decrease,

direct contact between particles in solution in the process of coagulation is not necessarily a must. The free energy may drop also in the case where the particles merely converge at some minimum distance, which allows them to interact through the hydration layers that are separating them [36, 44–46].

According to the theory of stability of lyophobic colloids, which was developed by Deryagin, Landau, Verwey, and Overbeck (the DLVO theory [47–50]), the particles that are in coagulation contact may be fixed at distances of short-range ( $\sim 1$  nm) and long-range ( $\sim 100$  nm) coagulation. It would have seemed that these solvation layers, which get in the way of exchange by electrons between the neighboring particles of FDCG in the agglomerates, are precisely the culprits responsible for the percolation phenomena that were discovered by the authors of [24]. However, this is not the case. In the first place, the aliquot in [24] was subjected to drying, which must have led to the annihilation of thick liquid layers ( $\sim 100$  nm). Secondly, owing to the effect of tunneling of electrons [51–55], thin hydration layers ( $\sim 1$  nm) are unlikely to serve as an obstacle for the exchange by electrons between the neighboring particles of FDCG. Thirdly, the percolation effects that were discovered by the authors of [24] begin manifesting themselves only at micrometer thicknesses of active layers, whereas the hydration connectors, should they have been playing a crucial role, were bound to have manifested themselves far earlier, as early as at nanometer thicknesses of an active layer, at distances that are commensurate with the dimensions of individual particles of FDCG.

In view of this, the authors of [24] put forth yet another assumption about the nature of percolation effects, which seems to our minds more reliable. The assumption in question consists of that the FDCG particles do not simply gather themselves into coagula but that agglomerates of particles of a carbonaceous material may have some peculiar structure and may be clusters of a peculiar kind—random fractal clusters (these are called also “Brownian fractals”).

A fractal cluster is an object with rarefied structure. The theory of fractal structures or, simply put, fractals was begun two decades ago by works of American mathematician B. Mandelbrot [56, 57]. He introduced new geometrical notions for the description of complicated structures and, in particular, porous media. Owing to him, lexicon of science acquired the notion “fractal.”

The theory of fractals is rendered in [58–63] (good reviews of the theory of fractals may also be found in [64–67]). If we start calculating the dimensionality of porous formations by methods intrinsic to the theory of fractals, then this quantity, which carries the name “fractal dimensionality”  $D$  will not at all be rigorously equal to 2 or 3, which are dimensionalities of two-dimensional or three-dimensional euclidean space ( $d = 2$  for a surface and  $d = 3$  for a volume). The fractal dimension-

ality  $D$  will be fractional and will always satisfy the inequality  $D < d$ . The noncoincidence of  $D$  with  $d$  testifies to the “defectness,” “imperfectness” of a two-dimensional or three-dimensional structure, to the degree of deviation of a porous structure from monolithic crystalline bodies.

Fractality causes also the rarefied nature of fractal clusters. When in a condensed state (for example, a model of a liquid drop) a cluster is an agglomerate of particles tightly pressed to one another. In this case the cluster radius  $R_c$  is connected with the number  $n$  of particles that are constituting the cluster through the relationship

$$R_c = R_0 n^{1/3}, \quad (3)$$

where  $R_0$  is the effective radius of an individual molecule. For a volumetric cluster of a fractal structure, on the other hand, relationship (3) must be replaced by the relationship

$$n = \xi R^D, \quad (4)$$

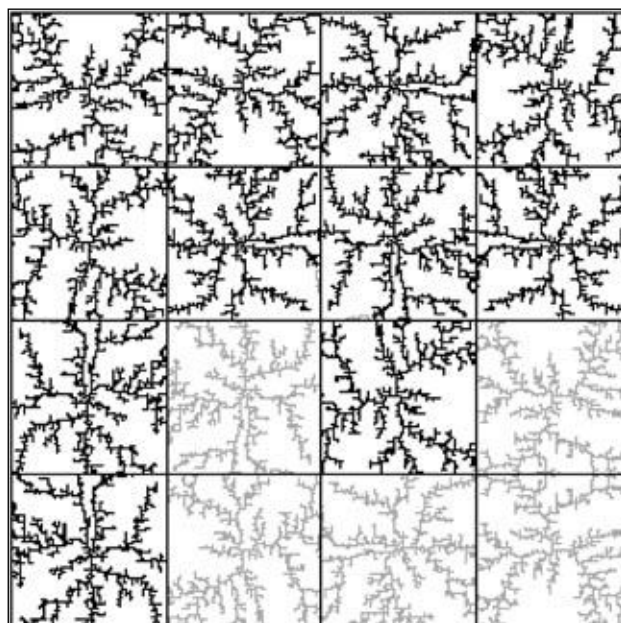
where  $\xi$  is a proportionality coefficient. The rarefied nature (looseness) of fractal clusters is caused by the fact that  $2 < D < 3$  in expression (4).

Of importance for us in this investigation is that, if particles of FDCG in solution, as a result the Brownian movement, do gather in agglomerates whose structure is a random fractal cluster, then, when bringing two such agglomerates, direct contact between these agglomerates and, consequently, the exchange by electrons become a problem. Such structures get in touch with one another by their peripheral parts, where fractal clusters are most rarefied. Therefore, the emergence of connecting, passing electrons, “bridges” between them is not a reliable event.

The hypothesis about the existence of fractal clusters was put forth by the authors of [24]. However, it was only of a qualitative character. The aim of this work is not only to describe the mechanism of such a phenomenon, where fractal properties of individual elements define percolation properties of the system as a whole, but also to perform quantitative evaluations in the framework of a complicated fractal-percolation model. Concretely, it is necessary to link the major parameter of the system—the concentration of FDCG particles in solution—with the size of the emerging random fractal clusters and with the magnitude of the probability of contact between two random fractal clusters that touch one another (parameter  $\gamma$ ). Thereafter it is necessary to perform percolation calculations, i.e. to determine how the electrons that take part in the electrochemical reduction of oxygen are distributed over the thickness of AL.

## THE COMPUTER SIMULATION

We will now pass to describing the essence of computer simulation of the fractal-percolation effect. Here, a number of simplifying assumptions was made. In the

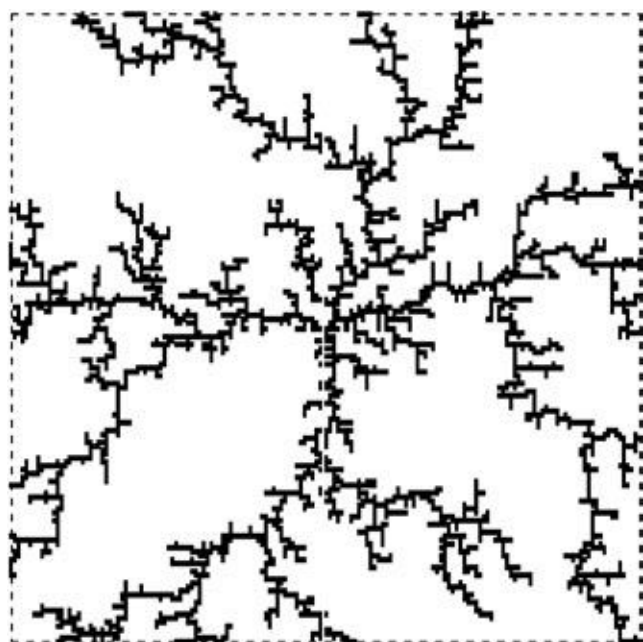


**Fig. 1.** Model for the active layer of a porous electrode. In each cell there are positioned random fractal clusters of size 71 by 71. The current lead adjoins the top side of the active layer. The cells that have access to the current lead and are provided for with electrons are marked with black color, and the cells that are isolated from the current lead are marked with gray color.

first place, for simplicity and obviousness, studied were two-dimensional, rather than three-dimensional, objects. Secondly, it was assumed that all fractal clusters have the same dimensions. And thirdly, an AL was presented in the form of a set of square cells of size  $L \times L$ .

Figure 1 shows an analysis of two-dimensional model of AL—a plane square lattice of points of size 4 by 4. In each square cell of this lattice of points there are present random fractal clusters of identical size 71 by 71, which have, as their centers, points that are located at centers of square cells. As the current lead is situated at the top of the model, all the cells of the top row that are in direct contact with the current lead are supplied with electrons. These are painted by black color. In 2nd to 4th rows of cells there now can emerge cells that are isolated from neighbors and are devoid of electrons. These are painted by gray color.

Agglomerates of FDCG particles that happened in every cell of the lattice (Fig. 1) were constructed in the following manner. There exists a large number of computer models of aggregation and growth of fractal clusters of liophobic colloids [68–71]. We selected the simplest technique, used quite frequently, which was suggested in [72] (see also reviews given in [73–77]), which is a diffusion limited aggregation (DLA). The essence of the DLA procedure consists of the following. The first step consists of the positioning of the center of a future random fractal cluster, an inoculation particle is deployed here. Then, a particle is released out of



**Fig. 2.** The random fractal cluster of size 161 by 161 that was obtained as a result of computer simulation of the process of the Brownian movement of particles in a fluid, whose movement is directed toward the center of a square of size 400 by 400 (aggregation with limited diffusion). The rest of explanations are in text.

the perimeter of a very large circumference with its center in the inoculation cell. The particle moves in a random fashion (emulation of the Brownian movement, diffusion) until it either leaves the circumference limits or reaches the perimeter of the inoculation cell and docks with it (act of coagulation of colloid particles). Then a second particle is released and the process is repeated, but this time this particle has a chance to somehow settle on an agglomerate formed by two particles. In this manner there emerges a cluster that contains now three particles. Such a procedure is then repeated many thousands of times, until there forms (“grows”) a random fractal cluster of large dimensions.

To determine fractal dimensions of the obtained random fractal clusters, we will consider a family of squares of area  $R_i^2$  with the center in the inoculation cell and count the number  $M_i$  of cluster cells that are present inside every square. Having calculated values  $y = \ln(M_i)$  and  $x = \ln(R_i)$ , we will find parameters of a function of linear regression [78]

$$y = b + dx, \quad (5)$$

which describes in the best manner possible the obtained data by the procedure of the least squares. The range of variations in linear dimensions  $R_i$  was selected so as the shift  $b$  was the least.

The next stage of the computer simulation we performed consisted of that, out of the initial fractal cluster of large dimensions, there were cut squares of a small

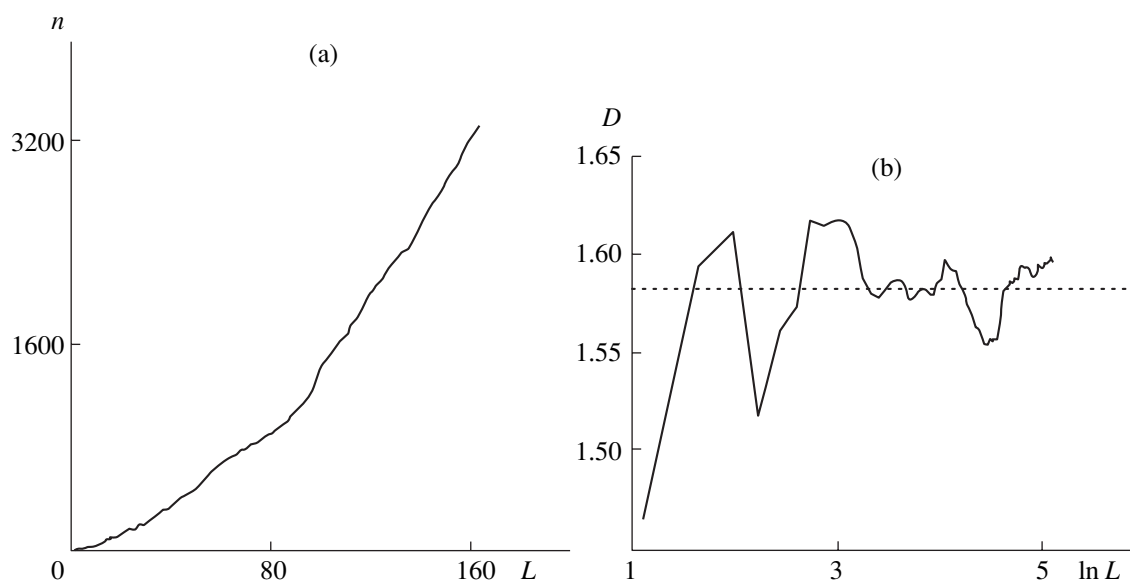
size  $L \times L$  with parts of a random fractal cluster imprisoned in them. This is precisely what was one of the cells of the model lattice under investigation (Fig. 1). Then this procedure was repeated, another fractal cluster was generated, a portion of size  $L \times L$  was cut out of it for the next cell, and so forth. Then it was necessary to find a way to somehow estimate the probability  $\gamma$  of that the neighboring cells in a square lattice were percolationally connected with one another.

Here, there was suggested what was probably a simplest technique. Two different random fractal clusters of large dimensions were “engendered.” Having selected a value of  $L$ , two square cells of size  $L \times L$  were cut out of these two clusters. The first cell served as a basis, while the second cell was docked with the first cell by turns by all its four sides and additional versions that were obtained when rotating it around two mutually perpendicular axes parallel to the sides of the initial square. That produced 32 possible versions of the docking of two different clusters of size  $L \times L$ . Then it was counted how many times the docking was crowned with success (this meant that electrons could pass from one cell into the other). Finally, the number that was obtained in this fashion was divided by the overall number of all versions, i.e. by 32. It is precisely this ratio between two numbers that was taken to be the probability of contact of cells in the lattice with cells of size  $L \times L$ .

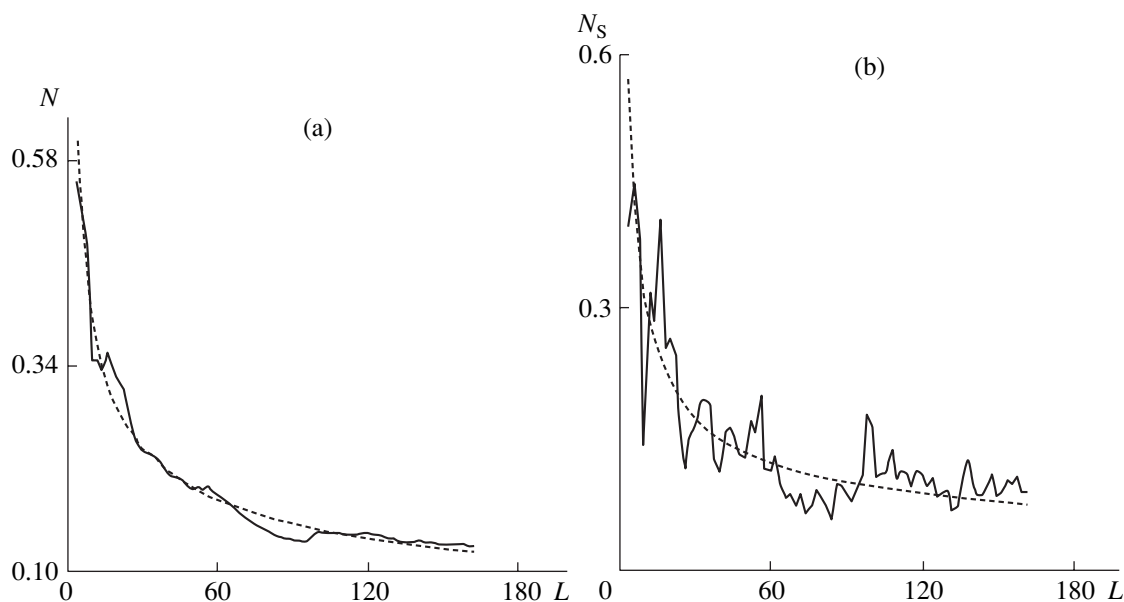
The last stage of computer-aided calculations was the solution of a percolation problem. In a model lattice of large dimensions of the type that is depicted in Fig. 1 (emulation of AL) it was necessary to find the absolute and reduced distribution of cells provided with electrons in the lattice. This was the manner in which modeled were the experiments on the measurement of capacitive  $C/\Delta, \Delta$  curves performed by the authors of [24], which we have mentioned in the foregoing.

## DISCUSSION OF THE RESULTS OF CALCULATIONS

We will now pass to a discussion of the concrete results of computer-aided calculations. In Fig. 2 we present a random fractal cluster of size 161 by 161, which was obtained as a result the Brownian movement of particles in a fluid (DLA model), whose movement was directed to the center from the walls of a square of size 400 by 400. The principal characteristic of a cluster, which is the fractal dimension  $D$ , was determined with the aid of procedures that were pointed out in the foregoing. In addition, there was calculated the dependence of the power of a fractal  $n$  (formula (4))—the number of particles constituting the fractal—on the dimensions of a square area  $L \times L$ , which geometrically correctly embraces the center of the cluster (obviously,  $L$  must take on only odd values). A dependence of  $n$  on  $L$  for the random fractal cluster that is presented in Fig. 2 is presented in Fig. 3a. It is obvious that the slopes of the obtained curve are proportional to  $D$  (formula (4)),



**Fig. 3.** Determination of the average value of the fractal dimension for the random fractal cluster that is depicted in Fig. 2. (a) Dependence of the power (number of particles) of the cluster on the magnitude of the side of the square that is limiting the cluster and (b) dependence of the fractal dimension on the magnitude of the side of the square that is limiting the cluster. The value of the fractal dimension (dashed line)  $D = 1.58$ .



**Fig. 4.** Dependence of major characteristics of the random fractal cluster that is depicted in Fig. 2 on the magnitude of the side of the square that is limiting the cluster. (a) The density of particles that make up the fractal and (b) the density of the particles of the fractal that exit onto its boundaries (sides of the square); the dashed line shows the run of theoretical curves.

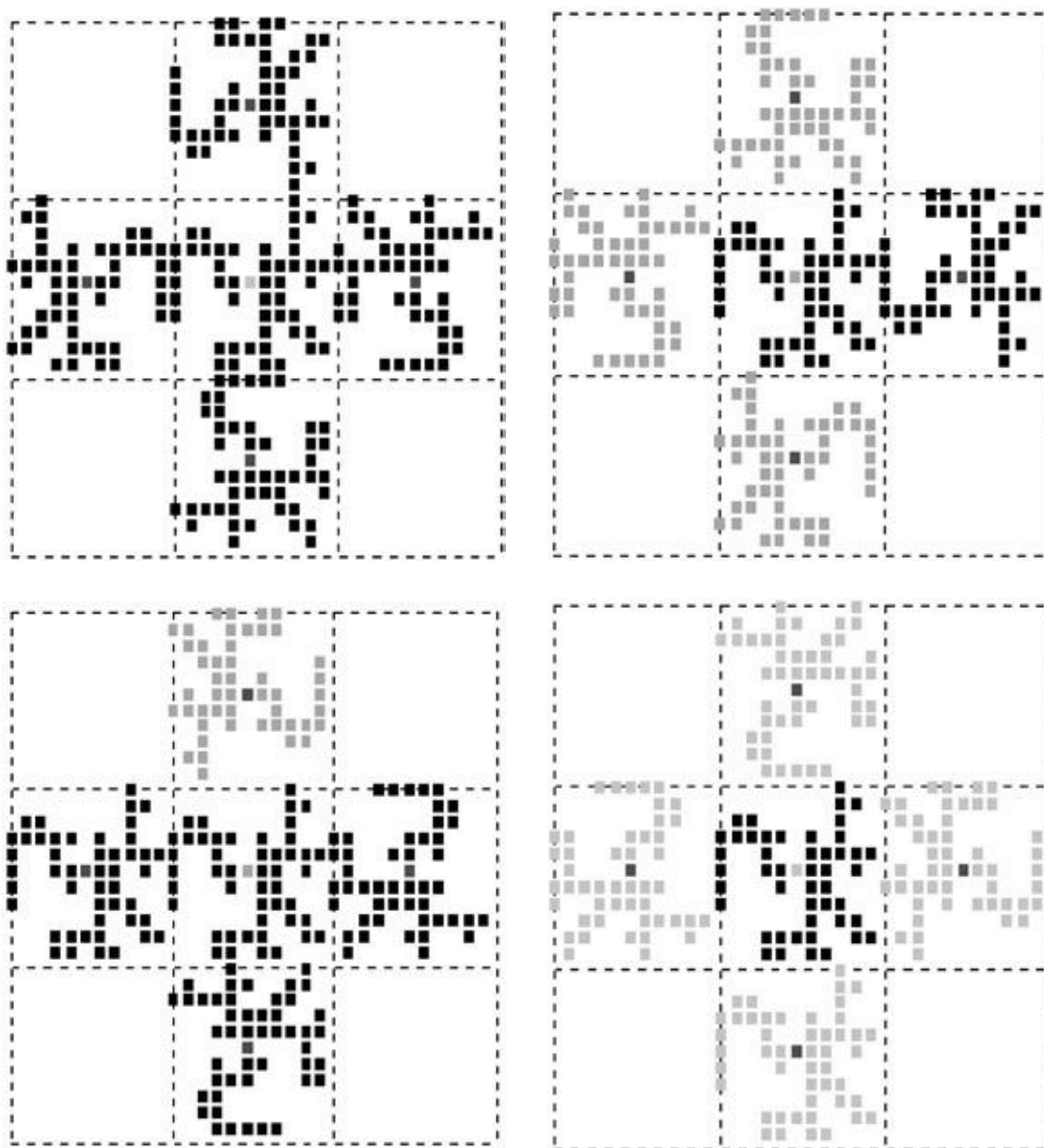
this circumstance permits an estimation of the fractal dimension. As seen in Fig. 3b, it is fluctuating, but little by little converges at the value  $D = 1.58$ .

The major parameter of this theory, which defines values of all the other quantities, is the density of the number of FDCG particles  $N$  in solution. Our intuition assures us that the larger the dilution of solution, the larger the size of a fractal cluster  $L$ . The density  $N$  is

defined as the ratio of the power of a cluster  $n$  to the overall number of particles that are capable of occupying an area of size  $L \times L$ . Having replaced  $R$  by  $L$  in (4), we obtain

$$N = \xi L^D / \xi L^2 = L^{-(2-D)}. \tag{6}$$

The volumetric density of the FDCG particles drops with increasing parameter  $L$ .



**Fig. 5.** Half (16 out of 32) of the possible realizations of contact between two random fractals positioned in neighboring cells of the lattice that emulates the active layer of a porous electrode. The rest of explanations are in text.

The run of an  $N, L$  dependence for the fractal cluster presented in Fig. 2 is presented in Fig. 4a. The solid broken line—computer-aided calculations, the dashed line—the theoretical curve, which was calculated with the aid of relationship (6). Up to the values  $L = 160$  there is observed good agreement between these curves. The value of density  $N \sim 0.13$  corresponds to a cluster of size 161 by 161. It is understandable that at  $N = 1$  the clusters shrink to a unit size (to inoculation particles).

In order to quantitatively characterize the obvious property of a fractal (Fig. 2), which is its ever increasing rarefied nature following the tendency to periphery,

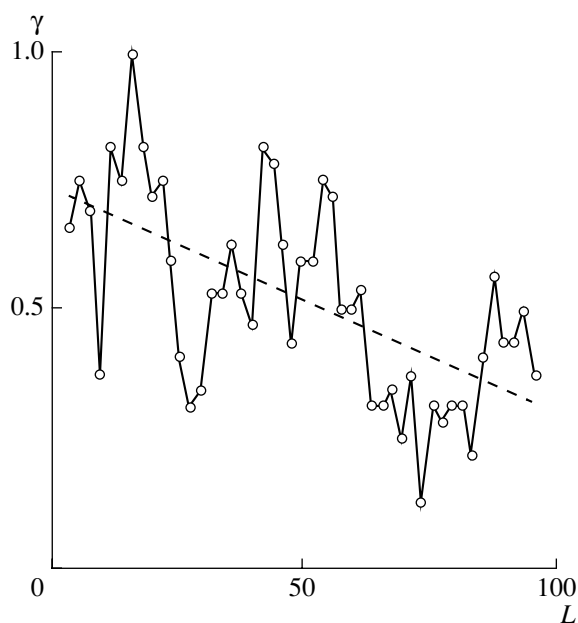
it is useful to also estimate the density of particles of a fractal cluster that happened on its perimeter (on the sides of a square of size  $L \times L$ ). It is a trivial matter to infer that the sought-for quantity, we will designate it as  $N_S$ , is equal to

$$N_S = [n(R + \Delta R) - n(R)] / (2\pi r \Delta R) \quad (7)$$

$$\sim (\partial n / \partial R) \Delta R / (2\pi R \Delta R) \sim (\partial n / \partial R) / R.$$

With allowance made for relationship (4), having replaced  $R$  by  $L$ , we finally obtain

$$N_S \sim L^{-(2-D)}. \quad (8)$$

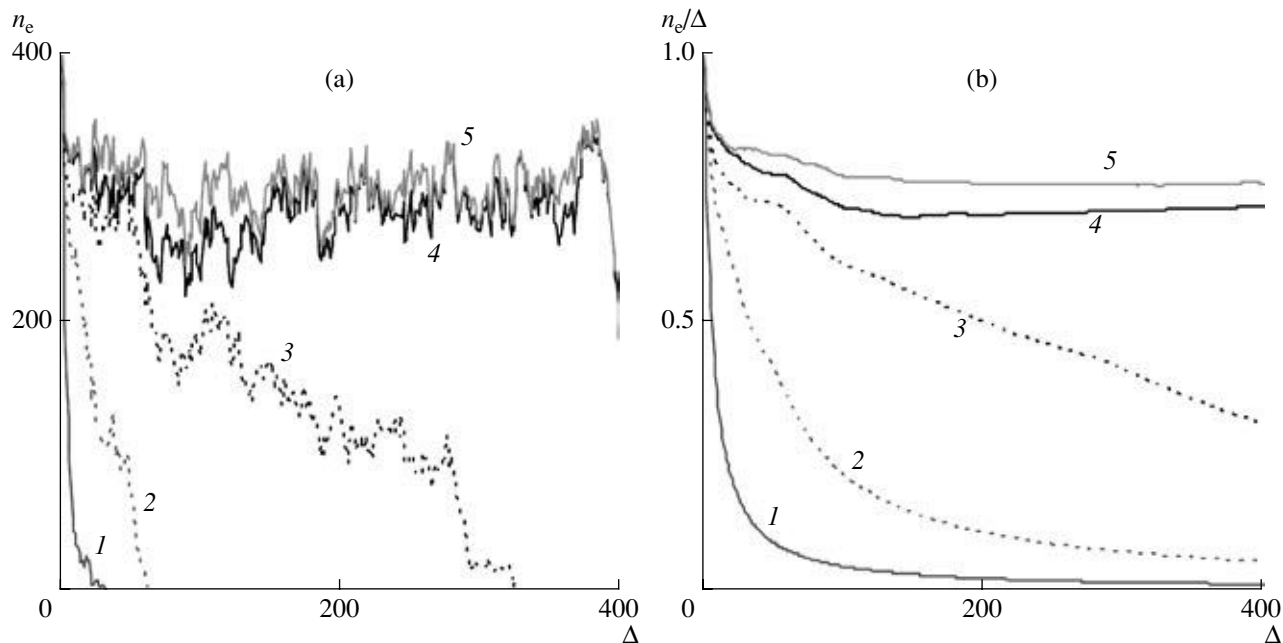


**Fig. 6.** Dependence of the probability of contact between two neighboring cells of the lattice that emulates the active layer of a porous electrode on the magnitude of the side of the square that is limiting the cluster. The dashed line is an approximation of the calculated curve.

Thus, dependences of densities  $N$  and  $N_S$  on  $L$  happened to be similar. Figure 4b shows the calculated on a computer (broken solid line) and theoretical (dashed line, which was calculated with the aid of formula (8))

run of the  $N_S, L$  curves. The character of the behavior of the calculated and theoretical curves in Fig. 4b has an important significance. As the dimensions of a fractal cluster increase, as its parts approach the walls of a square, from which there begins the Brownian movement of the FDCG particles in a fluid, which move to the growing cluster, the FDCG particles begin crowding on its periphery, and the calculated  $N_S, L$  curve begins therefore ascending and deviating from the theoretical curve. It is obvious that, if we want to have to deal with a nondistorted, "correct," random fractal cluster, which has the same value of the fractal dimension  $D$  no matter its dimensions, it is necessary to restrict ourselves to such values of quantities  $L$ , for which there is retained the correspondence between the calculated and theoretical  $N_S, L$  curves.

Let us now embark on the estimation of the probability of contact between fractal clusters that are contained in neighboring cells of a plane square lattice (Fig. 1). As an example (the procedure of the calculation of parameter  $\gamma$  is described in the previous section), 16 out of 32 realizations of a meeting of two clusters of size 11 by 11 are presented in Fig. 5. With the aid of a computer there was realized percolation of a "fluid" (electrons) out of the center of the first cell (basis, it is the same in all versions in Fig. 5, all its elements are painted black) into the four cells that are in touch with it. If percolation took place with one of the four peripheral cells, then all its elements were painted by black color, but if on the other hand the flowing of the "fluid" did not occur, the cells received gray color. The depen-



**Fig. 7.** The distribution of electrons in cells of a square lattice of size 400 by 400 that emulates the active layer of a porous electrode. (a) Dependence of the degree of the providedness of layers of the cell with electrons on the distance from the current lead and (b) dependence of the degree of the relative providedness of layers of the cell with electrons on the distance from the current lead. The probability of contact  $\gamma$ : (1) 0.4, (2) 0.475, (3) 0.5, (4) 0.51, and (5) 0.515.



dence of the probability of contact  $\gamma$  on  $L$  that was obtained in this fashion is presented in Fig. 6. We see a broken, “dancing” line, which, however, has an obvious tendency to an infallible decay. Its approximation is shown in Fig. 6 by a dashed line. The probability of contact  $\gamma$  drops twofold—from 0.7 to 0.35—following an increase in the dimensions of cells in the lattice that is emulating an AL (Fig. 1) from 3 to approximately 100, which corresponds to a decrease in the concentration of FDCG particles in solution approximately from 0.5 to 0.1 (Fig. 4a).

The knowledge of the value of  $\gamma$  allows us to turn our attention at last to the calculation of a percolation problem. The distribution of a “fluid” (electrons) in the cells of a square lattice of size 400 by 400—the number of cells  $n_c$  in a layer located at distance  $\Delta$  from the current lead (Fig. 1), as a function of the magnitude of parameter  $\gamma$  is presented in Fig. 7a. As was predicted by theory of percolation [35], the percolation threshold in a square lattice of links (every side that is connecting two cells in contact with one another becomes a “link”) is reached at  $\gamma = \gamma^* = 0.5$ . At  $\gamma < \gamma^*$  (Fig. 7a; curves 1, 2), electrons are capable of penetrating only into layers of cells that are intimately adjoined to the current lead (Fig. 1). At  $\gamma > \gamma^*$  (Fig. 7a; curves 4, 5), electrons are now practically uniformly distributed over any thickness of AL.

It will be remembered that the authors of [24] registered not the absolute ( $n_c \Delta$  dependence in Fig. 7a) but the specific capacitance, an analogue of such calculated curves ( $n_c/\Delta, \Delta$  dependence) is presented in Fig. 7b. Before the critical value of parameter  $\gamma^*$ , there is observed a sharp drop of curves (Fig. 7b; curves 1, 2), and after the passing of the percolation threshold by parameter  $\gamma$ , the curves take on a practically horizontal position (Fig. 7b; curves 4, 5). Thus, in the case of dilute solutions of particles of FDCG, the fractal–percolation effect is capable of explaining experimental data. It is precisely the case that was observed by the authors of [24]. Assuming that the density of carbon  $\rho = 2 \text{ g cm}^{-3}$ , we will find the bulk concentration of the FDCG particles in solution; it is equal to  $2 \times 10^{-3} \text{ g/2 g cm}^{-3}/10^{-1} \text{ cm}^3 = 0.01$ .

An important conclusion follows from the theory that we have developed. In order to avoid limitations of a fractal–percolation character following an increase in the thickness of AL, it is necessary to increase the concentration of the FDCG particles in solution. This will lead to a decrease in the average size of a random fractal cluster  $L$  (Fig. 4a) and to an increase in parameter  $\gamma$  (Fig. 6). If the concentration of particles of a cluster exceeds a critical value (value of parameter  $\gamma^*$  will be reached), then the fractal–percolation effect will vanish.

Concretely for the model of an active layer studied here (Fig. 1) we have the following. The value of parameter  $\gamma$  must be greater than 0.5 (Fig. 7b; curves 4, 5). But this, according to Fig. 6, means that the dimensions

of a fractal cluster  $L$  must be smaller than 50. Then, according to Fig. 4a, it will be necessary to raise the bulk concentration of the FDCG particles in solution  $N$  to values that exceed  $\sim 0.2$ . Unfortunately, this value cannot be directly compared to the experimental quantity 0.01 obtained by the authors of [24], because in this communication we restricted our consideration to considering clusters on a plane. However, it would require no great effort to extend the methods we proposed for the estimation of fractal–percolation limitations also to the case of volumetric fractal clusters.

## REFERENCES

1. Katz, E., Willner, I., and Kotlyar, A.B., *J. Electroanal. Chem.*, 1999, vol. 479, p. 64.
2. Chen, T., Barton, S.C., Binyamin, G., Gao, Z., Zhang, Y., Kim, H.-H., and Heller, A., *J. Am. Chem. Soc.*, 2001, vol. 123, p. 8630.
3. Morozov, S.V., Karyakina, E.E., Zadvornyi, O.A., Zorin, N.A., Varfolomeev, S.D., and Karyakin, A.A., *Elektrokhimiya*, 2002, vol. 38, p. 113.
4. Tarasevich, M.R., Bogdanovskaya, V.A., Zagudaeva, R.M., and Kapustin, A.V., *Elektrokhimiya*, 2002, vol. 38, p. 378.
5. Kapustin, A.V., Bogdanovskaya, V.A., and Tarasevich, M.R., *Elektrokhimiya*, 2003, vol. 39, p. 893.
6. Chirkov, Yu.G. and Rostokin, V.I., *Elektrokhimiya*, 2003, vol. 39, p. 667.
7. Chirkov, Yu.G. and Rostokin, V.I., *Elektrokhimiya*, 2002, vol. 38, p. 1130.
8. Chirkov, Yu.G. and Rostokin, V.I., *Elektrokhimiya*, 2003, vol. 39, p. 677.
9. Chirkov, Yu.G. and Rostokin, V.I., *Elektrokhimiya*, 2003, vol. 39, p. 811.
10. Chirkov, Yu.G. and Rostokin, V.I., *Elektrokhimiya*, 2003, vol. 39, p. 1476.
11. Chirkov, Yu.G. and Rostokin, V.I., *Elektrokhimiya*, 2004, vol. 40, p. 34.
12. *Porous Carbon Solids N-4*, London: Academic, 1968.
13. Tarasevich, M.R., *Elektrokhimiya uglerodnykh materialov* (Electrochemistry of Carbon Materials), Moscow: Nauka, 1984.
14. *Uglerodnye adsorbenty i ikh primeneniye v promyshlennosti* (Carbonaceous Adsorbents: Properties and Industrial Application) Plachenov, T.G., Ed., Moscow: Nauka, 1983.
15. Stails, E.B., *Nositeli i nanesennyye katalizatory* (Carriers and Deposited Catalysts), Moscow: Khimiya, 1991.
16. Fenelonov, V.B., *Poristy uglerod* (Porous Carbon), Novosibirsk: Nauka, 1995.
17. *Kolloidnyi grafit* (Colloidal Graphite), Andreev, P.N., Ed., Moscow: Institut Prikladnoi Mineralogii, 1932.
18. Szymanowitz, R., *Colloid Chemistry*, New York: Reinhold, 1946, vol. 6, p. 436.
19. Fialkov, A.S., *Uglegrafitovyye materialy* (Carbonaceous Materials), Moscow: Energiya, 1979.
20. Chizmadzhev, Yu.A., Markin, V.S., Tarasevich, M.R., and Chirkov, Yu.G., *Makrokinetika protsessov v poristyykh sredakh: Toplivnye elementy* (The Macrokinetic

- ics of Processes in Porous Materials: Fuel Cells), Moscow: Nauka, 1971.
21. Chirkov, Yu.G., *Doctoral (Chemistry) Dissertation*, Moscow: IELAN SSSR, 1975.
  22. Chizmadzhev, Yu.A. and Chirkov, Yu.G., in *Kinetika slozhnykh elektrokhimicheskikh reaktsii* (The Kinetics of Complex Electrochemical Reactions), Kazarinov, V.E., Ed., Moscow: Nauka, 1981, p. 240.
  23. Chizmadzhev, Yu.A. and Chirkov, Yu.G., *Comprehensive Treatise of Electrochemistry*, Bockris J.O'M., et al., Eds., New York: Plenum, 1983, vol. 6, p. 317.
  24. Kapustin, A.V., Tarasevich, M.R., Chirkov, Yu.G., and Bogdanovskaya, V.A., *Elektrokhiimiya*, 2004, vol. 40, p. 1049.
  25. Berezin, I.V., Bogdanovskaya, V.A., Varfolomeev, S.D., Tarasevich, M.R., and Yeroplov, A.I., *Dokl. Akad. Nauk SSSR*, 1978, vol. 240, p. 615.
  26. Bogdanovskaya, V.A., Gavrilo, E.F., and Tarasevich, M.R., *Elektrokhiimiya*, 1986, vol. 22, p. 105.
  27. Tarasevich, M.R., Bogdanovskaya, V.A., and Kuznetsova, L.N., *Elektrokhiimiya*, 2001, vol. 37, p. 969.
  28. Broadbent, S.R. and Hammersley, J.M., *Proc. Camb. Phil. Soc.*, 1957, vol. 53, p. 629.
  29. *Phase Transitions and Critical Phenomena*, Domb, C. and Green, M.S.L., Eds., New York: Academic, 1972, p. 208.
  30. Shklovskii, B.I. and Efros, A.L., *Elektricheskie svoystva legirovannykh poluprovodnikov* (Electrical Properties of Doped Semiconductors), Moscow: Nauka, 1979.
  31. *Percolation Structures and Processes*, Deutscher, G., Zallen, R., and Adler, J., Eds., Bristol: Hilger, 1983.
  32. Mason, G., *Characterisation of Porous Solids*, Amsterdam: Elsevier, 1988, vol. 39, p. 323.
  33. Isichenko, M.B., *Rev. Mod. Phys.*, 1992, vol. 64, p. 961.
  34. Stauffer, D. and Aharony, A., *Introduction to Percolation Theory*, London: Taylor & Francis, 1994.
  35. Chirkov, Yu.G., *Elektrokhiimiya*, 1999, vol. 35, p. 1449.
  36. Voyutskii, S.S., *Kurs Kolloidnoi Khimii* (A Textbook of Colloid Chemistry), Moscow: Khimiya, 1975.
  37. Adamson, A.W., *Physical Chemistry of Surfaces*, New York: Wiley, 1977.
  38. Sheludko, A., *Kolloidnaya khimiya* (Colloid Chemistry), Moscow: Mir, 1984.
  39. Frolov, Yu.G., *Kurs kolloidnoi khimii* (A Textbook of Colloid Chemistry), Moscow: Khimiya, 1989.
  40. Fridrikhsberg, D.A., *Kurs kolloidnoi khimii* (A Textbook of Colloid Chemistry), St. Petersburg: Khimiya, 1995.
  41. Shchukin, E.D., Pertsov, A.V., and Amelina, E.A., *Kolloidnaya khimiya* (Colloid Chemistry), Moscow: Vysshaya Shkola, 1992.
  42. Zimon, A.D. and Leshchenko, N.F., *Kolloidnaya khimiya* (Colloid Chemistry), Moscow: Agar, 2001.
  43. Einstein, A. and Smolukhovskii, M., *Brounovskoe dvizhenie* (The Brownian Motion), Moscow: OZIS RSFSR, 1936.
  44. Polak, A.F., *Tverdenie monomineral'nykh vyazhushchikh veshchestv* (The Solidification of Monomineral Binding Substances), Moscow: Stroiizdat, 1966.
  45. Efremov, I.F., *Periodicheskie kolloidnye struktury* (The Periodical Colloidal Structures), Leningrad: Khimiya, 1971.
  46. Ur'ev, N.B., *Vysokokontsentrrovannye dispersnye sistemy* (The High-Concentration Finely Divided Systems), Moscow: Khimiya, 1980.
  47. Deryagin, B.V. and Landau, L.D., *Zh. Eksp. Teor. Fiz.*, 1945, vol. 15, p. 663.
  48. Verwey, I.W. and Overbeck, J.C., *Theory of the Stability of Lyophobic Colloids*, Amsterdam: Academic, 1948.
  49. Deryagin, B.V., *Kolloidn. Zh.*, 1954, vol. 16, p. 425.
  50. Deryagin, B.V., *Trudy III Vsesoyuz. konf. po kolloidnoi khimii* (Proc. III All-Union Conf. on Colloid Chemistry), Moscow: Akad. Nauk SSSR, 1956, p. 225.
  51. Chernavskaya, N.M. and Chernavskii, D.S., *Tunnel'nyi transport elektronov v fotosintezе* (The Tunneling Electron Transport in Photosynthesis), Moscow: Mosk. Gos. Univ., 1977.
  52. Zamaraev, K.I., Khairutdinov, R.F., and Zhdanov, V.P., *Tunnelirovanie elektronov v khimii: khimicheskie reaktsii na bol'shikh rasstoyaniyakh* (The Tunneling Electron Transport in Chemistry: Chemical Reactions at Great Distances), Novosibirsk: Nauka, 1985.
  53. Minkin, V.I., *Kvantovaya khimiya organicheskikh soedinenii: Mekhanizmy reaktsii* (Quantum Chemistry of Organic Compounds: Reaction Mechanisms), Moscow: Khimiya, 1986.
  54. Gol'danskii, V.I., Trakhtenberg, L.I., and Flerov, V.N., *Tunnel'nye yavleniya v khimicheskoi fizike* (The Tunneling Phenomena in Chemical Physics), Moscow: Nauka, 1986.
  55. Chernavskii, D.S. and Chernavskaya, N.M., *Belok— mashina: Biologicheskie makromolekulyarnye konstruktii* (Protein as a Machine: Biological Macromolecular Structures), Moscow: Yanus-K, 1999.
  56. Mandelbrot, B.B., *Fractals: Form, Chance and Dimension*, San Francisco: Freeman, 1977.
  57. Mandelbrot, B.B., *The Fractal Geometry of Nature*, San Francisco: Freeman, 1982.
  58. Guyon, E., Metiscu, C.D., Hulin, J.P., and Roux, S., *Fractals in Physics*, Aharony, A. and Feder, J., Eds., Amsterdam: North-Holland, 1989, vol. 38, p. 172.
  59. Feder, J., *Fractals*, New York: Plenum, 1988.
  60. Peitgen, H.-O. and Richter, P.H., *The Beauty of Fractals: Images of Complex Dynamical Systems*, Berlin: Springer, 1986.
  61. Morozov, A.D., *Vvedenie v teoriyu fraktalov* (Theory of Fractals: An Introduction), Novgorod: Nizhegorod. Univ., 1999.
  62. Pomogailo, A.D., Rozenberg, A.S., and Uflyand, I.E., *Nanochastitsy metallov v polimerakh* (Nanosized Metal Particles in Polymers), Moscow: Khimiya, 2000.
  63. Chirkov, Yu.G. and Rostokin, V.I., *Elektrokhiimiya*, 2002, vol. 38, p. 1437.
  64. *The Fractal Approach to Heterogeneous Chemistry*, Avnir, D., Ed., Chichester: Wiley, 1989.
  65. *Fractals and Chaos*, Crilly, A.J., et al., Eds., New York: Springer, 1991.
  66. Birdi, K.S., *Fractals in Chemistry, Geochemistry and Biophysics*, New York: Plenum, 1993.

67. *Fractals in Soil Sciences*, Baveye, P. *et al.*, Eds., New York: CR, 1998.
68. Vold, M.J., *J. Colloid Sci.*, 1963, vol. 18, p. 684.
69. Sutherland, D.N., *J. Colloid Interface Sci.*, 1966, vol. 22, p. 300.
70. Sutherland, D.N., *J. Colloid Interface Sci.*, 1967, vol. 25, p. 373; *Nature* (London), 1974, vol. 226, p. 1241.
71. Sutherland, D.N. and Goodarz-Nia, I., *Chem. Eng. Sci.*, 1971, vol. 26, p. 2071.
72. Witten, T.A. and Sander, L.M., *Phys. Rev. Lett.*, 1981, vol. 47, p. 1400.
73. *Proc. Int. Conf. on Kinetics of Aggregation and Gelation*, Family, F., Landau, D.P., and Athens, G.A., Eds., Amsterdam: North-Holland, 1984.
74. Witten, T.A. and Cates, M.E., *Science*, 1986, vol. 232, p. 1607.
75. *On Growth and Form: Fractal and Nonfractal Patterns in Physics*, Stanley, H.E. and Ostrowsky, V., Eds., Dordrecht: Martinus Nijhoff, 1986.
76. Schuster, H., *Deterministic Chaos: An Introduction*, Weinheim: Physik, 1984.
77. Smirnov, B.M., *Fizika fraktal'nykh klasterov* (The Physics of Fractal Clusters), Moscow: Nauka, 1991.
78. D'yakonov, V.P., *Spravochnik po MathCad Plus 7.0 Pro* (A Reference Book on MathCad Plus 7.0 Pro), Moscow: SK, 1998.