

Nucleation and growth of metallic clusters at electrochemical crystallization

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Abstract. The review is devoted to the main aspects of the formation of crystalline nuclei (nucleation) during electrochemical crystallization of metals and outlines the current state of both theory and experiment in this field. It is emphasized that electrochemical deposition of metals is both a useful model system and a rapidly developing method for obtaining new materials. Theoretical provisions related to the thermodynamics of nucleation and the kinetics of formation and growth of individual crystals and mass crystallization are presented, taking into account diffusion and overlap processes with further cluster growth. The methods of electrochemical and structural studies are briefly considered, as well as the results of studying the electrochemical nucleation and growth of a number of metals on surfaces of various nature.

Keywords: nucleation, crystallization, electrochemistry, metals

1. Introduction

Phase transitions accompanied by the formation of a condensed phase, i.e. crystallization (from liquid or gas) or condensation of vapor, are of considerable interest from both

practical and fundamental points of view. Chemical processes in which a chemical reaction is accompanied by a phase transition are also related to this problem. Both the thermodynamic and kinetic aspects are important in this case.

Already in the first half of the last century, the main factors influencing crystallization and condensation were identified and fundamental dependences characterizing the energies and rates of these processes were found. It is enough to mention the names of J. Gibbs, M. Volmer, I. Stranski, Ya. Frenkel, and Ya. Zeldovich, who created a fairly complete classical pattern of such phase transitions.

The main results achieved at that time are described in some detail in the review by I. Stranski and R. Kaishev published in this journal in 1939 [1]. Even more complete information is contained in M. Volmer's monograph [2] published at the same time. To some extent, the present review shows progress in this area over the past decades.

The very strong dependence of the kinetics of phase transitions on such factors as supersaturation, supercooling, temperature and concentration in general, as well as on properties of the surface (for example, the presence of adsorbed matter that dramatically changes surface energy) in many cases does not allow predicting with sufficient accuracy (at least to an order of magnitude) the course of these processes in specific systems. In this regard, the creation of various model systems plays a significant role. In our opinion, one of the best model systems is electrochemical crystallization or condensation, that is, the formation of solid, less often liquid (mercury, gallium, amalgams, and gallams) metals or alloys, and sometimes also oxides, as a result of an electrochemical process at the interface between the solution (melt) and the surface of an electrically conductive material, both similar to the condensing matter or

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foreign. These are the same processes that occur during electroplating or electrometallurgical metal production.

Let us explain why this is so. Indeed, in the case of an electrochemical process, it is possible to precisely control the magnitude of the main factor influencing these processes, namely supersaturation (in the broadest sense of the word). The role of supersaturation in such systems is played by the displacement of the electrode potential from its equilibrium value. In electrochemistry this is called overpotential. Overpotential can be measured with an accuracy of about 10^{-4} V (some features of electrochemical systems do not allow it to be more precise). This is very high degree of accuracy as compared to the actual values of overpotentials that in real cases have the order of 0.1 V. At the same time strict control of temperature, concentrations of substances in the solution (melt), and, most importantly, the rate of the process is possible. This rate is determined directly by the value of electric current passing through the system (with the exception of the first few milliseconds, when part of the electricity is used to change the charge of the double layer at the phase boundary, but this can be easily taken into consideration).

Thus, in electrochemical systems, the most important aspect of measurements is to obtain the volt-ampere characteristics (I–V curves) and to study the current–time and potential–time dependences. It is equally important that what is happening on the surface itself is simultaneously monitored (for example, observing the by number, size, shape, and composition of the formed crystalline nuclei) using tunneling or scanning electron microscopy and other modern physical methods [3–5]. Thus, with the help of small-angle X-ray scattering (SAXS) and transmission electron microscopy, it is possible to study nanoparticles *in situ* and to obtain detailed information on the growth of nanoparticles in solutions. UV spectroscopy is a common method for determining the size of quantum dots, which is also directly relevant to the material in this review.

All of the above control methods, both electrochemical and structural ones, are equally important in the electrochemical synthesis of various metal and alloyed nanostructures such as nanowires, nanotubes, nanoscale powders, etc., which are increasingly used in modern technology. Electrochemical additive technologies are highly promising among the existing methods of nanoscale 3D printing, because they make it quite easy to obtain the desired objects, providing a high degree of control over their morphology and simple control of their composition, not to mention that the main object in this technique is not just small species, but individual ions.

The use of well-characterized low-index (including dislocation-free) or, conversely, high-index single crystal faces, which have, along with certain crystallographic orientations, micro- and nano-steps (including monatomic ones) and kinks on them, has become the routine of the modern level of research in this field [6–9]. This can currently be considered as the first field of research. Along with this, the second equally important direction is the nucleation of solid metals on a foreign (often structureless) surface, for example, on glassy carbon (such a surface is sometimes incorrectly considered as ‘inert’). Finally, there is the third area that remains as yet relevant: it is the study of the formation of liquid mercury nuclei on the surface of an oxidized platinum electrode [10]. The fact that the platinum surface is covered with a thin layer of oxide weakens the interaction of the depositing metallic mercury with the base metal, which brings the process closer

to a homogeneous one, and the liquid state of the clusters makes it closer to the classical pattern of spherical nucleation.

Thus, electrochemical crystallization is a good model system, in addition to many important applied technologies such as electrical connections in semiconductor chips [11], thin-film magnetic sensors [12], and nanoscale magnetic field generators [13], thermoelectric materials and nanostructures [14], as well as nanostructures for photovoltaic systems and energy conversion [15–18]. Rechargeable batteries (including lithium-ion and sodium-ion ones) and fuel cells should be added to this list, same as electrocatalytic electrodes for the production of hydrogen and other products, electrochemical sensors, nanowires, and more.

Over the past 30 years or so (mainly over the last 10 years) in the USA, Europe, China, Russia and other countries, a number of new highly important results have been obtained in all these areas of experiment, as well as in theory, allowing us to clarify and often revise the existing views. In this time, the number of papers published annually in the field of electrocrystallization has increased (according to the Web of Science) from about one thousand to eight thousand. This review examines only a small part of these publications: the most important results of more than 160 modern works, including several earlier fundamental studies.

2. Cluster formation energy and cluster size. Thermodynamics of nucleation

The classical nucleation theory primarily postulates that the change in energy (in Joules) during the formation of a three-dimensional cluster of a new phase within a homogeneous parent phase can be represented as an algebraic sum of two independent parts (the surface part and the bulk part):

$$\Delta G = \sigma S - \frac{\Delta\mu V}{V_m} = 4\pi r^2 \sigma - \left(\frac{4\pi}{3}\right) r^3 \frac{\Delta\mu}{V_m}, \quad (1)$$

where S and V are the surface area and volume of the cluster, r is its radius, V_m is the molar volume of the metal, σ is the specific surface energy, and $\Delta\mu$ is the change in the chemical potential upon phase transition. Obviously, this formula refers to a sufficiently large cluster to which the concept of a surface is applicable (the volume is always equal to the sum of the atomic volumes), as well as to a homogeneous surface ($\sigma = \text{const}$).

This formula also applies to the formation of a liquid drop (mercury) on a surface that is not wetted with it.

The change in the chemical potential $\Delta\mu$, which is usually written as $\Delta\mu = RT \ln S$ (where S is not entropy, but supersaturation or supercooling), during the electrochemical process is $zF\eta$, and in terms of one atom, $ze\eta$. Here, F is the Faraday number, z is the number of electrons transferred during a single act of attaching one particle (often called ‘a monomer’ in this case) to a cluster, e is the absolute value of the electron charge, and η is the overpotential. *Overpotential is a shift in the electrical potential of an electrode compared to its equilibrium value (at which the observed current is zero).* What matters is how the magnitude of the overpotential in this formula is related to the experimentally measured value, usually ranging from a few millivolts to tenths of a Volt. This will be discussed below. Throughout the following text, the overpotential is considered to be positive for convenience, that is, its absolute value is considered. The current value is also considered positive.

Differentiation of ΔG by r (assuming $\sigma = \text{const}$) shows that the maximum energy expended is achieved at a cluster radius $r = r_c = 2\sigma V_m / \Delta\mu = 2\sigma v / ze\eta$ (v is the volume per atom in the nucleus).

A cluster of this size is called a critical nucleus. Its volume is

$$V_c = \left(\frac{32\pi}{3}\right) \sigma^3 \left(\frac{V_m}{\Delta\mu}\right)^3, \quad (2)$$

the corresponding value of ΔG_c is

$$\Delta G_c = \left(\frac{16\pi}{3}\right) \sigma^3 \left(\frac{V_m}{\Delta\mu}\right)^2, \quad (3)$$

The 'c' index stands for 'critical.' The critical nucleus is in thermodynamic equilibrium with the surrounding phase, its average growth rate being zero.

All the above facts are textbook knowledge, they are related, for example, in [19]. It can be added to this that recently, alongside with the model of a critical nucleus, the concept of a stable cluster has been used lately [20], in which the terms on the right side of equation (1) are equal in modulus: $\Delta G = 0$. The radius of such a cluster is 1.5 times greater than r_c , and the number of atoms in it is approximately 3.4 times greater. This concept is convenient from the point of view that these are the smallest clusters that are highly likely to continue their growth and can be relatively easily experimentally detected; this aspect is specifically discussed below.

It is less known that the dependence of ΔG_c on r in the vicinity of the r_c point can be approximated as

$$\Delta G_c = \left(\frac{4\pi}{3}\right) r_c^2 \sigma - 4\pi \sigma (r - r_c)^2. \quad (4)$$

This (Fig. 1) is a parabolic approximation very convenient for calculations [21]. In addition, this approximation shows that the free energy of nucleation can be represented as a certain power-law decomposition in a series in terms of the order parameter $(r - r_c)^2 / r_c^2$, without resorting to its division into bulk and surface parts. This is important for comparing the classical theory of nucleation with later models [22, 23]. In this decomposition, the coefficients will depend on specific thermodynamic conditions, such as temperature, supersaturation, etc.

In the general case, σ depends on the crystallographic indices of the corresponding face. Knowing this dependence permits calculating the equilibrium crystal shape (from the condition of the minimum total surface energy). The solution of this problem [24] leads to the well-known Wulff's rule: $h_i = \text{const} = 2\sigma_i V_m / \Delta\mu$, where σ_i is the surface energy of the i th face, and h_i is the distance from it to a certain characteristic point inside the crystal called its center. The equilibrium crystal shape consists of a set of flat surfaces with low Miller indices. The areas of these faces decrease sharply with increasing indices, and the equilibrium shape, along with the flat faces, contains rounded edges connecting them [24]. The equilibrium shape differs from the actual shape of a growing crystal: the latter is determined by the ratio not between the energies, but between the growth rates of the faces.

Equations (2)–(4) remain valid for faceted crystals, but with other values of the numerical coefficient, which depends on the crystallography. In general, if σ is considered a

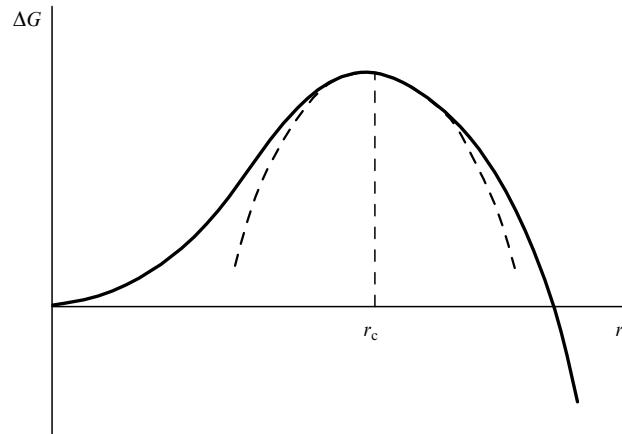


Figure 1. Dependence of the nucleation energy ΔG for a three-dimensional nucleus on its radius r . The parabolic approximation in the region of the critical nucleus size r_c is shown with a dashed line.

constant or averaged value, then the coefficient in equation (2) is $B = 8S^3 / (27V^2)$ and depends only on the shape of the cluster.

Note that $\Delta G_c = V_c \Delta\mu / (2V_m) = \sigma S_c / 3$; S_c is the total surface area of the critical cluster. These expressions are very general. They show that the energy barrier at nucleation is half the energy gain due to a decrease in the chemical potential or a one third of the energy spent on the formation of the phase boundary. This is true for a fairly large cluster.

Almost all of the above was known back in the 1920s. But it was not known then that critical clusters at electrocrystallization are quite small. And in this case, one should use not their sizes, but the number of atoms g in the clusters.

The number of atoms in a critical nucleus g_c is the ratio of its volume V_c to the volume of one atom $v = V_c N_A / V_m$, which yields

$$g_c = \left(\frac{32\pi}{3}\right) \frac{(\sigma v^{2/3} e^{-1})^3}{(ze\eta)^3} = \left(\frac{32\pi}{3}\right) \frac{\gamma^3}{(ze\eta)^3}, \quad (5)$$

where $\gamma = \sigma v^{2/3} / e$. The value of γ is a characteristic of each metal. It is expressed in Volts. Numerical values of γ for various metals at a temperature of about 300 K [25] range from 0.27–0.30 V (for low-melting metals) to 0.94–0.98 V (tungsten, rhenium). For most metals, $\gamma \approx 0.4–0.6$ V. It is worth noting that the average value of the overpotential, at which compact crystalline layers of metals are formed from ions with a charge $z = 2$ (these are the majority of metals which can be produced electrochemically) when they are deposited from solutions of simple (noncomplex) salts is about $\gamma/2$.

We will also give the relationship between g_c and the energy of a critical nucleus:

$$\Delta G_c = \frac{1}{2} ze\eta g_c = \left(\frac{16\pi}{3}\right) \frac{\sigma^3 v^2}{(ze\eta)^2}. \quad (6)$$

The coefficient of $1/2$ is accurate and does not depend on the shape of the nucleus and on all other conditions, such as the nature of the metal, the potential of the electrode, temperature, the presence of a foreign substrate, etc.

3. Heterogeneous nucleation

All that has been stated above describes the situation of homogeneous nucleation inside the parent phase, which is almost never actually observed during electrocrystallization and can only be considered as an idealized model. In fact, nuclei form heterogeneously at some interphase boundary.

In the presence of any active centers (surfaces, impurities, gas bubbles, droplets, etc.), the potential barrier ΔG_c decreases, and, unlike homogeneous nucleation, the nuclei do not have a spherical shape, but they are segments forming some contact angle α with the substrate. Their volume is reduced, and their surface is reduced too. Therefore, a correction factor Φ is introduced into the formula for homogeneous nucleation. This multiplier is due to the stronger interaction of the atoms with the above-listed active centers than with the rest of the cluster surface.

In the case of a liquid, the cluster takes the form of a spherical segment having a common circular boundary with a foreign substrate; its radius is $r \sin \alpha$, where α is the contact angle. As follows from the simple geometry, the volume of such a cluster is

$$V_{\text{het}} = \left(\frac{\pi r^3}{3} \right) (1 - \cos \alpha)^2 (2 + \cos \alpha) \\ = V_{\text{hom}} \left(\frac{1}{2} - \frac{3}{4} \cos \alpha + \frac{1}{4} \cos^3 \alpha \right), \quad (7)$$

where $V_{\text{hom}} = (4\pi/3)r^3$ is the volume of the corresponding sphere. The multiplier in parentheses is always less than one. An expression similar to (7) is also valid for the Gibbs energy of a critical cluster of the same shape: $(\Delta G_c)_{\text{het}} = (\Delta G_c)_{\text{hom}} (1/2 - 3/4 \cos \alpha + 1/4 \cos^3 \alpha)$.

Thus, the entire difference between homogeneous and heterogeneous nucleation in thermodynamics is described by a single factor $\Phi < 1$: $\Phi = V_{\text{het}}/V_{\text{hom}} = g_{\text{het}}/g_{\text{hom}}$.

The number of atoms in a critical nucleus may be approximately an order of magnitude lower (if $\Phi = 0.1$). However, the experiments performed so far have generally shown an even smaller number of atoms in critical nuclei.

If we use the adhesion energy σ_s instead of contact angle α and denote $\Delta\sigma = 2\sigma - \sigma_s$, then in these notations $\Phi = \Delta\sigma/2\sigma = 1 - \sigma/2\sigma$, and then for a cluster in the form of a polyhedron we can write [26] using the coefficient B introduced above:

$$\Delta G_{\text{het}} \approx \frac{1}{4} \frac{B\sigma^2 \Delta\sigma V_m^2}{(zF\eta)^2} = \frac{1}{4} \frac{B\sigma^2 \Delta\sigma v^2}{(ze\eta)^2}, \\ g_c \approx \frac{1}{2} \frac{Bv^2 \sigma^2 \Delta\sigma}{(ze\eta)^3}. \quad (8)$$

So, the transition from a homogeneously formed spherical nucleus to a nucleus located on the surface leads to the actual replacement of σ^3 by a smaller product $\sigma^2(\sigma - 1/2\sigma_s)$, which takes into account the adhesion of the nucleus to this surface.

When using the number of atoms in the nucleus instead of its size, the approximating expression (4) takes the form

$$\Delta G_3 = \Delta G_c - \left(\frac{ze\eta}{6g_c} \right) (g - g_c)^2. \quad (9)$$

So, the number of atoms in a three-dimensional nucleus is inversely proportional to the cube of overpotential, and the energy of its formation varies as the square of overpotential.

Further, for convenience of calculations, we can move from the atomic volume v to the surface area s of the contact between one atom of the nucleus and the base. Roughly approximating $s \approx v^{2/3}$, with an error of about 10%

$$g_c \approx \frac{1}{2} \frac{Bs^3 \sigma^2 \Delta\sigma}{(ze\eta)^3}. \quad (10)$$

Here is another rather general equation for the number of atoms in a critical nucleus without derivation:

$$g_c = -(ze)^{-1} \frac{d(\Delta G_c)}{d\eta}. \quad (11)$$

This equation obtained from completely different premises, is sometimes called the nucleation theorem, and was first formulated by Kashchiev and Oxtobi [27]. The nucleation theorem is very valuable for experimental works because it provides a reasonable estimation of the g_c value on the basis of experimental data.

The overpotential included in all the equations in this section is a deviation from the equilibrium potential only for the points of the surface where nucleation occurs. This means that two types of corrections should be introduced into experimentally measured values of electrical potentials: (1) a change in the concentration of the discharging ions in the zone of the solution or melt contacting the cluster (the so-called concentration polarization described by the Nernst equation) and (2) an ohmic voltage drop in the liquid phase. Under real conditions, at the same overall potential of the entire electrode, the components of the total overpotential may be different at different points on the surface, so the crystallization overpotential (which is included in the equations above) may vary from point to point. If the cluster is formed not by direct discharge from a solution (melt), but from a species (ad-ion) adsorbed on the surface, then it is necessary to subtract the overpotential of formation of this species by partial charge transfer. Therefore, in the theoretical consideration of nucleation processes, it is customary to consider separately the cases of direct discharge at the sites of growth and of surface diffusion. This tradition dates back to the early publications [28–31].

4. Two-dimensional nucleation and an atomistic approach to the thermodynamics of the process

Two-dimensional clusters are formed at high adhesion energy and especially when formed on the substrate of the same metal. But in the most general case, the higher the overpotential, the smaller the critical cluster, and it always becomes two-dimensional at a sufficient overpotential [32].

The change in the volume part of the energy in this case is $\Delta\mu V/V_m = \pi r^2 a \Delta\mu/V_m$, where a is the size of the atom. At the same time, the change in surface energy is $\pi r^2 \Delta\sigma = \pi r^2 (2\sigma - \sigma_s)$ due to the replacement of the substrate–solution boundary with the cluster–solution boundary. A third term should also be added, i.e., the edge energy of the nucleus perimeter $2\pi r a \sigma$. As a result, for the energy of a two-dimensional cluster ΔG_2 , it turns out

$$\Delta G_2 = -\frac{\pi r^2 a \Delta\mu}{V_m} + \pi r^2 \Delta\sigma + 2\pi r a \sigma. \quad (12)$$

Regarding the last term, it should be noted that it should also be taken into account for heterogeneous three-dimen-

sional nucleation, but in the latter case, this contribution is usually negligible.

Next, the area of a critical two-dimensional nucleus, the number of atoms in it g_c , and the energy of its formation are found. These values are usually expressed, as shown above, in terms of the area s occupied on the surface by one atom and the overpotential η . The number of atoms in a two-dimensional nucleus is

$$g_c \approx \frac{2.4s^2\sigma^2}{[ze\eta - s(2\sigma - \sigma_s)]^2}. \quad (13)$$

The case $2\sigma - \sigma_s = 0$ corresponds to crystallization on a substrate of the same material; then the formula takes the simplest form $g_c = 2.4s^2\sigma^2/(ze\eta)^2$. The numerical coefficient depends on the crystallographic faces of the base and cluster and can vary by a factor of 1.5 in both directions.

Consequently, as the overpotential increases, the g_c value decreases monotonously (moving from a cubic to a quadratic dependence in the small area), and for a certain $\eta = \eta(1)$ it becomes equal to unity. At higher overpotentials, crystallization proceeds without nucleation: each newly formed metal atom becomes a nucleus. Under these conditions, the use of the quantities σ and σ_s becomes incorrect; instead, the binding energies of ψ atoms with each other and with the substrate should be entered. However, in order not to complicate the text, we will leave the previous designations, taking into account the fact that these values vary only slightly in the case of for atomic-scale objects. The product $s\sigma$ is the specific surface energy per one atom of the surface.

Equating the g_c value to unity in (13), we obtain

$$\eta(1) \approx \frac{s(3.5\sigma - \sigma_s)}{(ze)}. \quad (14)$$

This value is of the order of one Volt. With an average value of σ_s equal to σ , $\eta(1)$ is thus $2.5s\sigma/(ze)$. Obviously, the coefficients in (13), (14) vary somewhat depending on the crystallographic features of both substrate and cluster.

The expression (14) allows finding overpotentials corresponding to the formation of nuclei containing several atoms (as long as they are all in contact with the surface). Thus, a nucleus containing three species occurs at an overpotential $\eta(3) \approx s(2.9\sigma - \sigma_s)/(ze)$.

It is significant that, when adhesion is taken into account, an infinitely large critical nucleus is not formed even at zero overpotential, but $g_c = 2.4(\sigma/\Delta\sigma)^2$. This indicates the possibility of nucleation at potentials more positive than equilibrium, that is, at negative overpotential, or *underpotential*. This phenomenon does indeed occur. The underpotential can reach $|\eta| = s(2\sigma - \sigma_s)/(ze)$. As experimentally established, this value correlates strongly with the difference in electronic work functions ϕ for the base metal and the cluster (in fact, $|\eta| \approx 0.5\Delta\phi$). This is quite natural, since the mutual adhesion of metals (as well as the coefficient of friction between them) is certainly related to the work function. This correlation has not yet been fully and quantitatively discussed.

Underpotential deposition (UPD) is characteristic not only for the deposition of metals on a foreign substrate, but also for the electrodeposition of components of electrolytic alloys, and is currently being intensively studied.

These are the sizes of critical nuclei and the energy changes during their formation and occurrence. The question arises,

as to how large a nucleus must grow before one can describe its further growth by the laws of macrokinetics? Obviously, such a cluster should be significantly larger, since the average growth rate of the critical nucleus is zero. To a first approximation, the radius of the above-mentioned cluster $r = 1.5r_c$, for which $\Delta G = 0$, can be taken as a macroscopic cluster.

Generally speaking, the fact that the number of atoms g_c in a critical nucleus becomes small at a sufficiently high overpotential, requires a change in approach to this subject, since the quantities σ , $\Delta\sigma$, and $\Delta\mu$ lose their usual meaning on the atomic scale. Under these conditions, these quantities should be expressed in terms of atomic interactions. Then the total energies corresponding to different cluster configurations should be calculated. Additionally, it is necessary to take into account interactions both with the nearest and the next-nearest neighbors.

The calculations performed [33, 34] showed that the above results remain generally valid down to the smallest clusters with the correction of numerical coefficients in the basic equations for variations in the energies of the clusters due to changes in their shape. Thus, a supercritical cluster of 14 atoms has a higher energy than a cluster of 13 atoms since the latter has 'a magical' structure (a shell of 12 atoms around one). Figure 2 shows the calculated energies of the formation of clusters of 2 to 19 atoms (broken lines) and a smooth curve corresponding to the above traditional calculation.

The atomistic approximation is more important when considering the kinetics rather than the thermodynamics of nucleation; in this field, it leads to more significant changes in theory.

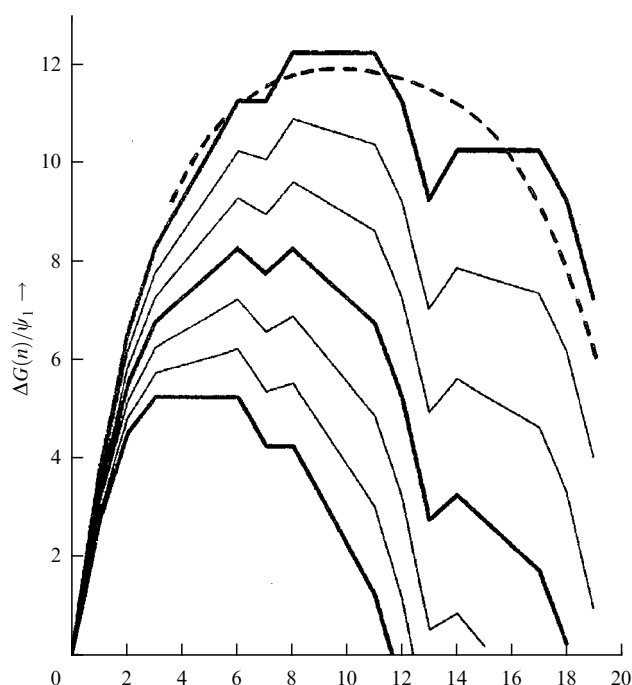


Figure 2. Calculated dependencies of the nucleation energy on the number of atoms in the nucleus (i.e., $\Delta G(n)$, up to $n = 19$ atoms) based on the data from [19, 34]. The energy is shown as a ratio to the binding energy of the atoms in the nucleus, ψ_1 . Curves are presented for overpotentials corresponding to values of η ranging from $2\psi_1/ze$ (upper broken line) to $3\psi_1/ze$ (lower broken line). The dashed line shows the calculation result for the continuous model with $\eta = 2\psi_1/ze$.

It is generally assumed that when the surface area, size, and volume of clusters are expressed in terms of the number of atoms g , the volume is proportional to g_c , and the surface and radius are proportional to $g^{2/3}$ and $g^{1/3}$, respectively. However, this is true only for sufficiently large clusters [35]. In the transition region from two-dimensional clusters of several atoms to larger three-dimensional clusters (with approximately the same dimensions in three directions), the cluster containing g atoms or molecules has the number of atoms or molecules belonging to its surface not equal to $g_s = \text{const } g^{2/3}$, as in the case of large objects, but close to $5g^{2/3} - 8g^{1/3}$ or more precisely,

$$g_s = Ag^{2/3} - \left(\frac{A^2}{3}\right)g^{1/3} + B,$$

where A varies from 4.5 to 6.5, depending on the shape and type of packing of the cluster, and B is several units; for a cubic cluster, $A = 6$ and $B = 6$. This formula has probably appeared for the first time in the world literature in [36].

In the same paper, it is shown that in the case of spherical clusters

$$g_s \approx 4.836g^{2/3} - 7.795g^{1/3} + \frac{4\pi}{3}.$$

For $g \rightarrow \infty$, this formula transforms into the usual limit expression for the sphere $g_s = 4.836g^{2/3}$. In the case of ‘magic clusters,’ which are obtained by adding layers to the simplest object consisting of 13 spherical particles (twelve around one central one), the number of surface atoms is several percent less, and for the first 25 shells it corresponds more closely to the expression

$$g_s(\text{magic}) = 4.54g^{2/3} - 7.38g^{1/3} + 4.$$

According to the classical theory of nucleation, it is necessary to find a cluster size at which $\Delta G = g\Delta\mu - g_s s\sigma$ passes through the extremum. Here $\Delta\mu$ is the change in the chemical potential per one atom. Substituting the expression for g_s here, we get

$$g\Delta\mu = \left(4.836g^{2/3} - 7.795g^{1/3} + \frac{4\pi}{3}\right)s\sigma, \quad (15)$$

and, differentiating by g , we obtain the number of atoms in g_c critical nucleus:

$$3.224(g_c)^{-1/3} - 2.599(g_c)^{-2/3} = \frac{\Delta\mu}{s\sigma}, \quad (16)$$

which is a quadratic equation with respect to $(g_c)^{-1/3}$. The exact solution g_c has the following form:

$$g_c = \left(\frac{4\pi C^3}{3}\right), \quad (17)$$

where $C = 1/[1 - (1 - \Delta\mu/s\sigma)^{1/2}]$.

This is the number of atoms in a critical nucleus corresponding to the change in the chemical potential $\Delta\mu$. It can be seen that equation (17) loses its meaning at $\Delta\mu > s\sigma$, or $\eta > \sigma/(ze)$, i.e., no critical nuclei exist at such high overpotentials. This is a stronger condition than (14).

Obviously, when $\Delta\mu \ll s\sigma$, the formula changes to the usual form $g_c = (32\pi/3)(s\sigma/\Delta\mu)^3$. However, at higher $\Delta\mu$, expression (17) yields, as shown in [37], significantly fewer atoms in a critical nucleus than expression (5).

So, a sharp acceleration of nucleation (due to the small size of critical clusters) should be expected when $\Delta\mu/s\sigma > 0.7$, that is, approximately at $g_c < 50$. In this case more than 70% of atoms are located on the surface and, as we noted above, the concept of surface energy changes its physical meaning, passing into the energy of unsaturated bonds, but its value expressed in J m^{-2} changes little. Interestingly, if, under these conditions, we try to approximate the dependence $g_c(\eta)$ by a power law, as in formula (10), then the exponent under overpotential will be much higher than 3 and closer to 5. This fully corresponds to the numerous experimental data on a very sharp increase in the rate of nucleation in a certain supersaturation region.

The last thing that needs to be noted in connection with the energy of nucleation is the fact that in the case of sufficiently large clusters *there is no sharp boundary between the surface of the cluster and its bulk* [38]. There are two ways to take this into consideration: (1) by introducing the dependence of the surface energy on the cluster size and (2) by considering 2 or 3 surface layers with gradually decreasing surface energy. Both of these methods are equivalent and lead only to changes in the coefficient in formula (17). It is also possible to abandon the classical approach in favor of theories of the Cahn–Hilliard type [22, 39].

5. Kinetics of nucleation

For the first time, the problem of calculating the rate of nucleation (under conditions of a certain specified deviation from equilibrium) was quantitatively considered by Volmer [40]; he suggested that the number of clusters J overcoming the critical size per unit of time (that is, the flux of clusters, since they are considered as moving in the dimensional space) is proportional to $\exp(-\Delta G_c/k_B T)$, as the rate of any process overcoming the corresponding potential barrier. However, to estimate the proportionality coefficient, it is necessary to consider the elementary processes of adding atoms to clusters and removing them away in a certain range of cluster sizes close to the critical one.

This calculation was performed by Becker and Döring [41] and independently by Zeldovich [42] (using a different method). Each of the methods has its advantages; their modern presentation is available in [19, 43–45].

Most briefly, the same result can be obtained using the ideology belonging to Frenkel [44]. He considered the chain of adding particles to a cluster, and then replaced finite increments by differentials. It is worth following how this approach produces a rather elegant final result.

Let us denote the cluster size distribution function as $Z(g)$. This function is nonequilibrium during the crystallization. The equilibrium function observed in the absence of the nucleation process is denoted as $Z_0(g)$. Let us call a cluster of g atoms a g -cluster, or a cluster of class g , and denote by ω_- the frequency of atom cleavage from a unit of its surface S_g . Then the flux of transition of g -clusters to class $(g-1)$ can be expressed as $Z(g)S_g\omega_-$. Similarly, the transition flux of $(g-1)$ clusters to class g is $Z(g-1)S_{g-1}\omega_+$. The dimension of the frequencies ω_+ and ω_- is $[\text{cm}^{-2} \text{ s}^{-1}]$. At a nonequilibrium distribution of $Z(g)$, there is some difference flux for the transition from $(g-1)$ to g :

$$J_g = Z(g-1)S_{g-1}\omega_+ - Z(g)S_g\omega_- . \quad (18)$$

But at equilibrium, all Z are the same, and the flux is zero, i.e., $Z_0(g-1)S_{g-1}\omega_+ = Z_0(g)S_g\omega_-$. It yields

$$J_g = Z(g-1)S_{g-1}\omega_+ \left[\frac{Z(g-1)}{Z_0(g-1)} - \frac{Z(g)}{Z_0(g)} \right].$$

This is the total flux J_g of the transition from $(g-1)$ to (g) , expressed in 1 s^{-1} . Similarly, we can find the flux J_{g+1} from (g) to $(g+1)$. The difference between these two fluxes is equal to the rate of change in the number of g -clusters: $dZ(g)/dt = J_g - J_{g+1}$. For not too small g $S_g \approx S_{g-1}$ and $Z(g) \approx Z(g-1)$. After replacing the finite increments with derivatives, one can obtain

$$J_g - J_{g+1} = -\frac{dJ}{dg}, \quad \frac{Z(g-1)}{Z_0(g-1)} - \frac{Z(g)}{Z_0(g)} = \frac{d(Z/Z_0)}{dg}. \quad (19)$$

Additionally, if we denote $S_{g-1}\omega_+ = D(g)$, equation (22) can be rewritten as

$$J_g = -D(g)Z_0(g) \frac{d}{dg} \left[\frac{Z(g)}{Z_0(g)} \right]. \quad (20)$$

This equation was first obtained by Zeldovich [42]. Considering that $Z_0(g)$ is proportional to $\exp(-\Delta G(g)/(k_B T))$, and also omitting the indices, we have $J_g = -D dZ/dg + (D/k_B T) Z \partial \Delta G/\partial g$, and finally

$$\frac{\partial Z}{\partial t} = -\frac{\partial J}{\partial g} = \frac{\partial}{\partial g} \left(D \frac{\partial Z}{\partial g} \right) + \left(\frac{1}{k_B T} \right) \frac{\partial}{\partial g} \left(D Z \frac{\partial \Delta G}{\partial g} \right). \quad (21)$$

This is the Fokker–Planck equation; it describes the ‘diffusion’ of a cluster along the coordinate axis of its size g , and the value $D(g)$ is the ‘diffusion coefficient’ along this axis. This is the number of particles attached per unit time to a class g cluster. It is expressed in reverse seconds. Thus, the transition of clusters from one class to another is described as a diffusion process moving in the direction of an increase in g . The similarity with conventional linear diffusion is related to the fact that in both processes an individual object can move in two opposite directions (a cluster can both receive and give away atoms), while the entire system moves in one particular direction.

The steady flux occurs as follows. For $g \ll g_c$ (the flux is small compared to a large number of clusters), the function $Z(g)$ is close to the equilibrium one $Z_0(g)$, that is, $Z(g)/Z_0(g) \approx 1$. On the contrary, for $g > g_c$ the nonequilibrium size distribution of nuclei is constant, $Z(g) = \text{const}$, as each cluster continues its growth. At the same time, the equilibrium function $Z_0(g)$ in this region increases sharply due to a decrease in ΔG ; therefore, in the subcritical region $Z(g)/Z_0(g) \rightarrow 0$.

The transition to the subcritical region from the state of $Z(g)/Z_0(g) \approx 1$ occurs in a certain range of sizes of Δg near g_c . If the cluster is within these limits, fluctuations can still transfer it back to the subcritical region, but at $g > g_c + 1/2\Delta g$, it will grow with a probability close to 100%. The width of the range Δg is determined by the function $\exp(-\Delta G(g)/k_B T)$, which has a sharp maximum at g_c . This width is most easily approximated by a Gaussian distribution

$$f(g) = \exp \left(-\frac{\Delta G}{k_B T} \right) \approx \text{const} \exp \left[-\left(\frac{ze\eta}{6g_c} \right) \frac{(g - g_c)^2}{k_B T} \right] \quad (22)$$

and it is close to $[(6\pi k_B T g_c)/(ze\eta)]^{1/2}$; this expression determines the value of Δg :

$$\Delta g \approx \left[\frac{(6\pi k_B T g_c)}{(ze\eta)} \right]^{1/2}. \quad (23)$$

So, the ratio of $Z(g)/Z_0(g)$ goes from unity to zero predominantly in this region of cluster classes. It means that on average

$$\frac{d}{dg} \left[\frac{Z(g)}{Z_0(g)} \right] \approx \frac{1}{\Delta g} = \left[\frac{(ze\eta)}{(6\pi k_B T g_c)} \right]^{1/2}.$$

Substituting this value, and $Z_0(g) = N_0 \exp(-\Delta G(g)/(k_B T))$ and also $D(g)$ into (20), one finally obtains

$$J = N_0 \left(\frac{S_c \omega_+}{g_c} \right) \exp \left(-\frac{\Delta G_c}{k_B T} \right) \left[\frac{\Delta G_c}{(3\pi k_B T)} \right]^{1/2}, \quad (24)$$

N_0 being the number of active centers suitable for nucleation. This equation contains an important factor

$$Z = g_c^{-1} \left[\frac{\Delta G_c}{(3\pi k_B T)} \right]^{1/2}, \quad (25)$$

which is called the *Zeldovich factor*, or the nonequilibrium factor. However, Becker and Döring [41] already knew about its role as far back as 1935, having found it with the help of another, formally simpler, but tediously lengthy method. This result is more than 90 years old, and it remains, nevertheless, an example of a very ingenious calculation within the limits of elementary algebra.

In electrochemistry, the most commonly used form of (25) is

$$J = N_0 \left(\frac{S_c \omega_+}{g_c} \right) Z \exp \left[-\left(\frac{16\pi}{3} \right) \frac{\sigma^3 v^2}{(ze\eta)^2 k_B T} \right], \quad (26)$$

from which, neglecting the weak dependence of the Zeldovich factor on ΔG_c , as well as the weak dependence of the surface energy on overpotential, after taking the logarithm, we obtain

$$\ln J = K_1 - \left(\frac{16\pi}{3} \right) \frac{\sigma^3 v^2}{[(ze\eta)^2 k_B T]}, \quad (27)$$

or

$$\ln J = K_1 - \frac{K_2}{\eta^2},$$

K_1 and K_2 are practically constant in any specific case. Consequently, in the case of three-dimensional nucleation, the logarithm of the steady-state nucleation rate is inversely proportional to the square of overpotential. A similar analysis of two-dimensional nucleation leads to a similar expression:

$$\ln J = k_1 - \frac{k_2}{[ze\eta - s(2\sigma - \sigma_s)]}, \quad (28)$$

that is, the overpotential should be corrected for the change in surface energy. However, a simplified form is more com-

monly used:

$$\ln J = k_1 - \frac{k_2}{\eta}, \quad (29)$$

which is accurate for crystallization on a substrate of identical material.

The resulting expressions show that if experimental data on the nucleation rate are plotted in coordinates $\ln J - 1/\eta^2$ or $\ln J - 1/\eta$, then in one of these cases, depending on the dimensionality of the nucleus, a straight segment should be obtained. From the equation of this straight line, data on the surface energy and exchange current density can be obtained.

Such results do indeed occur, but because the studied overpotential range is usually small, the information value of these data is insignificant. Moreover, it is often impossible to distinguish in which coordinates the linearization is better: for two-dimensional or for three-dimensional nuclei. Improvements have been proposed for modifying these coordinates (see, for example, [46]), but this has had little effect. Furthermore, the surface energy obtained from the slope of the curve differs significantly from the actual value, and no one has attempted to find the exchange current density from these data.

Nevertheless, the usefulness of the presented calculation lies at least in the fact that differentiating (27) by η , with account for (5) leads to an important expression for calculating g_c from experimental measurements of the steady-state nucleation rate (in fairly narrow overpotential ranges):

$$g_c \approx \left(\frac{k_B T}{ze} \right) \frac{\partial \ln J}{\partial \eta}. \quad (30)$$

This provides a thermodynamically independent method for determining the size of a critical nucleus (a detailed analysis shows that formula (30) overestimates g_c by no more than one atom). In this case, taking the logarithm of a dimensional quantity is acceptable since the result is independent of the dimension. This method is often used to determine the size of a critical nucleus [33, 47, 48]. Thus, in [10], the number of g_c atoms in a mercury nucleus formed on oxidized platinum at overpotentials of 92–100 mV was found to be 8 (at 20 mV, $g_c \approx 15$). The value of J (given in [10] per one cm^2 of surface area; in reality, the electrode area was much smaller) was approximately $5.5 \times 10^7 \text{ s}^{-1}$ during the steady-state period (at an overpotential of 20 mV, $J \approx 2.1 \times 10^7 \text{ s}^{-1}$). Note that the number of atoms in mercury nuclei formed at overpotentials from 3.0 mV to 8.5 mV was very high, ranging from 3.15×10^6 to 3.48×10^4 , respectively, which is closer to the classical model (although it was determined using a different method). This is a relatively rare example of determining the size of critical clusters at very low overpotentials. Typically, these are tens of mV, and the number of atoms is only a few.

Strictly speaking, when differentiating equation (26), we obtain also derivatives of ω_+ and N_0 by overpotential. However, as will be shown in the next paragraph, ω_+ for a critical nucleus does not depend on overpotential, just like N_0 , although in a number of works, for example, [49], it was assumed that different centers on the surface can be active at different overpotentials.

If continuous two-dimensional nucleation on a single crystal face is accompanied by the propagation of monatomic steps, and a growth current I occurs, then a combined

analysis of the kinetics of such growth and the nucleation kinetics [50] shows that

$$\begin{aligned} g_c &\approx \left(\frac{3k_B T}{ze} \right) \frac{\partial \ln I}{\partial \eta} - 2 \left[\exp \left(\frac{ze\eta}{k_B T} \right) - 1 \right] - 3(1 - \alpha) \\ &\approx 3 \left[\left(\frac{k_B T}{ze} \right) \frac{\partial \ln I}{\partial \eta} - 1 \right]. \end{aligned} \quad (31)$$

This provides another way to determine g_c . In this way, the number of atoms in two-dimensional silver nuclei on a dislocation-free Ag face [100] is found; it decreased from 30 to 17 in the overpotential range from 16 to 22 mV [50]. The factor of 3 on the right-hand side of (31) reflects the fact that the current I is approximately proportional to the nucleation rate to the power of 1/3, so equations (31) and (30) yield similar results.

The steps at the crystal surface in this particular case were monoatomic, and this has been repeatedly demonstrated experimentally [51, 52]. This applies, in particular, to elegant experiments in which silver was deposited onto the [100] or [222] face, which represented the end face of a cylindrical single-crystal silver electrode. Precautions were taken to ensure that the face was dislocation-free (see below, Section 11). Then, upon applying a small overpotential, a two-dimensional nucleus emerged after some time, and while growing, it filled the entire face. The current pulse recorded at this time exactly corresponded (according to Faraday's law) to a single monolayer of silver. Interestingly, the pulse shape (current versus time) depended on the random position of the nucleus on the surface: for example, when it formed in the center, the current increased linearly over time, in accordance with the length of the growth front, and abruptly stopped when this front reached the edge of the single crystal.

6. Frequencies of atom attachment and detachment

Under kinetic control of the process (i.e., in the absence of diffusion limitations), the attachment and detachment frequencies of ω_+ and ω_- per unit surface area coincide with the partial cathodic and anodic current densities at a given overpotential, divided by ze . However, for small clusters, these quantities differ from those for a flat surface because the electron term shifts due to the surface curvature. The cathodic component of the current per unit area (i.e., the attachment frequency) for a cluster with a radius of curvature r is

$$i_c(r) = i_0 \exp \left(\frac{\alpha ze\eta}{k_B T} \right) \exp \left(-\frac{2\alpha\sigma v}{rk_B T} \right), \quad (32)$$

where α depends on the shape of the potential barrier for electron transfer; for a symmetric barrier, $\alpha = 1/2$. The anodic component of the current (the detachment frequency) is

$$i_a(r) = i_0 \exp \left(-\frac{(1-\alpha)ze\eta}{k_B T} \right) \exp \left(-\frac{(1-\alpha)2\sigma v}{rk_B T} \right). \quad (33)$$

The equilibrium potential, defined by the equality $i_c(r) = i_a(r)$, differs from the case of a flat surface by the term

$$\Delta E_{eq}(r) = \frac{2\sigma v}{(zer)}, \quad (34)$$

coinciding with the Gibbs–Thomson thermodynamic equation. The exchange current density i_0 remains unchanged at this new equilibrium potential. (However, some studies have taken into account the effect of curvature on only one of the current components; in our opinion, this is incorrect.) Thus, for subcritical clusters, dissolution is faster than deposition. For critical nuclei, the rates ω_c are equal, and the value of ω_c coincides in meaning with the exchange current density i_0 (in A cm^{-2}), divided by ze (in Coulombs) transferred in a single act:

$$\omega_c = \frac{i_0}{ze}. \quad (35)$$

This quantity is independent of the overpotential or size of the critical nucleus. This shows that the total exchange flux (in inverse seconds) to a critical nucleus of radius r (area S_c) is

$$S_c \omega = D(g_c) = \frac{S_c i_0}{ze}. \quad (36)$$

For a hemispherical nucleus, $S_c = 2\pi r^2$, and then

$$S_c \omega = \frac{2\pi r^2 i_0}{ze} = \frac{8\pi v^2 \sigma^2 i_0}{[(ze)^3 \eta^2]}. \quad (37)$$

If the rate of addition is limited by surface diffusion, then this quantity depends on the surface diffusion coefficient and the adsorption ion concentration gradient near the nucleus. The other quantities retain their meaning, but the pre-exponential factor in this case is not the number of active sites, but the number of adsorbed atoms on the surface. This quantity, as shown in electrochemistry, depends on the overpotential:

$$N_{\text{ads}} = \text{const} \exp\left(\frac{ze\eta}{k_B T}\right). \quad (38)$$

This introduces an additional term $ze\eta/k_B T$ into the dependence of the logarithm of the nucleation rate on the overpotential.

7. Nonsteady-state (transient) nucleation

The duration of the nonsteady-state nucleation period (at the beginning of the process) is directly related to the frequency of atom addition to and detachment from the cluster. When the electrode potential switches from one value to another, establishment a new steady-state flux J_{st} requires some time τ . The most important case is when the initial electrode potential is the equilibrium one, i.e., a sharp increase in nonequilibrium occurs.

The nonsteady period τ is also called the induction time. A steady-state flux is established after a time interval that is 3 to 4 times greater than τ . The induction time is calculated for various cases. A common scenario is a slow redistribution of cluster sizes from equilibrium to a new steady state [53]. In this case, τ is close to $\tau \approx K\sigma k_B T / (zei_0 \eta^2)$, where K lies in the range of approximately 1 to 10. This expression can be derived [54] by calculating (approximately) the number of steps necessary for the cluster to grow to a critical size, or as an exact solution of the Fokker–Planck equation, or by another method.

Another reason for the initial slowdown of nucleation is that the curvature of the surface of the growing cluster reduces its growth rate. Indeed, the average growth rate of a

critical cluster is zero. It is only after the addition of one more atom that a nonzero growth rate appears. This rate reaches a macroscopic value only when the nucleus radius has already grown approximately 4 times larger than that of a critical nucleus [55] (and not 1.5 times, as assumed in [20]). The transition from the critical cluster to this size requires approximately the same time as the redistribution of cluster sizes.

Furthermore, initially there is still an insufficient number of adsorbed monomers or dimers on the surface, and time is required for their accumulation. In this case, such accumulation produces a nonzero initial current that decays exponentially, after which nucleation begins.

The case of the gradual emergence of active centers on the surface is examined in considerable detail in the literature, where either the initial presence of a certain number of centers or the initial absence of these centers is assumed [56]. Other causes of nonstationarity also exist, for example, a change in the number of active centers upon a shift in the electrode potential; this case is analyzed in detail in [57, 58].

8. An atomistic approach to the kinetics of the nucleation process

Macroscopic models assume a clear-cut separation between surface and bulk energies; this is not the case. Furthermore, the apparent discrepancy between macroscopic concepts of nucleation (suitable only for relatively large objects) and the actually observed nuclei consisting of only a few atoms led to the development of an atomistic model of nucleation [59, 60], in which the classical concepts are somewhat modified. Atomistic approaches to electrocrystallization were first developed in [61]. This approach later evolved into a significant research direction, which has yielded to date a number of important results.

At the same time, a discrepancy (often by several orders of magnitude) between calculated and experimental data not only on the sizes of critical nuclei but also on the number of nuclei formed on the surface under real conditions, as well as several other unresolved issues, still remain unresolved. It is not entirely clear, for example, why there is a threshold overpotential value below which no nuclei at all are formed on dislocation-free surfaces. This is particularly true for the formation of nanocrystalline objects down to amorphous ones, such as those found in certain types of alloys. Furthermore, it is clear that the concept of the surface curvature radius, which is a part of the Gibbs–Thomson equation, is meaningless for small clusters. Therefore, the frequency of particle attachment to them is determined not by the exchange current density, but by the current density corresponding to a given overpotential.

An alternative to the classical theory of electrochemical nucleation is the aforementioned atomistic model developed by Milchev et al. [34, 59, 60]. This model, like the classical one, describes the nucleation process as the successive addition of atoms and predicts a critical number of atoms in a thermodynamically stable cluster. The difference is that the atomistic model takes into account the energy associated with the interactions between individual atoms and their interactions with the electrode surface, instead of the interfacial energy of the cluster surface. We noted this above: see the discussion of Fig. 2. However, this only applies to the energetics of the process, not the kinetics.

One of the new approaches to the kinetics of such processes [62, 63] is as follows. Let us consider an ideal

surface (face) of a crystal containing N_0 places (per unit area) for the possible attachment of new species. Let some current state on this unit surface be characterized by the presence of N such species arranged randomly, with $N \ll N_0$. The coverage is $\theta = N/N_0$.

Let us find how many two-dimensional clusters of n ($n = 1, 2, 3$, etc.) species are located on the surface. In the literature, such clusters are called *monomers*, *dimers*, *trimers*, etc., respectively. If each species has m possible nearest neighbors (in reality, m is on average about 5), then m places out of the total number of $N_0 - N \approx N_0$ free places are in the immediate vicinity of a given species. A simple reasoning for the number of triplets $M(3)$, fours, fives, etc. shows that the number of n -s $M(n)$ per unit surface area is

$$M(n) \approx \frac{N^n (n-1)! m}{N_0^{n-1}} = N_0 m \theta^n (n-1)! \quad (39)$$

It is assumed that for $n > 2$, the number of places where a new species can attach itself to the perimeter of the cluster is equal to the number of species already present in the cluster, which is quite acceptable for $n < 50$. Thus, for $m=5$ and $\theta = 10^{-2}$ $M(3) \approx 10^{-5} N_0$.

If the coverage is θ_0 at equilibrium potential (that is, at zero overpotential) (equilibrium coverage), then at a given overpotential η it will increase and amount to

$$\theta = \theta_0 \exp\left(\frac{e\eta}{k_B T}\right) \quad (40)$$

due to the exponential acceleration of the deposition of new monomers onto the surface and at the same time to the slowing down of the detachment of species already present there into the solution.

Hence, for the number of clusters of class n available at overpotential η , the following expression is obtained:

$$M(n) \approx m \theta_0^n N_0 \exp\left(\frac{ne\eta}{k_B T}\right) (n-1)! \quad (41)$$

It is further postulated that the growth of a new phase begins only after the formation of at least one cluster of a certain class $n = g_c$. In other words, clusters containing one less species are assumed to be subcritical.

Further calculations [63] show that during the stochastic process of ion discharge on the electrode surface with the formation of adatoms, the stationary rate J of the formation of g -clusters can be expressed as

$$\ln J = g \ln \theta_0 + \ln(g!) + \left[\frac{(g + \alpha)ze\eta}{k_B T} \right] + \text{const}, \quad (42)$$

where θ_0 is the equilibrium degree of surface coverage with adatoms, and the remaining notations are standard. The electrochemical transfer coefficient α is close to 0.5 and always less than unity. In this case, J is defined as the total number of species added per unit time to all n -clusters located on the electrode surface. It was noted in [63] that using the relation that follows from (42):

$$\frac{d \ln J}{d \eta} = \frac{(g + \alpha)ze}{k_B T}, \quad (43)$$

it is possible to determine the value of g_c (in a given potential range) from experimental measurements of the nucleation

rate (at several potentials in a narrow potential range), and if these measurements are performed at significantly different potentials, then other information can be obtained. It is important to note that expression (43) provides the number of atoms in a critical nucleus, which differs by only α , that is, by less than one, from that given by equations (30) and (31), obtained from completely different premises.

Note that in deriving the above formulas, no concepts or considerations related to nucleation energy, specific surface energy, equilibrium and nonequilibrium cluster size distribution functions, etc. were used.

Here, it is necessary to pay attention to the fact that the existence of a critical value g_c in this concept is caused by a very simple reason. To make this obvious, let us differentiate expression (43) with respect to g at a constant overpotential. Such differentiation, if we use the fact that $d \ln(g!)/dg \approx \ln g$, yields

$$\frac{d \ln J}{dg} = \ln \theta_0 + \ln g + \frac{ze\eta}{k_B T} \quad (44)$$

and since θ_0 is significantly lower than unity, i.e., $\ln \theta_0 < 0$, then for some $g = g_c$ the said derivative passes through zero:

$$\ln g_c + \frac{ze\eta}{k_B T} + \ln \theta_0 = 0,$$

or

$$g_c = \left(\frac{1}{\theta_0} \right) \exp\left(-\frac{ze\eta}{k_B T} \right). \quad (45)$$

For a given value of g , the value of the flux J passes through a minimum. Consequently, it is the transition from a g_c -cluster to a $(g_c + 1)$ -cluster that is the limiting step, that is, it determines the rate of the entire further growth process (which in the steady state is equal to the rate of this transition). This actually coincides with the definition of a critical nucleus: it is from this size that sustainable growth begins, the rate of which can be (in principle) higher than the rate of the indicated transition.

A comparison of formula (45) with the available experimental data on the size of critical nuclei shows the following. In [64], for example, it was shown (by an independent method) that $g_c = 4$ for silver on a glassy carbon substrate at $\eta = +25$ mV. Since in this case $(ze\eta/k_B T) \approx 1$, then $\theta_0 \approx 0.09$, which is a plausible value.

Next, we can find the value of that sufficiently high overpotential η at which the critical nucleus will consist of a single atom: $(1/\theta_0) \exp(-ze\eta/k_B T) = 1$, whence

$$\eta = -\left(\frac{k_B T}{ze} \right) \ln \theta_0. \quad (46)$$

With the approach developed here, the sought-for overpotential depends only on the equilibrium coverage θ_0 , and not on the specific energies σ and σ_s , as in equation (18). These quantities, however, are related to each other by the adsorption isotherm equation for the adsorbed metal adatoms on the surface: $\theta_0 = f(\sigma, \sigma_s)$. If we postulate that $\ln \theta_0 = -s(3.5\sigma - \sigma_s)/k_B T$, then expression (46) takes on a form that coincides with (14). In this case, the equation for g_c takes a very clear form:

$$k_B T \ln g_c \approx -ze\eta + s(3.5\sigma - \sigma_s), \quad (47)$$

or, more generally, $k_B T \ln g_c \approx -ze\eta + s(A\sigma - B\sigma_s)$.

Returning to the nucleation rate, it may be concluded that the logarithm of the nucleation rate in this interpretation depends linearly on the overpotential, in contrast to the picture obtained in the macroscopic case, precisely for the above-mentioned reason that the frequency of species attachment to clusters is determined not by the exchange current density, but by the current density that corresponds to a given overpotential.

Indeed, experimental data on this dependence in many cases are well linearized [65].

9. Growth kinetics of a single hemispherical cluster

It is assumed that, in general, nucleation and growth processes occur simultaneously. Continuous nucleation and simultaneous surface growth occur, under entire or partial diffusion control. This approach works well in a fairly large number of cases [15, 43–45]. Indeed, phenomenologically, cluster nucleation and growth are the same process: if we consider a critical cluster, the addition of the previous species to it can be regarded as nucleation, while the addition of the next one is considered growth. However, nucleation occurs at a potential which is equilibrium with respect to the cluster, and therefore its rate is determined only by local processes of a species addition and detachment, while growth can depend on diffusion factors. In the limiting case, however, instantaneous nucleation followed by continuous growth is also considered; this occurs when active sites on the surface are rapidly depleted, or the monomer concentration near the cluster drops sharply as a result of nucleation.

Growth is usually considered separately in kinetic or diffusion modes. This means that the rate of the overall process is determined either by the rate of the surface process of addition and detachment from the cluster or by the supply of monomers to the cluster boundary. However, it rarely happens that a predominantly kinetic or predominantly diffusion regime is maintained throughout the entire growth period. Initially kinetic growth with increasing diffusion limitations is significantly more probable. For the sake of the most compact presentation, we will consider the general case of the growth of *an individual cluster* at certain specified values of both electrochemical and diffusion parameters.

This type of growth was considered in most detail by Fletcher [66], alongside with a significant number of works by other authors.

We consider *the hemispherical diffusion* of discharging ions with a concentration of C_0 to the cluster surface, followed by charge transfer [67], which is described by the Butler–Volmer equation $i = i_0[(C_s/C_0) \exp(\alpha z f \eta) - \exp(-(1-\alpha)z f \eta)]$. In this equation, $f = e/k_B T$, η is the overpotential (we still assume it is positive), z is the number of electrons transferred in a single discharge event, i_0 and α are the electrochemical parameters: exchange current density and electron transfer coefficient. The ion concentration near the surface is denoted as C_s , where $C_s < C_0$. The cluster is assumed to be on a flat surface, and diffusion to it occurs from the half-space.

The three-dimensional growth rate of a single cluster is expressed by various equations, depending on the nature of the rate-determining stage of the growth process [59, 68].

In a fairly general case, the growth of a hemisphere of the radius R is described by the equation

$$\frac{dR}{dt} = D(C_0 - C_s)V_m[(\pi D t)^{-1/2} + R^{-1}], \quad (48)$$

(D is the diffusion coefficient in the solution). Since $R \ll (\pi D t)^{1/2}$, and, moreover, in the case of mixed kinetics (i.e., comparable rates of diffusion and surface processes), the surface concentration C_s at current density i decreases to [68]

$$C_s = C_0[\exp(-z f \eta)] + \left(\frac{i}{i_0}\right) \exp(-\alpha z f \eta),$$

then $(\pi D t)^{-0.5}$ in (48) drops out, and with satisfactory accuracy

$$\frac{dR}{dt} = D V_m C_0 \frac{[1 - \exp(-z f \eta)]}{(R + [D z F C_0 \exp(\alpha z f \eta)]/i_0)}. \quad (49)$$

Generally speaking, both terms in the denominator of this expression can be of the same order of magnitude, so neither can be neglected. For simplicity, we will neglect only the factor $[1 - \exp(-z f \eta)]$, which tends to unity as η increases. The solution of this equation for t has the following form:

$$t = \frac{R^2}{(2 D C_0 V_m)} + R z F \frac{\exp(-\alpha z f \eta)}{(V_m i_0)}. \quad (50)$$

The first term on the right-hand side is diffusional in nature, while the second one is kinetic. At a high exchange current density i_0 , the last term tends to zero, and then, with account for the smallness of the last exponent, $R \approx (2 D C_0 V_m t)^{1/2}$, which means that a diffusion-controlled process occurs. At low i_0 , $R \approx i_0 \exp(-\alpha z f \eta) v t / z e$, meaning the process rate is determined by the kinetics of charge transfer across the surface. From this, after simple transformations, the following expression for the total current is obtained:

$$I = I^* \varphi\left(\frac{t}{t^*}\right) = I^* \left[\left(1 + \frac{t}{t^*}\right)^{1/2} + \left(1 + \frac{t}{t^*}\right)^{-1/2} - 2 \right], \quad (51)$$

where I^* and t^* are the characteristic current and the characteristic time.

Expression (51) contains both electrochemical and transport characteristics of the process. It contains time only in the form of t/t^* , and therefore the dependence of $I(t)$ is similar for different parameters.

At the very beginning

$$I \approx 2\pi V_m^2 i_0^3 z^{-2} F^{-2} [\exp(\alpha z f \eta)]^{-3} t^2. \quad (52)$$

At the final stage, the course of the process is determined solely by diffusion:

$$I \approx 4\pi (D C_0)^{3/2} z F V_m^{1/2} t^{1/2}, \quad (53)$$

and during the intermediate stages, the dependence of the current on D and i_0 turns out to be more complicated. There is a rather long period when the overall current increases almost linearly over time.

During the simultaneous independent growth of many clusters formed in the course of progressive nucleation, the dependence of the overall current on time $I(t)$ can be found by

integration (in the case of instantaneous nucleation, it is sufficient to multiply the current by the number of growing clusters). For a cluster that began its growth at the moment τ , the current I at the moment t is $I^* \varphi[(t - \tau)/t^*]$.

Approximately the same result was obtained in [19] and [69], but it was presented in a more complicated form. The expressions obtained by Fletcher for a set of hemispheres [69] also take into account the multiplier $[1 - \exp(-zf\eta)]$, which we neglected.

10. Mass crystallization without overlapping and with overlapping

The basics of these processes are described in [70–74]. Let the nucleus grow under potentiostatic conditions at a certain current density i , determined by the kinetics of charge transfer, that is, constant over time and uniform over the entire surface. In this case, the velocity of the growing surface moving along the normal is iV_m/zF , so that a cluster located on the surface at the moment t is a hemisphere with the radius $R = iV_m t/zF$ and surface area $2\pi R^2$.

Thus, when a cluster grows in the kinetic mode, the total current $I(t)$ (not the current density) to this cluster at the moment t is

$$I(t) = 2\pi R^2 i = 2\pi i^3 \left(\frac{V_m}{zF} \right)^2 t^2. \quad (54)$$

For lateral growth of a cylindrical cluster of constant height h , the corresponding expression takes the form

$$I(t) = 2\pi R h i = 2\pi h i^2 \left(\frac{V_m}{zF} \right) t. \quad (55)$$

In the diffusion regime, the cluster grows according to the law $R = (2CV_m D t)^{1/2}$ (where C is the concentration of electroactive species). Hence, for hemispherical clusters

$$I(t) = 4zF\pi(DC)^{3/2}(V_m t)^{1/2}. \quad (56)$$

If N_0 nuclei are formed simultaneously at the first moment, the current $I(t)$ will be N_0 times greater (in the case of independent growth, that is, when the clusters are not too close to each other).

In fact, the simultaneous formation of the entire ensemble of nuclei is an idealized model; this means that the time interval of their formation is much shorter than the duration of growth. In general, the dependence $N(t)$ can be expressed as

$$N(t) = N_0 [1 - \exp(-At)]. \quad (57)$$

If such a decrease in the nucleation rate is simply due to a decrease in the number of active sites, equation (57) is accurate (the induction period is assumed to be negligible). Then, at $t \gg A^{-1}$, nucleation can be considered instantaneous, and the recorded expressions remain valid. But in the opposite case, when $t < A^{-1}$, nucleation proceeds at a constant rate AN_0 , or, equivalently, J . In this case, nucleation is called ‘progressive.’ Formula (57) approximates another case where nucleation slows down due to a decrease in the concentration C around each growing cluster; such zones are called ‘nucleation exclusion zones,’ or, more precisely, zones with a reduced probability of nucleation.

Comparison of all the results for instantaneous and progressive, two-dimensional and three-dimensional nucleation, and growth in the kinetic and diffusion modes (8 possibilities in total) shows that the initial dependences of the measured current on time $I(t)$ have the general $I = \text{const } t^\alpha$ form

$$\log I = \text{const} + n \lg t, \quad (58)$$

while n can have 6 different values: 0; 0.5; 1; 1.5; 2; 3, depending on the mode of nucleation and growth, and, consequently, the experimentally found values of α can serve as a diagnostic criterion for the type of processes occurring [75].

If the simultaneous parallel growth of a large number of clusters is considered, their overlapping must be taken into account. Exclusion zones of nucleation (depleted zones) may begin to overlap at a fairly early stage of growth, as a result of which both the area of these zones and the kinetics of cluster growth change.

Consider the case when clusters are formed randomly with an average velocity $\mathbf{J}$ (here $\mathbf{J}$, typed in bold, refers to a unit of surface area, i.e., its dimension is $[\text{cm}^{-2} \text{s}^{-1}]$). Let the clusters grow at a linear rate iV_m/zF . At the same time, the depleted zones begin spreading in accordance with the laws of diffusion. The radius R_z of the zone formed during the time t around the cluster which started its growth at an earlier moment τ is known to be

$$R_z = 2D^{1/2}(t - \tau)^{1/2}, \quad (59)$$

and the area of this zone is $4\pi D(t - \tau)$. While the growth is controlled by diffusion, the increment of this area over an infinitesimal time interval dt is equal to $4\pi D dt$ (regardless of the moment τ). Therefore, for the total number of clusters $\mathbf{J} d\tau$ formed during dt , the increment of this area (per unit surface area) is

$$dS = 4\pi \mathbf{J} D dt d\tau, \quad (60)$$

and the same value corresponds to a decrease in the area free of diffusion zones. Please note that both sides of equation (60) are dimensionless, as they mean an increase in the area of clusters per unit of total surface.

At a certain point, the zones start overlapping (Fig. 3), as a result of which the area no longer grows linearly, and it is necessary to find laws describing the overlapping of these zones. The description of the method used for such an analysis in Kolmogorov’s classic work is very complicated, and we will use a simpler approach. Let us denote the dimensionless fraction of the surface free of zones at time t as $q(t)$. Integrating over τ and over all clusters formed from time $t = 0$ to a given moment t , we obtain:

$$dS = 4\pi \mathbf{J} D q(t) t dt. \quad (61)$$

However, on the other hand, this increase in the area of diffusion depleted zones is equal to a decrease in the free surface fraction $-dq$. From this we obtain the differential equation for q :

$$\frac{dq}{q} = -4\pi \mathbf{J} D q(t) t dt. \quad (62)$$

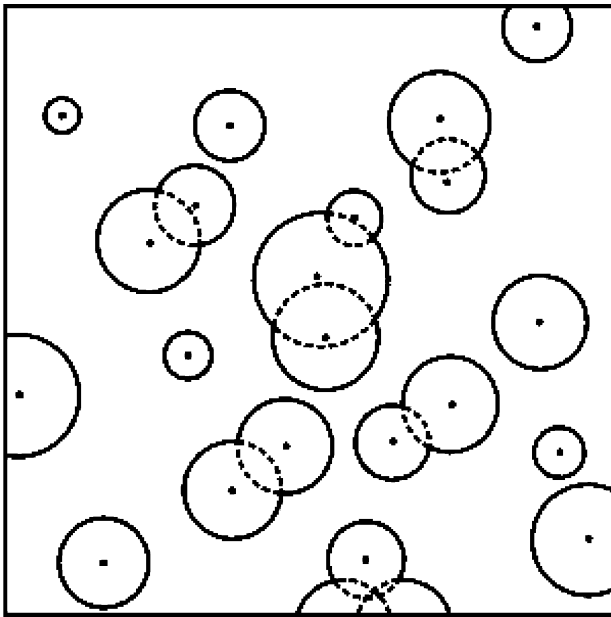


Figure 3. Formation and overlap of circular zones with a reduced probability of nucleation due to diffusion depletion. Each zone grows around a newly formed nucleus according to the law $r \sim (Dt)^{1/2}$. The size of the zones varies because the nuclei (shown as dots at the centers of the zones) are formed at different moments.

Since $q(t=0) = 1$ (the entire surface is free at the initial moment), we obtain

$$q = \exp(-2\pi JDt^2). \quad (63)$$

At the moment t , this is the fraction of the surface on which nucleation can continue. The proportion of the surface covered by diffusion zones around growing clusters is $1 - q = 1 - \exp(-2\pi JDt^2)$, respectively.

This result, which fully describes the overlap process, was first obtained by Mumpel [76]. Besides, at the same time, Johnson, Mehl, Avrami, Kolmogorov, and Yerofeyev dealt with this problem. This model can be used for both diffusion and kinetic growth modes, for two- and three-dimensional nuclei, etc.

Inside the diffusion depleted zones, the nucleation process also takes place, but at a reduced rate, gradually increasing near the zone boundaries. The rate of nucleation in them was considered in [77], and it was shown that it depends not only on the diffusion coefficient, but also on the properties of the depositing metal. The total number of nuclei per unit surface area formed does not exceed $(J/8D)^{1/2}$ with account for the depleted zones [63, 78].

The overlapping slows down the current growth over time, so then current passes through the maximum $I_{\max}$ at the moment $t_{\max}$, after which it decreases in accordance with the Cottrell equation. The experimental dependences of the measured current on time $I - t$, obtained under various conditions, correspond to this result. At the same time, the shape of the curves for instantaneous and progressive nucleation are significantly different.

The combination of these results with equations describing the growth of clusters without overlapping leads to the currently generally accepted expressions for the $I - t$ dependences for instantaneous and progressive nucleation [79]. By

joining the solutions obtained at various stages of the process, the following expression is obtained:

$$I(t) = zFC \left(\frac{D}{\pi t} \right)^{1/2} \left\{ 1 - \exp \left[-N_a \pi k D \left(t - \frac{1}{J} + \frac{\exp(-Jt)}{J} \right) \right] \right\} \quad (64)$$

with a dimensionless parameter $k = (8\pi CV_m)^{1/2}$. Hereafter, J again refers to the entire working surface and has a dimension of 1 s^{-1} , the concentration of ions in the solution C is expressed in moles per unit volume, and N_a is the number of active centers per unit surface. Here, we call the value I "the current (per unit surface)," and not the current density, since in this case it is simply the integral current for all clusters located on a unit surface.

For the extreme cases of instantaneous and progressive nucleation ($t \gg J^{-1}$ and $t \ll J^{-1}$) equation (64) yields

$$I(t) = zFC \left(\frac{D}{\pi t} \right)^{1/2} [1 - \exp(-N_a \pi k D t)], \quad (64a)$$

and

$$I(t) = zFC \left(\frac{D}{\pi t} \right)^{1/2} \left[1 - \exp \left(-\frac{1}{2} N_a \pi k D J t^2 \right) \right]. \quad (64b)$$

When dimensionless coordinates $I^* - t^*$ are used, where $I^* = I/I_{\max}$, $t^* = t/t_{\max}$, this expression is transformed in the case of instantaneous nucleation into

$$(I^*)_{\text{(inst)}}^2 = 1.9542(t^*)^{-1} [1 - \exp(-1.2564t^*)]^2, \quad (65)$$

and in the case of progressive nucleation into

$$(I^*)_{\text{(progr)}}^2 = 1.2254(t^*)^{-1} [1 - \exp(-2.3367t^{*2})]^2. \quad (66)$$

The product $(I^2 t)_{\max}$ depends only on D and C and is equal in the first case to $0.1629D(zFC)^2$, and in the second case to $0.2598D(zFC)^2$. This allows calculating the diffusion coefficient of the discharged species with fairly good accuracy (and at the same time allows checking the adequacy of the model):

$$D = \frac{K(I^2 t)_{\max}}{(zFC)^2}, \quad (67)$$

where K depends on the nucleation conditions and ranges from 0.16 (with instantaneous formation of all nuclei) to 0.26. However, the diffusion coefficient can be more reliably found from independent measurements.

The shape of the corresponding curves (Fig. 4) is very close to that for experimentally obtained transients, which allows calculating not only the diffusion coefficient, but also the total number of nuclei N (per unit surface), etc., based on experimental data. Currently, there are quite a lot of such data. As an example, we give the formula for finding N in the cases of instant nucleation:

$$N \approx \frac{0.08}{[Dt_{\max}(V_m C)^{1/2}]}. \quad (68)$$

However, the actual overlap conditions are more complex than those based on theory. For example, active centers are rarely randomly located. Therefore, it is doubtful that the coordinates of the extreme point should be used for calcula-

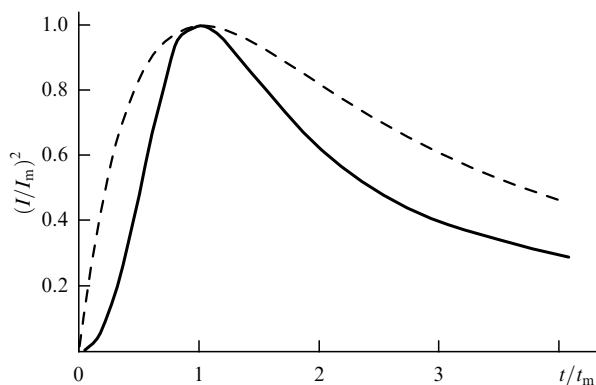


Figure 4. Theoretical dependence of the square of the dimensionless current I/I_m on the dimensionless time t/t_m in the case of instantaneous nucleation (dashed line) and progressive nucleation (solid line). The coordinates (current and time) of the maxima on the curves are taken as I_m and t_m .

tions; the initial sections of the curves are more informative. The crosslinking of solutions for the initial stage of hemispherical diffusion (increasing current) with the late stage of Cottrell decay is not entirely correct, so the maximum current point is doubtful, especially since the initial model includes a distortion of flux continuity, that leads to the introduction of an additional coefficient $4/3$ in equation (64b). In addition, this theory does not take into account the overall shape of the $i-t$ dependence for the growth of a single cluster. As a result, a comparison of the calculated value of N with that directly recorded by electron microscopic methods yields a 2–3-order discrepancy [80–82]. Nevertheless, this theory is still often regarded as the standard one.

It has been suggested that this discrepancy is due to errors in the mathematical calculation, which interprets the transition from a hemispherical diffusion process to each individual cluster to planar diffusion to the entire array after the overlap of the diffusion zones. However, an alternative calculation of the diffusion process [83], performed from a completely different perspective, confirms the correctness of the commonly used model with subsequent modifications (see, e.g., [84]). Therefore, the reason for the shortcomings of the specified model is different. The calculation performed in [83] suggested that the discrepancy between the experimental and calculated values of the number of nuclei formed on the surface under potentiostatic electrocrystallization conditions is caused by a lack of consideration of the kinetics of the electrochemical process stage. *At the moment corresponding to the current maximum, kinetic and diffusion parameters play comparable roles.*

Accordingly, in [85], cluster growth was calculated in the mixed kinetics mode, that is, taking into account the electrochemical stage. Therefore, the final formula includes the parameters of the charge transfer stage. For instantaneous nucleation in dimensionless coordinates

$$I^* = \frac{3t^*}{[1 + 2(t^*)^{3/2}]}, \quad (69)$$

and for progressive nucleation

$$I^* = \frac{5(t^*)^2}{[1 + 4(t^*)^{5/2}]}. \quad (70)$$

The product $I_{\max}^2 t_{\max}$ turned out to be $0.14D(C_0 n F)^2$, which is close to the value determined by the traditional equation for diffusion growth after instantaneous nucleation, namely $0.16D(C_0 n F)^2$. Therefore, the value of the diffusion coefficient calculated by this method differs little from that found in the traditional way. However, the expressions for the number of growing clusters N (based on $i_{\max}$ and $t_{\max}$) turn out to be significantly different, namely, for the total number of clusters at instant nucleation

$$N = \frac{3I_{\max}}{(4DCV i_{\text{kin}} t_{\max})}, \quad (71)$$

and for progressive nucleation, the number of clusters formed at the moment t is

$$N(t) = \frac{5I_{\max} t}{(3DCV i_{\text{kin}} t_{\max}^2)}, \quad (72)$$

where i_{kin} is the usual current density of the ion discharge process at a given overpotential.

These formulas yield results that are much closer to experimental data than those obtained from the Sharifker–Hills formula (68).

The described method for calculating the number of clusters on the surface allows identifying a significant difference between metal crystallization on a metallic substrate and on a structureless substrate. In the latter case, in contrast to the monocrystalline surface of metals and coarse-grained metals in general, as a rule, the number of nuclei weakly depends on the potential. *It is probably mainly determined by the total number of active centers on such a substrate, regardless of their nature. But the number of nuclei on a crystalline surface does not correlate with the number of specific centers.*

It is of interest that a number of researchers report that in a wide variety of systems [87–95] not only the number of growing centers differs from the calculated value (68), but also the shapes of the curves of current versus time deviate from the theoretical ones. In most cases, deviations were observed at times greater than $t_{\max}$. For example, when cobalt was deposited on a Pt/Si substrate [96], the instantaneous nucleation was followed by progressive one and then deviated from the latter. This was also observed in [97]. Upon electrodeposition of cobalt onto glassy carbon [98], an early deviation from the gradual nucleation process was observed at approximately $t/t_{\max} = 2.8$ at a high cathode potential (–1.275 V according to SCE). Similar effects are also described in [88, 99] and in a number of other papers. Along with the role of mixed kinetics, as mentioned above, kinetic complications during electrodeposition, as well as a deviation in the shape of clusters from hemispherical, were cited as the cause of such deviations. All these assumptions are qualitative in nature; no quantitative analysis has been attempted.

In some cases, it is reported that in the course of deposition, the instantaneous nucleation mechanism is replaced by a progressive one and vice versa, or the nucleation rate constant changes continuously [100]. Obviously, this speaks not about the actual processes, but about the imperfection of the model.

Nevertheless, the reasons for the deviations from the Sharifker–Hills model may be different. At the same time, a clear understanding of the deviations from the model can help to choose the appropriate electrolyte composition, operating

potentials, mixing conditions, etc., in order to obtain the necessary structure of the deposit.

Further crystal growth usually occurs via one of three mechanisms: the Volmer–Weber mode of growth of three-dimensional clusters, Frank–van der Merwe mode of layer-by-layer growth (when the atoms in a layer are more strongly bonded to the substrate than to each other, as a result of which the growth of the next layer does not begin until the formation of the previous one is completed), and Stranski–Krastanov mode, in which a two-dimensional monolayer is first formed, on top of which three-dimensional clusters grow [101]. The last mode of growth occurs when the adhesion of the monolayer to the substrate surface is stronger than the adhesion of the species to each other.

Fractal (dendritic) growth, which is characteristic for very high process rates, as well as for special cases such as lithium battery electrodes, is also considered as a specific case. This mode of growth, which is also particularly characteristic for zinc and some other metals, is often observed at high overpotentials and can be described by aggregation limited by diffusion, suggesting irreversible adhesion of adatoms upon initial contact with the crystal surface [102, 103].

In the case of *two-dimensional nucleation* and two-dimensional growth according to Frank–van der Merwe during the growth of a thick metal layer, even when an incomplete first layer is formed, nucleation and growth of the second layer can begin on it, etc., forming incomplete layers. Therefore, the overall dependence of current on time consists of a set of transients discussed above. The corresponding curves for subsequent layers are delayed in time and somewhat blurred, as growth occurs on incomplete layers. The experiment actually demonstrates the oscillations of the current, which dies out at about the 5th or 6th layer. The calculations yield approximately the same result, and the steady-state current is close to the maximum current at the formation of a monolayer. The electric charge passed from the start of the process to the first maximum current is approximately equivalent to the formation of a monolayer.

In the case of *three-dimensional growth*, there are no such oscillations, and — both theoretically and experimentally — only one current maximum is manifested. This maximum, or, rather, the subsequent decrease in current, is associated with the so-called geometric levelling of the surface after the three-dimensional clusters merge together. The overlapping of the growing three-dimensional clusters occurs in the same way as the overlapping of diffusion zones when they begin to form a continuous coating. The problem of cluster overlap during electrodeposition was considered in [104], where four possibilities were discussed: (1) instantaneous nucleation with diffusion-limited growth; (2) progressive nucleation with diffusion-limited growth; (3) instantaneous nucleation with kinetically controlled growth; and (4) progressive nucleation with kinetically controlled growth. All these cases correspond to extremal dependences of current on time, but the type of dependences is significantly different. In particular, the time in which half the maximum current is achieved in these cases is $0.12t^*$, $0.40t^*$, $0.44t^*$ and $0.56t^*$, respectively. In addition, the shape of the initial sections of the curves differs.

The subsequent slight decrease in current is of nondiffusion nature. In the case of diffusion limitations, there is a much more significant Cottrell current drop, although not to zero: the steady-state thickness of the diffusion layer δ corresponds to a minimum current of $zFCD/\delta$.

Recently, the processes have been identified [105, 106] that cannot be described exclusively by the classical theory. In some publications, for example, [107] the concept of under-critical clusters (of the order of nanometers in size) is introduced; such clusters are stable aggregates, unlike monomers (individual atoms or molecules) in classical theory. In other words, there are processes of growth due to aggregation of particles (and not just the addition of monomers to clusters, as is assumed in the classical theory of Zeldovich and others). However, when discussing these results, the same concepts of surface diffusion and nanocluster growth are used as in the classical theory. In particular, the concept of a nanocluster as a structural unit was used in the development of a generalized mechanism of electrochemical aggregative growth for electrodeposition of metals on a low-energy surface.

In addition, in the general case, it is necessary to take into account that the coefficient of surface diffusion, as well as the rates of aggregation and recrystallization, increase with increasing overpotential η . As a result, the values of J and N calculated using the classical model may differ significantly from the experimental results obtained during local surface studies.

11. Electrochemical and structural methods used in the study of nucleation

Let us list and briefly describe the main electrochemical and then structural methods used in the analysis of nucleation processes. First, we will consider the classical methods, which are described in detail in [68], and then we will focus on the newer ones.

Chronopotentiometry is an electrochemical research and analysis method based on the study of changes in the electrode potential E over time at a given value of the electrolysis current. It is used relatively rarely in the study of nucleation, as it is not informative enough in this regard. When a current passes through the interface, the ions of the solution are first transformed into atoms adsorbed on the surface. These adatoms further accumulate up to a certain surface concentration (coverage θ , which is a fraction of the monolayer), after which the nucleation starts. At the same time, the overpotential increases at first, and then starts diminishing; nuclei do appear approximately at the moment of the beginning of its decline. The amount of electricity that has passed allows judging which potential and which overpotential corresponds to the beginning of nucleation at various specified current densities.

Chronoamperometry is a more widely used method. This is the study of the dependence of current on time at a given potential (overpotential) or, in other words, the study of potentiostatic transients. Most of the nucleation studies have been performed using this method. It is the chronoamperograms that reflect the course of the nucleation and growth of nuclei at a given overpotential, the overlap of diffusion zones, the transition from hemispherical to flat diffusion, etc. The diffusion coefficient and the number of nuclei were calculated in many modern publications using the position of the maximum on the dependence of current on time.

The two-pulse method. A very short (10^{-7} – 10^{-4} s) overpotential pulse is first applied to the electrode, at which a certain number of nuclei occur; but they are very small and are not visualized by most available methods. Therefore, immediately after the first pulse, a second one with a lower

overpotential is applied, but for a sufficiently long time. During the second pulse, practically no new nuclei are formed, and those formed during the first pulse grow to the required size so that they can be detected using electron or even optical microscopy. After that, it is enough to calculate the number of grown crystals n and consider the dependence of n on the overpotential of the first pulse, its duration, the electrolyte temperature, etc.

The method of waiting for the first nucleus, or finding the probability of formation of 1–3 clusters. This is one of the earliest methods dating back to 1948. At some moment $t = 0$, a certain overpotential is set on the electrode, and after some time t_1 , a current arises in the circuit, indicating the appearance of a nucleus. If this experiment is repeated several times, the average t_1 value is inversely proportional to the nucleation rate. Sometimes a variation of this method is used, namely, the selection of the duration of the first pulse so that the nucleus occurs in half of the cases. The method is still used.

Thus, the study of the t_1 time of the appearance of Ag nanoparticles on platinum electrodes in the form of a nanodiscs during deposition from solutions in acetonitrile was used to determine the critical size of the nuclei and the energy of their formation.

Another method is based on the sharp dependence of the nucleation rate on overpotential, which was used in [10] in the study of mercury nucleation on oxidized platinum. After a potential pulse, at which a relatively large number of nuclei appeared, the overpotential was sharply reduced to such a magnitude that some of the nuclei became subcritical and dissolved. Then the minimum nucleus size of the remaining ones was critical one.

Electrochemical Impedance Spectroscopy (EIS). Impedance spectroscopy, that is, the study of the dependence of the active and reactive components of the complex electrical resistance of an electrochemical system on the frequency of a small-amplitude alternating potential (superimposed on the constant potential of the electrode), allows obtaining quite significant information about the system. In common EIS practice, an alternating potential with an amplitude of no more than 15 mV is applied to the system. In this case, the system remains quasi-linear. The impedance Z depends on the frequency. For example, in a Nyquist diagram, each point represents an impedance at some frequency ω . Based on the shape of the diagram (distorted semicircle, linear dependence, etc.), well-founded conclusions can be drawn about the relative role of kinetic and diffusion factors in the process under study, and in general about the mechanism of the electrochemical process.

The use of small electrodes (microelectrodes). Although very small electrodes have been used in crystallization studies for many years, in recent years the ultramicroelectrode method is actively used [107–110]. Ultramicroelectrodes are called electrodes with a diameter of less than 25 micrometers. Recently, submicron and nanoelectrodes with a size of even less than 500 nm have become possible [109, 111, 112], and have been used to study the electrocrystallization of various materials. The ultramicroelectrode method provides operation and measurements with hypersensitivity down to a single object, which makes it ideally suited for fundamental research of the early stages of electrodeposition. Combined with the modern imaging equipment, this allows determining the characteristics of nanoparticle formation in real time. In addition, very small

electrodes eliminate a number of problems of a purely electrochemical nature.

In the course of *in situ* electrochemistry studies on Pt, an electrochemical cell was constructed with an electrolyte drop in a capillary in contact with a working electrode to limit the electroactive area of study [113].

The capillary method of growing dislocation-free facets belongs to the same group of methods. Studies of nucleation on the surface of single crystal faces are complicated by the fact that dislocations are often present on such surfaces, which become predominant local nucleation centers. In order for all points of the electrode to be equivalent, it is necessary to have a dislocation-free face. To obtain such a face, a method is used that can already be called classical [47]. The same metal is deposited on the surface of the face (usually silver or copper), so that the face grows inside a capillary with a diameter of about 0.1 mm. As it grows, the existing dislocations gradually reach the edges of the capillary (since it is unlikely that the directions of the dislocation axis coincide with the capillary axis). This is monitored by applying anode current pulses from time to time, after which etching pits appear at the dislocation outlets (they are observed using an interference microscope). It has been established that nucleation on dislocation-free faces requires the supply of a certain threshold overpotential (at least 8 mV in the case of silver deposition from a nitrate solution).

The use of single-crystal electrodes. Work with single crystals is typical in the field of metal nucleation. The modern stage of work with monocrystalline electrodes is associated with the name of J. Clavilier, who proposed in 1980 an original method for manufacturing single crystal electrodes [8]. This method consists in melting the lower tip of a metallic vertically fixed wire (including platinum or gold) in a burner flame, slowly raising the flame and increasing the hanging drop of a molten metal to a size of 2–2.5 mm. The drop is then slowly cooled, and the resulting spherical electrode acquires an almost perfect monocrystalline structure.

The Clavilier method is widely used because of its relative simplicity, although it really requires considerable skill to master this technique. A working sample is then made from the resulting faceted single crystal metal drop, fitting the desired face using a goniometer with a laser, mechanical and thermal treatment.

Structural methods: probe microscopy and X-ray methods. Direct observation of clusters on the electrode surface at the first stages of their study was carried out using optical methods, including interference techniques. Then various types of electron microscopy were used, and currently the most important method is scanning probe microscopy, which provided unique opportunities for studying the atomic structure of electrodes and allowed observing of the processes on the surface during the adsorption of solution components, changes in the potential, location of clusters and even of individual molecules are located, the types of active centers involved, etc. The surfaces of platinum, gold, silver, and copper single crystals, the processes of surface reconstruction and the deposition of adatoms, such as copper on gold, have been studied. An example of such a study is, for example, [114], where individual gold atoms and nanoparticles were observed deposited on a boron-doped diamond substrate for 5 to 30 milliseconds.

Scanning electrochemical probe microscopy (SEPM) methods comprise a family of methods including scanning

electrochemical microscopy (SECM), electrochemical scanning tunneling microscopy (ECSTM), electrochemical atomic force microscopy (ECAFM) and scanning electrochemical cell microscopy (SECCM) and possibly other similar methods, which are described in [115]. We briefly describe the features related to electrodeposition in these methods, in particular, electrochemical atomic force microscopy. In the SECM method, ultramicroelectrodes are used as scanning probes to determine the electrochemical characteristics of surfaces [116, 117]. The scanning probe moves above the surface of the substrate in a solution located in an electrochemical cell, and electrodeposition is performed in either a potentiostatic or potentiodynamic mode. The conductive sensor allows obtaining electrochemical currents in addition to topographic images. The spatial resolution in this case is limited by the size and geometry of the sensor. The ECAFM method is similar, it provides improved spatial resolution compared to SECM by using a sharp but nonconductive probe and a three-electrode electrochemical cell. ECAFM and ECSTM make it possible to carry out *in situ* measurements during electrodeposition on conductive surfaces [118]. For example, this method was used to study the deposition and dissolution of silver [119], and the electrical circuit consisted of a four-electrode cell operating in the bi-potentiostatic mode, so that the Faraday current (i.e., the metal reduction current) at constant potential could be controlled in parallel with the tunnel current between the tip of the STM and the working surface of the electrode. Using ECSTM, it was possible to fix a single Ag nanoparticle, the morphology of which corresponds to the mechanism of crystal growth of a 3D island. This method has also been used to simultaneously determine the size and electrochemical properties of individual Pt nanoparticles on the silicon surface during electroless deposition [119]. Compared to STM, ECAFM is more versatile and only requires connecting the sample to an external potentiostat.

Over recent years, other methods have been developed that are close to those considered, for example, see [120–122].

In situ small-angle X-ray scattering (SAXS), X-ray absorption spectroscopy (XAS), and high-energy X-ray diffraction (HE-XRD) are used in combination with probe methods. During nucleation and at an early stage of growth during electrodeposition, surface X-ray diffraction (SXRD) or X-ray diffraction at low angles in combination with synchrotron radiation allows studying the structure of the atomic layers of a crystal, as well as to detect particles near the electrolyte/electrode interface by the solution side [123]. Other modern techniques include energy dispersive SXRD, high-energy SXRD, translucent SXRD, and coherent surface X-ray scattering. *In situ* X-ray imaging can be combined with spectroscopic methods such as Raman spectroscopy. The results can also be complemented by molecular dynamic modeling [124].

In [108], a fairly detailed review of *in situ* observations of the kinetics of crystal nucleation and growth is presented.

In situ transmission electron microscopy (LCTEM) and scanning transmission electron microscopy (STEM) use very thin electrochemical cells for monitoring crystal nucleation and growth at early stages in real time [125, 126]. In these studies, the cells had a thickness of about micrometers, and the solution was placed between windows made of silicon nitride, on one of which a gold microelectrode was formed (electrodes made of glassy carbon and platinum were also used).

12. Studies of the processes of electrochemical nucleation and early stages of crystal growth of various metals

Numerous experimental studies carried out in recent years by the methods discussed above have, in the majority of cases, confirmed the correctness of the theoretical concepts outlined. For a number of deposited metals and substrates, it was possible to establish induction times and nucleation rate constants at various overpotentials and concentrations of solutions, the number of nuclei, the number of atoms in critical nuclei, the correspondence of the structures formed to the structure of the support, the mode of crystallization, etc.

The following is a brief and incomplete summary of the most important results for several metals. It is necessary to note the following trend over recent years: quite a lot of work uses nonaqueous electrolytes (organic solvents or eutectic mixtures with a low melting point, that is, ionic liquids).

As a rule, refractory metals behave significantly differently from low-melting ones during electrodeposition. This is primarily due to the fact that the latter have a significantly lower surface energy, and therefore a low crystallization overpotential. Let us first consider metals with a higher melting point.

(a) Metals with a high melting point: silver, copper, platinum, palladium.

Investigation of the initial stages of silver electrodeposition on the surfaces of Pt [111], Au [111], and Au [100] single crystals in low-viscosity ionic liquids by electrochemical methods in combination with *in situ* scanning tunneling microscopy (STM) and *ex situ* atomic force microscopy (AFM) both during pre-phase deposition (UPD) and under some overpotential [127] showed that the substrate material significantly affects the mechanism of nucleation and growth of silver deposits. While no underpotential growth was observed on Pt[111], the formation of Ag UPD monolayer on the Au[111] electrode in ionic liquids is clearly visualized using *in situ* STM. The formation of an Ag adsorption layer on gold electrodes during UPD promotes Ag crystallization, which begins on Au[111] and Au[100] at much lower negative potentials than on Pt[111]. There is a correspondence between, on the one hand, electrochemical and, on the other hand, structural data demonstrating the nucleation and growth of individual Ag crystallites on Pt[111] in accordance with the Volmer–Weber mechanism and the layered growth of silver on Au[111] and Au[100]. Only at high overpotentials does the growth of silver on gold electrodes switch to the Stranski–Krastanov mode after the appearance of three-dimensional crystallites.

Scanning electrochemical microscopy in a cell was used in [94] to study the deposition of silver on pyrographite. Discrete current peaks corresponding to Ag nanoparticles with a diameter of 30 nm were recorded. Transient processes were studied at overpotentials of 50, 100, and 200 mV in a highly dilute AgNO₃ solution in the presence of KNO₃. The formation of a lot of critical Ag nuclei was established, and as the nuclei turned into nanoparticles, the nearelectrode concentration of Ag⁺ ions decreased, and the rate of growth became limited by diffusion. In this work the aggregation of nanoparticles was observed due to the system's tendency to minimize surface energy.

In the already mentioned work [111], the induction time during the nucleation of a single Ag nanoparticle was measured at overpotentials from –130 to –70 mV. Pt

microelectrodes ranging in size from 5.1×10^{-10} to 2.6×10^{-11} m² were used to detect a single Ag nucleation event during the experimental observation time, which ranged from 150 ms to 1000 s. Multiple measurements of the Ag nucleation induction time were performed to determine the nucleation rate as a function η of overpotential. The number of atoms g_c in the critical cluster was 1–9 atoms at an overpotential in the range from –130 to –70 mV. The energy of nucleation varied from $3.3 k_B T$ to $13 k_B T$ in the same overpotential range.

Finally, let us note once again the rather remarkable publication [50], in which the number of atoms in two-dimensional silver nuclei on the dislocation-free Ag[100] face was found. It decreased from 30 to 17 in the overpotential range from 16 to 22 mV.

In 1992, the initial stage of copper deposition on monocrystalline gold electrodes was studied using *in situ* ECSTM [128]. It was found that Cu forms a monolayer in the UPD region on gold and small clusters at low overpotential. Later, a similar result was obtained on platinum single crystals: A.I. Danilov and collaborators [129] studied the initial stages of copper deposition at low overpotentials on Pt [100] and Pt [111], as well as on stepped surfaces of Pt [610], Pt [410]. The process included the formation of an adsorbed Cu layer, an epitaxial monolayer, and three-dimensional copper crystallites on [100] terraces, while there was no two-dimensional Cu layer on the surface of Pt [111]. At sufficiently high overpotentials, a three-dimensional copper phase appeared on a monolayer of copper adatoms on top of Pt [111]. In all the cases studied, the Stranski–Krastanov mechanism of nucleation and growth was implemented. Thus, nucleation began only after the formation of the copper monolayer was completed, and the growth proceeded in a mixed kinetics mode. At the same time, electrochemical pretreatment of the surface strongly influenced the number of active centers. In contrast, on a glassy carbon substrate, copper nucleation occurred according to the Volmer–Weber mechanism, while the surface oxygen-containing groups on glassy carbon served as active centers.

In [130] (also at copper deposition), the combination of LCTEM and chronoamperometry allowed obtaining results that were also consistent with the classical three-dimensional model of island growth. It was concluded that copper electrodeposition occurred in accordance with the first-order kinetics and diffusion-limited three-dimensional growth. Frame-by-frame images of copper deposition during linear voltammetry have recently been obtained on a combined W–Au ultramicroelectrode [131]. After the Cu clusters first originated on a small area of the exposed W, and then on the Au part of the overall surface, they grew when more negative potentials were applied. Multiple points of nucleation were found.

When using high-speed ECAFM [132, 133], the formation of nuclei and rapid growth of multilayer islands of copper were observed within a few seconds after applying the potential. At the same time, there was a gradual transition from hemispherical to planar diffusion. In addition, the number of nuclei increased significantly with overpotential. Unlike Au and Ag, these results for Cu electrodeposition were fully consistent with the classical theory for mixed reaction control and mass transport (i.e., for mixed kinetics).

Electrodeposition of *platinum* nanoparticles for use in catalysis has a number of advantages over other synthesis methods. The advantages include high purity of the products

(without surfactants or additives), relatively low cost, and ease of morphological control [134]. Many studies on the electrocatalytic activity of Pt nanoparticles often lack quantitative information on the rates and mechanisms of crystal nucleation and growth; in contrast, paper [135] provides fairly detailed information about these processes on the surface of a platinum [111] face. At the first stage, nucleation and growth were observed, in which nanoribbons originated and grew laterally; later, the nanoribbons coalesced and subsequently grew mainly along the normal to the surface.

In [136], the electrodeposition of a single Pt nanoparticle on a platinum ultramicroelectrode with a thickness of 10 μ m from an aqueous glycerol solution was observed using droplet technology (single nanodrops method). The small volume of the droplets provided a sharp decrease in the near-electrode concentration of discharged particles, allowing the deposition of individual Pt nanoparticles to be observed (in the kinetic mode at low overpotentials, and in the diffusion mode at high overpotentials). In this work, the crystal growth rate constant for Pt electrodeposition was determined for the first time: it was 0.003 cm s^{-1} .

The electrodeposition of isolated Pt atoms and nanoclusters of several platinum atoms on a bismuth electrode was studied in [137]. The deposition of a single Pt atom was detected by the minimum diffusion current of 55 pA. This result is important for the development of the theory and practice of single atom catalysis. Individual nanoclusters (consisting of about nine atoms) with a radius of less than 1 nm and Pt nanoparticles with a size of 1 to 10 nm were also studied for their electrocatalytic activity in the reaction of electrochemical hydrogen evolution. It was found that the rate of this process increases with growing radius of Pt nanoparticles until it reaches a plateau at a radius of about 4 nm.

Palladium in the form of various nanostructures is promising for production and storage of hydrogen by water electrolysis [138, 139]. It was shown in [140] that the nucleation of Pd nanoparticles on carbon (in the form of nanotubes) occurs faster than in a millisecond, which indicates predominantly instantaneous nucleation. In [141], the electrodeposition of Pd onto a carbon-coated grid was studied by two-stage chronoamperometry and it was shown that most of the deposited Pd nanoparticles were 1–2 nm in size.

In a very extensive study [142], potentiostatic palladium deposition was performed at overpotentials of –0.380, –0.280, –0.230, –0.210, and –0.180 V in a mixture of 0.056 M PdCl₂ + 0.1 M HCl on an Au substrate. The transients fully corresponded to the Sharifker–Hills models for both instantaneous and progressive nucleation, and deposition of Pd occurred mainly by instantaneous nucleation up to $t_{\max}$. The calculated charge density and surface coverage of Pd nanostructures up to $t_{\max}$ (confirmed by analysis using scanning electron microscopy), decreased with increasing overpotential. The deposition took place at a partial coverage (20–30% at –0.380 V and 50–60% at other potentials) up to $t_{\max}$. Further deposition occurred due to progressive nucleation on a free (uncoated) surface as a result of three-dimensional and two-dimensional growth in the diffusion regime. At the same time, the experimental graphs deviated from the Sharifker–Hills theory. Moreover, the results of electrochemical impedance spectroscopy performed at deposition potentials showed mixed charge and

mass transfer at the electrolyte–substrate interface. In this case, mixed kinetics is considered as the reason for the deviation from the Sharifker–Hills model.

(b) Low-melting metals: zinc, lithium, mercury.

There is relatively little research of the *zinc* deposition, although this metal, along with its widespread use in electroplating, is important for rechargeable current sources, since batteries based on it have a high capacity and a very negative electrode potential [143]. Thus, in [144], epitaxial electrodeposition of thin Zn films onto graphene was carried out to obtain a material for electrochemical processing (as a base for rechargeable batteries). In general, no significant deviations from the classical models of nucleation and growth were observed during the deposition of zinc.

A distinctive feature of work [145] is the use of trimethyl phosphate to reduce surface energy and increase crystallization overpotential. For this purpose, tetramethylene sulfone was also used in [146] as a second solvent, which provided a more uniform distribution of the process rate over the surface. Cyclic tetramethylene sulfone molecules were preferably adsorbed on the [0001] zinc lattice plane and formed oriented dipole lattices with low electron density, which, according to the authors, slows down the adsorption of zinc ions on the electrode surface. This effectively reduces the reaction rate and, as has been shown, improves the stability of the battery.

Back in [147], a constant growth rate of zinc dendrite was established for the kinetic growth and an exponential decrease in time was found for diffusion. In [148] it was shown using the ECTEM method at an early stage of zinc crystallization that a potential jump first occurs during the galvanostatic process, after which, at an almost constant overpotential, dendrite growth takes place. In this case, the process as a whole follows the classical pattern, in which equilibrium critical clusters first appear, which then (at a lesser overpotential) continue to grow.

The work [149] is devoted to the phase formation of zinc on a tungsten electrode from a zinc solution, and in the range of current densities 200–600 mA cm⁻². The following parameters were determined: the transition overpotential (100–200 mV), crystallization overpotential (50–60 mV), phase formation work (of the order of 10⁻¹⁹ J), number of atoms in a nucleus (from 2 to 10). The assumption was substantiated that the phase formation was carried out on the reduced areas of the oxidized surface of tungsten. In the studied range of overpotentials, nuclei were formed at energetically homogeneous electrode centers. A low value of the transfer coefficient ($\alpha = 0.26$) was noted, which reflects the weak influence of the electric field of the double layer on the activation energy of charge transfer.

A rather interesting and apparently general result was obtained in [150] when observing the deposition of zinc on polycrystalline copper using ECAFM. In this case, it was found that CuO particles present on the copper surface (and often remaining on it after various pretreatment methods, including single crystals) act as nucleation centers for zinc during its electrodeposition. This probably applies to other metals as well.

Lithium is an anode material for many new chemical energy sources with high energy density [151]. When lithium is deposited, the most important problem is the stability of its growth form [152]. In [153], the processes of nucleation and growth during the formation of an interfacial medium in lithium-ion batteries were considered, and the key mechan-

isms were identified: heterogeneous nucleation and early-stage growth; surface diffusion with a tendency to one-dimensional growth (due to a high surface diffusion barrier) and the emergence of a preferred crystallographic orientation, which promotes dendrite formation. During rapid deposition of lithium, the concentration of Li⁺ ions decreased, creating a depletion zone of Li⁺ ions on the surface of the anode and causing the formation of a space charge, which leads to the growth of dendrites. These considerations were also developed in earlier works [154, 155].

Scanning electron microscopy was used [156] to study the nucleation process of metallic lithium on a copper substrate, and the data obtained were described in accordance with the classical theory of nucleation. It was found that the size of lithium nuclei is proportional to 1/ η , and the density of the number of nuclei is proportional to the third degree of overpotential. ECTEM and STEM (*in situ*) methods were used in [157–160]. In particular, STEM was used to study the deposition and dissolution of lithium at the interface between a working platinum ultramicroelectrode and an electrolyte solution [160].

In [157, 158], STEM *in situ* was used to visualize the interfacial boundary during Li deposition on a glassy carbon electrode with a thickness of 30–50 nm from an organic solution used in lithium batteries. The images showed that metal nuclei were formed at the edge of the electrode and then grew normally to its surface. At the same time, the deposits did not have the classical fractal shape characteristic of dendritic growth, but were spherical clusters. After the initial growth to a critical diameter of 400–500 nm a second period of nucleation was observed. Spheroids were also observed by Kushima and co-authors in an *in situ* ECTEM study of the formation and first growth period of Li nuclei on structured Au electrodes [161]. The images show the various stages of Li electrodeposition: initially, spherical nuclei appear on the surface of gold. Their size increases proportionally to the square root of time, indicating growth limited by diffusion. Then, the growth of Li whiskers takes place, with the predominant deposition of Li at the Li/Au interface rather than at the tips of the dendrites. In time, the growth rate decreased, after which a fracture appeared on the whisker, dividing it into two segments under the influence of accumulated internal stresses. A more complex model of nucleation and growth, taking into account the decomposition process of the electrolyte itself, was proposed in [162].

The deposition of metallic lithium was also studied in [163]. The process began with progressive nucleation, which further turned into an instantaneous one and then stopped. The heterogeneity of the electrode surface caused a local change in the overpotential, which depended on the size of the nucleus. During the first 75 seconds of deposition, stochastic nucleation took place on the surface, and upon further deposition (up to 140 s), the electrochemical heterogeneity of the surface decreased, and a uniform growth of a thin lithium film was observed after very rapid formation of new nuclei.

The nucleation of *mercury* on platinum and some other electrode materials was studied in detail and repeatedly in early works in this field. Actually, it was the work with mercury (mainly by the Bulgarian school created by Kaischew and Budevski) that allowed the creation of a modern theory of the process. Recently, there have been fewer such works, but they are still published from time to time. Thus, the nucleation and growth of mercury micro-

droplets during electrochemical reduction from an acidified nitrate solution on a specially prepared (oxidized) platinum surface was studied in some detail by the two-pulse method described above [10]. The duration of the nucleating pulse ranged from 1 to 30 ms, with overpotentials of 0.092–0.10 V. The clusters were grown at an overpotential of 0.04 V for 20 to 120 s. The number of registered clusters reached 8×10^5 per cm^2 and was approximately proportional to the duration of the nucleating pulse, and the nucleation rate was $(1.4\text{--}26) \times 10^7$ per second per cm^2 , depending on the overpotential and on the state of the platinum surface (apparently, in fact, on the density of active centers). The critical nuclei consisted of 8 mercury atoms, and the induction period was about 2 ms. We would also like to note the older work [164] on the deposition of a mercury–silver alloy from a nitrate solution at overpotentials near 0.07 V. In this case, the nuclei consisted of 7–9 atoms of both metals. Such studies allowed determining the order of magnitude of the rates of such processes, the characteristic times and the number of atoms in the nuclei.

13. Conclusion

The presented results, in our opinion, show that the theory of the formation and growth of metal nuclei under electrochemical conditions has received significant development over the past decades and well describes the numerous experimental data. However, the experiment is ahead and allows observing the behavior of the smallest individual species and to achieve controlled growth of various objects such as nanowires or deposits with the necessary catalytic properties. Further development of the theory is likely to rely heavily on computer modeling and experiment on the rapidly developing new capabilities of modern electronic equipment.

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