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Size effects in electrochemistry

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Abstract. General characteristics of size-dependent phenomena in electrochemical systems are given. Primary attention is paid to methodical achievements of nanoelectrochemistry, which is a line of research created over the last 15 years. The development of the main concepts of electrochemistry initiated by the stream of nanoscopic information is considered. The prospects for local studies of processes on charged interfaces, elementary steps of these processes and application of nanoelectrodes and related systems in interdisciplinary fields are discussed. The bibliography includes 198 references.

I. Introduction

Electrochemistry studies homogeneous condensed ionic systems (solutions, melts, solid electrolytes) and heterogeneous systems which include electrified interfaces. The spatial scales of heterogeneous electrochemical systems vary over a wide range (Table 1). Correspondingly, the size effects observed in them are numerous and diversified, and quite a number of them are analogous to those in homogeneous electrochemical systems. However, the latter are beyond the scope of this review.

Characteristic dimensions of conventional components of electrochemical systems (electrodes, electrolytes and membranes) cover 5 – 10 orders of magnitude. The lower boundaries of the corresponding intervals approach typical sizes of specific space regions (layers) that arise only at the electrode – electrolyte, electrode – membrane and electrolyte – membrane junctions. In electrochemical systems, the concentration distribution of components near the electrode differs from that in the bulk. As the distance from the interface increases, this distribution changes, *i.e.*, the system contains nonuniform regions. The structure of such a region is considered in detail in Refs 1 – 3. Below, we only briefly comment on the concepts employed in this article.

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Table 1. Characteristic scales of elements of electrochemical systems and devices.

Elements	Size intervals /m	Components
Electrodes for practical applications	0.1 – 10	metals, semiconductors, composition materials
for research	10^{-3} – 10^{-2}	
microelectrodes	10^{-5} – 10^{-4}	
ultramicroelectrodes	10^{-8} – 10^{-6}	
thin-film electrodes	$< 10^{-8}$	
Electrolyte layers		solutions, melts, solid electrolytes
electrolysers	0.1 – 10	
research cells	10^{-3} – 0.1	
thin-layer cells	10^{-6} – 10^{-5}	
microcells	10^{-7} – 10^{-6}	
Membranes	10^{-7} – 10^{-2}	polymers, porous inorganic materials
Diffusion layers	10^{-6} – 10^{-4}	all electrolyte components
Chemisorption layers	10^{-10} – 10^{-9}	the same
'Electronic tails' and near-surface layers in semiconductors	$< 10^{-11}$	electrons and other charge carriers

When an electrode process occurs on an interface, the boundary layer is depleted of the corresponding reactant and(or) enriched with the products formed. Insofar as diffusion rates are finite, a region always exists in which the concentration of one or several components depends on the distance. We call this region the diffusion layer and usually consider it as an electrolyte component.

A uniform distribution of components can also be disturbed under equilibrium conditions. Boundary regions that arise in the process are called the 'electrical double layer' (EDL).† Charged species are distributed in the EDL under the effect of different electrostatic interactions, the concentration of ions either decreasing or increasing with an increase in the distance from the

† This name is associated with the concept of metallic and ionic plates of a hypothetical capacitor commonly used as the interface model.

boundary. If the interaction of an ion with a charged electrode is much stronger than its interaction with induced charges, then the concentration distribution much resembles the diffuse distribution of charges in an ionic atmosphere and is described by a parameter having the meaning of the Debye screening length and equivalent to the effective thickness of the diffuse part of EDL, namely, the ionic diffuse layer.

If certain components of a system specifically interact with the electrode material, then a chemisorption layer (the dense part of EDL) is formed between the surface and the diffuse layer. For the vast majority of electrode–solution systems, dense layers are formed involving solution molecules and often exclusively by such molecules.

According to modern notions of the interface structure, the adsorbate layers and the 'edges' of surface atoms on metal electrodes are spatially separated with a gap in between attributed to the emerging electronic gas ('electronic tail'). In electrochemical systems, the properties of this gap depend on the electrode potential (charge). For semiconducting electrodes, the spatial dispersion of charge carriers is also characteristic of near-to-surface solid-phase layers.

We can assess the properties of electrochemical systems from electrochemical responses, *viz*., different dependences of electrical signals (current, potential, voltage) on time and also on polarisation conditions (for instance, modulation frequency and amplitude during ac polarisation). Size effects arise when the system's parameters are commensurate with the characteristic quantities that determine a particular response.

We can distinguish several basic groups of size effects caused either by the scale commensurability of two and more subsystems, or 'intrinsic' size-dependent properties of individual subsystems. Each of these groups merits special consideration (*e.g*., see Refs 4–30). In this review, we consider the general features of size effects in electrochemical systems and give them a sort of classification. The prospects of using size effects for intensifying electrode processes and also for technological (including nanotechnological) applications are discussed. The presented list of references does not exhaust all the literature (otherwise, it would be extremely large) and contains, apart from reviews, only representative papers of recent years.

Size-dependent thermodynamic properties of electrochemical systems related to equilibria involving two-dimensional adsorption layers and nanocrystals are the subject of an interdisciplinary research field that shares its frontiers with colloid chemistry, surface science and solid-state physical chemistry. Studies of other electrochemical size effects also show a trend for integration and are combined by a recently formed separate research field, *viz*., nanoelectrochemistry. Along with inherent electrochemical techniques, this actively developing new scientific discipline extensively uses probe techniques for local surface studies,[14,16,17,20,21,31–34] diffraction[35] techniques, and also optical[36,37] and small-angle X-ray methods[38] (including those *in situ*[39]).

Originally, nanoelectrochemistry was developed on the basis of studying classical size effects (for instance, the dependences of surface conductivity on film thickness[8]). However, during the past decade, it has begun to encroach more actively on the province of quantum size-dependent phenomena. The development of nanoelectrochemistry is also stimulated by the progress in electronics; the latter branch, in turn, diversifies its elemental basis due, in particular, to the introduction of micro- and nanoelectrochemical technologies. The reason for such a 'feedback' resides in the fact that by extending the scope of electrochemical systems to the nanoscale, one substantially strengthens the material basis of electrochemistry and sharply enhances its experimental potentialities.

The possibilities of experimental studies of micro- and nanoelectrochemical systems are largely determined by the facilities for measuring small currents and charges. The characteristic settling times usually lie within hundreds of milliseconds, and, even if we pass to the femtoampere range, the lower limit of measured charge will fall within 10^{-16} and 10^{-15} C. These values exceed the charges consumed in electrochemical reactions of single ions and molecules approximately by three orders of magnitude. At present, the unique measurements with nanosecond resolution have severe restrictions on the lower limit of the measured current. The crucial obstacle that prevents lowering of the limit mentioned results from the fact that characteristic polarisation capacities of micro- and nanoelectrochemical systems are commensurable with the inherent capacities of the measuring devices.

II. Size effects in diffusion kinetics. Microelectrodes and microcells.

The uppermost limit on the scale of size-dependent properties of electrochemical systems is occupied by those manifesting themselves in electrochemical processes with diffusion-controlled rates. Such properties are studied in detail for the systems in which the dimensions of either electrodes or layers of electrolyte solutions are commensurable with the diffusion layer thickness (micrometer range that may be upscaled, for instance, due to gravitation effects). That is why, when separating microelectrodes and microcells into a special class of electrochemical systems, the upper limits of sizes (volumes) cannot always be determined unambiguously, being dependent on the configuration and convection conditions.

For the majority of microelectrodes, such a limit is ~ 10 μm. For disk, spherical, semispherical, conical and microdrop liquid electrodes exact relationships for the dependences of the limiting diffusion current I_d on the characteristic size r were obtained.[40–42] Similar size limits for microcells are determined by a condition of the overlapping of diffusion layers for two electrodes between which the current flows.[43] The corresponding quantitative expressions are very complicated; hence, the applications of microcells are largely related to *in situ* surface spectroscopy (the so-called thin-layer cells for minimising absorption in the solution bulk) and microtechnologies. In those cases, the cell volume contains actually no regions with constant concentrations of reactants, and different non-steady-state size-dependent distributions of solution components can arise.

The most important basic application of microelectrodes deals with the determination of kinetic parameters of electrode processes and is limited by the ratio between the corresponding rate constants and the limiting currents of reactant delivery.

As an example, we consider the limiting diffusion current density i_d, which corresponds to the rate of an electrode process at a slow delivery of a reactant. For an electrode of a common (macroscopic) size r exceeding substantially the diffusion layer thickness, i_d is independent of the electrode configuration and determined only by the diffusion coefficient of the reactant D and its concentration c. Correspondingly, for an electrode of a geometric surface area S, the diffusion current

$$I_d = i_d S = \text{const}\ cD^m r^2, \qquad (1)$$

where the power index $m < 1$.

The values of the constant and m are determined by the parameters that characterise the convection conditions (rotation velocity of a solid electrode, streaming velocity of a liquid metal from a capillary, *etc*.) and by the electrode shape and described by the rigorous relationships deduced within the framework of the planar diffusion model. Inasmuch as i_d and the rate of electron transfer stage are proportional to c, it is difficult to overcome the diffusion limitations and determine the rate constant for the electron transfer on common-size electrodes for quick processes.

When the diffusion layer thickness is commensurable with electrode dimensions, the planar diffusion model does not operate due to a significant role of edge effects. For example, for a disk microelectrode,

$$i_d = \text{const}'\ c\sqrt{D} r^{-1}. \qquad (2)$$

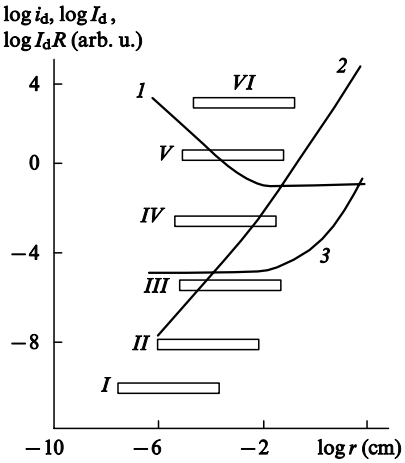


Figure 1. Size dependences of electrochemical responses (*1–3*) and typical scales of various nanotechnological processes (*I–VI*); (*1*) i_d, (*2*) I_d, (*3*) I_dR; (*I*) nanostructurisation in STM configuration, (*II*) electron-beam technologies, (*III*) ion-beam technologies, (*IV*) holographic lithography, (*V*) X-ray lithography, (*VI*) photolithography. Plotted on the basis of the results taken from Refs 19, 24.

Correspondingly, I_d turns out to be proportional to r rather than to r^2, which affects the dependence of the ohmic potential drop I_dR on r (where R is the resistance of the solution layer between the working electrode and a point in which the potential is measured by a reference electrode). Figure 1 illustrates how the most important characteristics of electrochemical systems tend to vary.

In the case of fast delivery of a reactant, regardless of the electrode size, the rate of an electrode process is proportional to the surface area (in the absence of other types of size effects, see Sections IV and V). Hence, with a decrease in r, it becomes possible to overcome the diffusion limitations for still faster reactions. Microelectrodes allow quantitative measurement of the rate constants of an order of magnitude of centimetres per second, whereas the limits of conventional rotating and dropping electrodes do not exceed 10^{-2} cm s^{-1}.

To determine the rate constants of fast reactions, the arrays of microelectrodes which include flow-through channel systems with ensembles of microband electrodes are also widely used.[44] A rotating ring-disk electrode can be considered as the first array electrode which allowed measurement of the kinetics of separate steps of electrode processes, owing to its optimum hydrodynamics.[45] The electrochemical responses of electrode arrays are characterised by special types of size dependences determined by the relative positions of their fragments (for instance, by the spaces between them).

Microelectrodes are widely used in electroanalysis,[46,47] especially for solving environmental and biological problems (for example, in electrochemical measurements *in vivo* in the monitoring of the composition of biological media, diffusion of drugs and poisons, accumulation of glucose, *etc.*). These applications stimulated further miniaturisation of electrodes. As a result, a large class of the so-called ultramicroelectrodes with surface areas of less than 1 μm^2 was developed.[48,49]

Modern methods of insulation of the surfaces of metal wires and other items provide electrodes of characteristic sizes of $\sim$ 10 nm (sometimes named nanodes). Standardisation of the geometry (shape) of nanodes presents a particular problem which can be solved by using nanosize materials of known structures, for example, carbon nanotubes as the electrodes.[50]

The term 'nanoelectrodes' is sometimes used in a different context when considering the phenomena in solutions of monodispersed colloidal metals. Thus when stabilising colloidal gold particles in dichloroethane by ferrocene-containing organic molecules, the responses of redox transformations of the latter could be detected in the single contacts of particles (nanoelectrodes) with the polarising macroelectrodes.[51] In this case, an analogy can be traced with well known suspension electrodes in which macroelectrodes play the role of current collectors.[52]

A new impact for the development of microelectrode technology was made in the end of the 1980s when Bard *et al.*[15] proposed a basically new method for carrying out local studies of surface processes and phenomena, namely, the technique of scanning electrochemical microscopy (SECM). This technique is based on the possibility of measuring the current on a probe microelectrode as a function of the distance h between the probe and the surface of an electrode under study of arbitrary dimensions dipped into a solution containing a redox system with a high electron-transfer rate constant and known diffusion coefficients of redox forms. When the diffusion layers of the probe and the electrode under study overlap (which occurs if h is commensurable or less than r), the processes on both electrodes can either be accelerated or decelerated, depending on the potentials of the probe and the electrode. The corresponding relationships for steady-state and non-steady-state currents in SECM configuration were derived as two-dimensional integral equations (for example, see Ref. 26) for systems with different geometry of probes and surfaces under study as applied to both heterogeneous and homogeneous processes.

Inasmuch as the diffusion layer boundary repeats to a certain extent the surface relief, the SECM technique allows one to visualise the latter with submicron resolution. Scanning tunnelling microscopy (STM) in air may be considered as a version of SECM, because the surface under study always bears an ultrathin film of condensed moisture playing the role of a liquid electrolyte.[53] The resolution that can be achieved depends largely on the curvature radius of the probe tip (even for tips of uncertain general geometry). Moreover, the size of the tip exerts the most critical effect on distortions of the images of surface fragments with small curvature radii. The corresponding size effects can be simulated numerically,[54] and there is a prospect of using advanced models for different convolution procedures (*e.g.*, for recovery of real images of the surface studied and for the determination of the tip geometry from the distortions of standard surface images). The development of the STM method provided special procedures for the pretreatment of well characterised tips, which are common for all probe techniques including SECM.[55,56]

The resolution in the SECM technique is enhanced if a non-uniform surface contains areas of different nature where the rates of local processes differ. Various specialised versions of SECM are developed, for instance, those for the studies of enzymic processes,[57] combined technique (SECM – probe microscopy[43]) and related techniques for investigations on the boundaries of two immiscible liquids.

A unique result achieved in SECM configuration is the measurement of responses of an electrochemical transformation of a single molecule.[58–60] This became possible owing to the accumulation of the signals from multiple successive reversible transformations of a reactant and its product in a limited solution volume between a deepened probe ultramicroelectrode ($r \approx 10$ nm) and a planar surface (Fig. 2). It is the localisation of small solution portions in micro- and nanocells the volumes of which can be reduced down to 10 nl and realisation of systems with two ultramicroelectrodes arranged along a common axis at a small distance from one another that will determine further progress in this field.[61]

Certain basic problems of microelectrochemistry formulated only recently[24,26,48] still remain unsolved. They pertain to the analysis of the potential distribution for overlapped diffusion and diffuse layers (including the case of diffuse layers of two closely spaced electrodes). This is observed, for example, in the configuration of electrochemical tunnelling microscopes (*in situ* STM). Under these conditions, certain anomalies are observed which have not yet found unambiguous explanations.[62] Thus the cathodic deposition of a metal phase can occur at electrode potentials

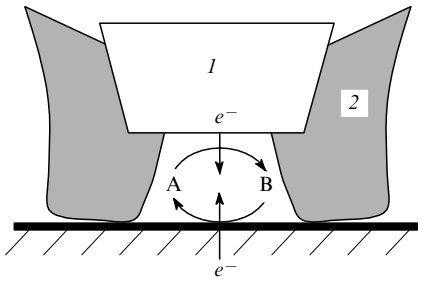


Figure 2. A scheme of a microcell for measuring electrochemical transformations of single molecules.[15]
(*1*) Ultramicroelectrode, (*2*) insulation; A and B are oxidised and reduced reactant forms, respectively.

banned by formal thermodynamics. Hence, one cannot rule out the possibility that distortions in the surface equipotentiality can occur in the vicinity of the tunnelling gap. It is still more probable that the configurations used do not provide correct measurement of the potential drop between the working and reference electrodes.

III. Electrical double layer as a nanostructure

As noted above, an electrochemical interface demonstrates a sufficiently complicated space distribution of components, due to chemisorption and electrostatic factors.[23, 63, 64]

Being the most important EDL characteristic, the zero-charge potential is directly related to the physical properties of electrodes (for example, the electronic work function).[63] Its value depends on both the electrode material nature and the crystallographic orientation of the surface. For a thin-film (especially, semiconducting) electrode, such a thickness can be reached that permits the work function to manifest size-dependent effects;[65] correspondingly, variations of film thickness can cause changes in the electrode charge *vs*. potential dependence.[7]

The models of EDL structure deal with space distributions of the potential in the dense and diffuse parts. For electrodes with pronounced heterogeneous structures and compositions, the potential can vary not only along a normal to the surface but also in parallel to it, both in the dense and diffuse parts. Comprehensive phenomenological models are developed for size-dependent parameters of EDL on polycrystalline surfaces constructed from different lattice faces with different values of zero-charge potential.[66] For small heterogeneities, EDL structure is well approximated by a model with a uniform diffuse layer. With an increase in the heterogeneity size, transition layers appear between neighbouring regions of diffuse layers of different structures. Probe techniques make it possible to study the heterogeneities of the potential distribution near the surface and describe quantitatively the interaction between the diffuse layers of the electrode and the probe.[62] This may be considered as further development of the approaches dealing with interaction of crossed filament electrodes.[63]

In the general case, the EDL is a multicomponent system in which not only concentrations but also the states of species may differ from those in the bulk. For example, the lateral Coulomb repulsion of ions adsorbed with charge transfer [67] weakens so that their surface coverage can reach a complete layer. The phenomenon of the formation of adatomic submonolayers stabilised by the interaction with the support is called *underpotential deposition* (UPD), because it provides deposition before the redox system involved reaches its equilibrium potential (for example, the deposition of adatoms M at potentials more positive than the equilibrium potential of an M/M^{n+} system). The different rates of formation and dissolution of adatomic monolayers compared with metal phases also point to the differences between these systems. Apparently, the properties of a layer start to approach those of a phase only after the deposition of the third or fourth monolayer.

Like adatoms, the molecules of organic adsorbates form structurally non-uniform adsorption layers. In the case of strong lateral interactions, different domains appear on a supporting surface, their structures being dependent on the surface geometry and charge as well as on the presence of other adsorbates. Two-dimensional condensation [68] typical of adamantane and camphor derivatives and of certain amino acids is a spectacular manifestation of lateral interactions. For adsorption with partial charge transfer (or without it at all), the co-adsorption of anions and cations can be responsible for the formation of closely packed monolayers. For example, the adsorption of multicharged polyoxometalate anions is accompanied by the formation of the so-called salt-like layers.[69–71]

Many adsorbates were reliably shown to preferentially adsorb on defective surface sites and behave specifically with respect to surface areas of different coordination.[72, 73] Figure 3 shows, as an example, the results on CO adsorption on high-index faces of a platinum single crystal. A size effect manifests itself in an increase in the surface coverage by CO molecules on areas with a high density of steps (*i.e*., with a decrease in the terrace length). For well characterised systems, the general thermodynamic approach was applied for the analysis of the contributions made by terraces and steps into reversible adsorption processes and, in particular, for the elucidation of the effects of surface crystallography on the observed zero total charge potential value.[72] Moreover, we can assume that the electronic work function is different in different surface points and, apparently, it makes sense to invoke the concept of the local work function (and, correspondingly, the local zero free charge potential [74]). An argument for such an assumption may be the difference in adsorbabilities of the surfaces of terraces and steps.

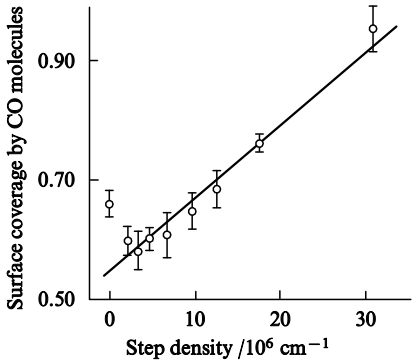


Figure 3. Surface coverage by adsorbed CO species determined from the coulometric data in 100 mM $HClO_4$ as a function of atomic step density on Pt[n(111) × (111)] single-crystal faces.[72]

It should be noted that, along with equilibrium properties of adlayers, the characteristic sizes of areas of given configurations also strongly affect the dynamic characteristics of adsorption processes. For instance, STM data at high time resolution showed that during the formation of the second layer of silver adatoms on a gold electrode surface diffusion on terraces proceeds more quickly than that on sites near the steps.[75] As a result, the adatoms are stabilised near the steps, which is beneficial for the smoothing of the relief in the early deposition stages (Fig. 4). The dynamics of adatomic-layer fragments can be followed in STM experiments with high time resolution.[24]

Unusual nanosize structures with barrier properties are formed by alkanethiol molecules adsorbed on metal atoms

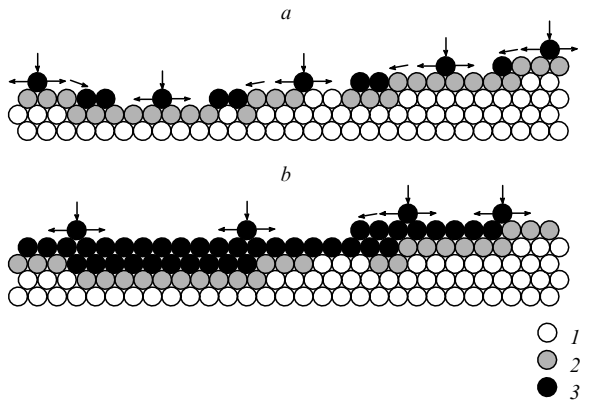


Figure 4. Schematic representation of a mechanism of silver deposition on an Au(100) surface.[75]
(*a*) Initial stages, (*b*) formation of multilayer deposit; (*1*) gold atoms, (*2*) silver atoms in equilibrium states, (*3*) mobile adatoms (marked by arrows) and silver adatoms incorporated into the lattice.

owing to chemical (virtually irreversible) interaction of terminal thiol groups with metals.[76–78] For example,

$$RSH + Hg - e^- \longrightarrow Hg(SR) + H^+.$$

By changing the alkyl chain length, one can obtain, with high precision, a sufficiently closely packed interlayer of molecules arranged in parallel (the area occupied by a thiol centre is ~ 20 Å^2) with a thickness invariant over the surface. The capacitances of alkanethiol-modified electrodes do not exceed several microfarads per square centimetre and decrease for longer alkyl chains.[79] This suggests that the solvent is practically completely forced out from the EDL dense part, and a uniform dielectric interlayer is formed on the interface. Alkyl chains are shown not to be arranged along a normal to the surface but to be bent at a substantial angle (up to 40°). Peculiarities of the formation and properties of alkanethiol layers are sensitive to surface defects,[77] which offers a unique possibility of diagnosing the latter, for example, by following different manifestations of the barrier properties of alkanethiol layers during charge-transfer processes. These systems can also be applied for studying the discrete charging of double layers formed on small particles that operate as nanoelectrodes.[80]

Considerable progress in studies of nanosize structures became evident with the possibility of visualisation of adsorbates *in situ* by probe techniques.[17, 76, 81, 82] Special attention should be drawn to the potentialities of these techniques for studying adsorption-induced phenomena, such as the appearance of surface stresses and the surface reconstruction.[83, 84] Thus the latter can be simulated on the atomic level according to the results for faces of single crystals of gold and platinum (Fig 5).

However, the problem of interpretation of STM data still remains sufficiently complicated, because the electrical double layers of a probe electrode and a scanned surface tend to overlap and interact with one another.[62]

Studies of the EDL structure on an atomic level is important for quantitative description of the interaction of reactants with electrified interfaces, *i.e.*, for the solution of problems of electrochemical kinetics. These studies can also shed light on the microscopic origin of discreteness-of-charge effects arising in the specific adsorption of ions, the effects exerted by metal hydrophilicity on the dense-layer capacitance, *etc.*, which were considered so far within the framework of phenomenological approaches. Modern approaches to building physical models of charged interfaces are surveyed in Ref. 23.

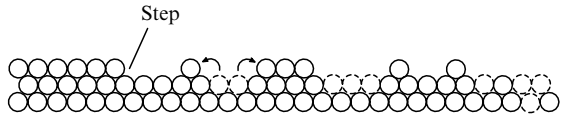


Figure 5. A scheme of island formation on a Pt(111) surface induced by potential cycling in a region that includes oxygen adsorption.[84]

IV. Size effects in electrocatalysis

Size-dependent electrochemical phenomena occur in chemisorptive and electrocatalytic processes that take place on highly dispersed, small (for instance, ultrathin) and surface-heterogeneous electrodes. In such processes, the heterogeneities of characteristic sizes commensurable with either the thicknesses or lateral periods of adsorption layers (nanosize range) play a significant role.

Many active electrocatalysts represent the so-called nanostructurised materials that exhibit periodic inhomogeinities not only on the surface but also in the bulk.[22, 85] Nanostructures are at equilibrium only in rare cases, most commonly they are metastable, but long-lived.

Nanosize materials were introduced into the practice of electrochemical studies long before the methods of their structural, morphological and electronic characterisation became available. First of all, these were the electrodes with well developed surfaces (the ratio of the real surface area S_{real} to the geometric area S being equal to 1000 and higher) of platinum-group metals consisting of nanocrystals.[4, 6, 7] For them, the experimentally determined rates of electrocatalytic processes, the surface coverages by adsorbates and the polarisation capacitances were referred not to the individual characteristics of small particles but to the values of S_{real}.[86, 87] It is the dependence of the specific (calculated per S_{real}) activity on the fabrication method that was the subject of numerous studies aimed at intensification of practically important processes applied mainly in fuel cells.

The concepts of the related structural (size) effects in heterogeneous catalysis[88] as applied to dispersed electrodes have also generated certain simplified notions based on the analysis of 'electronic' and 'structural' factors. For example, the latter factor was considered in the mitohedral approach,[89] which was developed further in the 1980s–1990s. During this period, well characterised electrode materials of similar compositions but substantially differing in surface coordination became available, *viz.*, faces of single crystals and polycrystalline materials with pronounced preferential crystallographic orientations.[10] Numerous attempts were undertaken (for example, see Refs 4, 12) to describe the activities of small metal particles in terms of an additive approach to the contributions of low-index faces. Usually, the ratio of faces on the surface was calculated for ideal equilibrium crystals (in the nanosize range, it strongly depends on the grain size).

Although a number of activity–surface coordination relationships have been revealed, the attempts to substantiate the decisive role of crystallographic orientation in electrocatalysis by dispersed materials have failed for virtually all actively studied processes of oxidation of organic compounds and hydrogen, as well as of oxygen reduction. Undeniably, the main reason for the deviations between experimental and model dependences lies in the non-equilibrium nature of small particles of real catalysts. It is also significant that the particle sizes used in the calculations were not necessarily determined by direct methods.

The technique of high-resolution electron microscopy[90–92] made it possible to refine the data on the real geometry of nanosize particles for a number of materials. However, the potentialities of this technique for the analysis of multilayer deposits and dispersed electrodes are limited. Reliable results are obtained mainly for smooth carbon supports with low surface coverages by catalysts. It should be noted that the interactions of small particles with the support substantially complicate the behaviour of these systems;[6, 7] no adequate models exist for the description of these

interactions. The activity – particle size relationships for different electrocatalytic processes are analysed in several papers (*cf.* Refs 92–98). However, these relationships pertain to relatively narrow intervals of particle sizes. Moreover, the technological methods of fabricating catalysts with different particle sizes do not provide permanence of several important structural characteristics. In different studies, the specific activity was shown either to increase or to decrease with an increase in the particle size not only in the nanometre range but also in submicron range for which one can hardy expect any manifestations of equilibrium 'structural' (and, all the more, 'electronic') size effects.

To date, different dispersed materials based on platinum and palladium have been examined by means of the STM technique with a nanometre resolution.[99–101] A comparative analysis of the data on the real surface area, porosity [102] and characteristic sizes of surface fragments (independently determined by different techniques) allows highly reliable conclusions to be drawn on the real structures of nanosize electrocatalysts: the latter include globules constituted by quasispherical particles. Sufficiently wide size distributions of particles and globules are revealed for electrodeposited dispersed catalysts. This result requires that a great number of property – size relationships be reconsidered for those cases where the sizes were estimated from S_{real}: the particle size thus determined certainly exceeds that corresponding to the distribution maximum. At a high degree of screening (or coalescence) of particles in the globules, the aforementioned differences can reach an order of magnitude, as in the case of certain materials based on electrodeposited palladium.[101]

At present, the controversial views on the structure of different boundary regions in nanosize electrocatalysts, first of all, of intergrain boundaries in globules of metal crystals pose a problem which is extremely difficult to solve experimentally. Probably, as in the case of other nanostructurised materials,[22,85] it is these highly defective regions that play a significant role in adsorption and electrocatalytic phenomena. For a number of cases, a phenomenological analysis [103,104] based on an assumption of high surface defectiveness of these electrocatalysts makes it possible to find a self-consistent set of experimental results. However, it fails to rationalise the nature of defective surface regions.

Yet another aspect of size-dependent electrocatalytic effects that manifest themselves on the scale of molecular sizes is associated with the structure of chemisorption layers. The mechanisms of the vast majority of electrocatalytic processes involve strongly bound adsorbates for which co-adsorption and competitive adsorption play important roles.[9]

A rather universal type of size effect occurs within the framework of the mechanism known as bifunctional catalysis.[9] This mechanism is realised on bi- and milticomponent surfaces where the process is controlled by the chemical reaction of two different adsorbates. Electrocatalytic hydrogenation of organic substances involving hydrogen atoms and their oxidation involving adsorbed hydroxyl radicals may serve as examples of these processes. The activity of a catalyst proves to be highest where its surface contains simultaneously two components which selectively chemisorb the species involved in the slow stage of the reaction. In this case, both the mutual arrangement of components and the ratio of their surface concentrations are of importance. Particularly, there exists an optimum (depending on the reactant structures) size of surface areas with one or another composition which provides the greatest number of reaction sites. Such an area is always commensurable with the size of the adsorbate species. Homogeneous alloys which exhibit no pronounced segregation and adatomic submonolayers are typical bifunctional catalysts. Figure 6 shows the rate of electrocatalytic oxidation of ethylene glycol on platinum covered by different amounts of tin adatoms as a function of the electrode potential.[105] Tin adatoms are the adsorption centres for active oxygen species and exhibit the maximum activity at medium surface coverages.

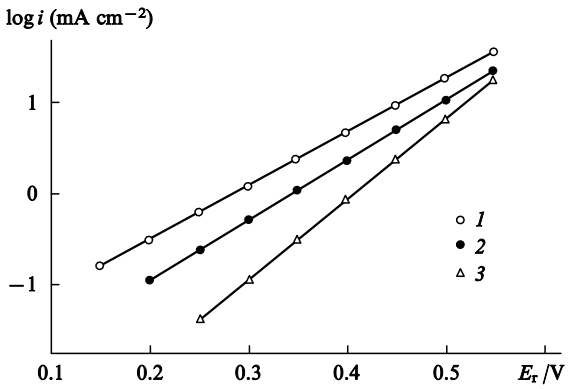


Figure 6. Steady-state polarisation curves of ethylene glycol oxidation (0.5 M, in the presence of 1 M NaOH) on platinised platinum modified by tin adatoms.[105]
Surface coverage by adatoms: (*1*) 0, (*2*) 0.76, (*3*) 0.48; E_r is the potential referred to the reversible hydrogen electrode.

If a process is controlled by the recombination of atoms, then, conversely, optimisation of the electrocatalyst requires an increase in the number of neighbouring active adsorption centres of the same nature. For this mechanism, the dependence of the process rate on the geometry and sizes of reaction sites can be well simulated by hydrogen evolution on platinum-group metals modified by different adatoms. Depending on their sizes, adatoms can occupy one, two or three neighbouring positions otherwise available for adsorbed hydrogen. In real systems, we cannot always provide a uniform distribution of a modifying additive over the surface; therefore, the observed effects of recombination inhibition appear to be smaller than is expected. This situation can be used for solving the inverse problem, *viz.*, studying the geometry of island structures.

Yet another typical mechanism of electrocatalysis (first of all, for processes involving organic substances on platinum-group metals, Fig. 7) occurs for two and more parallel processes of

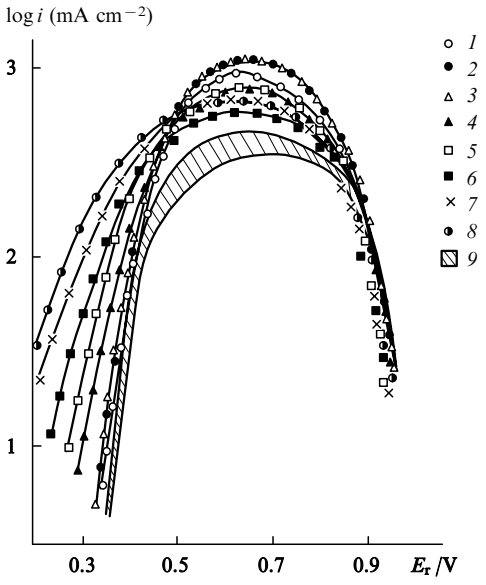


Figure 7. Steady-state polarisation curves of formic acid oxidation (1 M, in the presence of 0.5 M H_2SO_4) on platinised platinum modified by thallium adatoms.[106]
Concentration of added Tl^+ /mM: (*1*) 0.01 (*2*) 0.033, (*3*) 0.1, (*4*) 0.33, (*5*) 0.48, (*6*) 0.96, (*7*) 1.9, (*8*) 4.8, (*9*) 0. In the vicinity of the maximum, current fluctuations occur with the amplitude shown by the dashed area.

reactant chemisorption, one of which produces non-reactive strongly bound adsorbates that partly block the surface. For such self-inhibited catalytic processes, the selective suppression of the inhibitor adsorption is an important size-dependent factor. In systems with organic reactants, the blocking adsorbate occupies usually several neighbouring surface sites; hence, its formation is hindered by foreign adatoms that modify the surface (the so-called 'third-body effect'[9]). This is exemplified in Fig. 7 by the data on the acceleration of formic acid oxidation on platinum modified by thallium adatoms each blocking three neighbouring adsorption centres, according to estimates. The 'third-body' effect is manifested only in the ascending branch of the curve in the potential region where the process is inhibited by strongly adsorbed CO-like species.

Blocking adsorbates of this and nearby components are formed in both the destructive adsorption of various organic molecules and immediately in the adsorption of CO molecules. Thus the problem of designing systems with a pronounced 'third-body effect' is of prime significance for the solution of an urgent applied problem, *viz.,* preparation of CO-tolerant catalysts.

In principle, macrokinetic effects in systems with porous catalysts can be also assigned to size effects. These are discussed in detail by Chizmadzhev *et al.*[107]

V. Size effects in the elementary act of charge transfer

At present, subnanometre-scale size effects are actively studied on the molecular level within the framework of theoretical descriptions of electrochemical interfaces and attendant processes of the transfer of charged species (for example, see Refs 108–112). In such a consideration, both the sizes of molecular subsystems (reactant and product species involved in the charge transfer, solvent molecules adsorbed on electrodes) and the characteristic scales of electron density distribution are of substantial importance. Charge transfer processes cannot be studied without invoking quantum-mechanical approaches, which in turn requires a changeover from spatial scales to spatial–temporal scales.

The probability of electron transfer in an electrode–reactant system is determined by a number of factors that depend on the characteristic sizes of reaction layers.[108] The most 'large-scale' and complex factor is the distance of the closest approach of a reactant to the surface $z_{\lim}$, which is determined by steric restrictions and by chemisorptive and electrostatic interactions.

For ionic and molecular reactants, such distances do not usually exceed fractions of several tenths a nanometre. If $z_{\lim} > 1$ nm, we speak of the 'long-range' electron transfer. The limiting value $z_{\lim}$ is arbitrary and is determined by a substantial attenuation of the electron overlap, which exponentially depends on the electrode–reactant distance. By introducing the transmission coefficient K, one may represent this dependence as follows:[108]

$$K = \text{const}'' \exp\left(-\frac{z}{b}\right), \tag{3}$$

where the parameter b depends on the degree of electron delocalisation and is of an order of magnitude of a hundredth part of a nanometre. Usually, the delocalisation of reactant electrons plays the decisive role, in particular, the greatest b values (< 0.1 nm) are known for transition-metal complexes in which the charge transfer proceeds to orbitals of a mixed nature.

In principle, all reactant species located at any distance from the surface contribute to the observed rate; however, the contributions of species located in a thin near-surface layer not exceeding $z_{\lim}$ prevail. In place of the parameter $z_{\lim}$, another parameter of the same order of magnitude δz known as the reaction layer volume is used, for example, in the expression for the current density (rate of the process)

$$i = \text{const}''' (z_{\lim})\, \delta z \exp\left(-\frac{E_a}{RT}\right), \tag{4}$$

where E_a is the activation energy, R is the universal gas constant, T is the temperature. In modelling the electron transfer, δz is determined by integrating the expression (3) within the limits from $z_{\lim}$ to the infinity.

The 'long-range' transfer can be observed in systems with barrier layers on the electrode surfaces[79, 113, 114] and is studied most comprehensively for thiol systems. In particular, unambiguous dependences of the transfer rate on the barrier layer thickness are established. Thiol layers with redox-active terminal substituents that provide rigid localisation of the reactant are widely used.[115] The introduction of two redox centres, with a variable distance between them, into a thiol molecule is an interesting extension of this approach (Fig. 8).

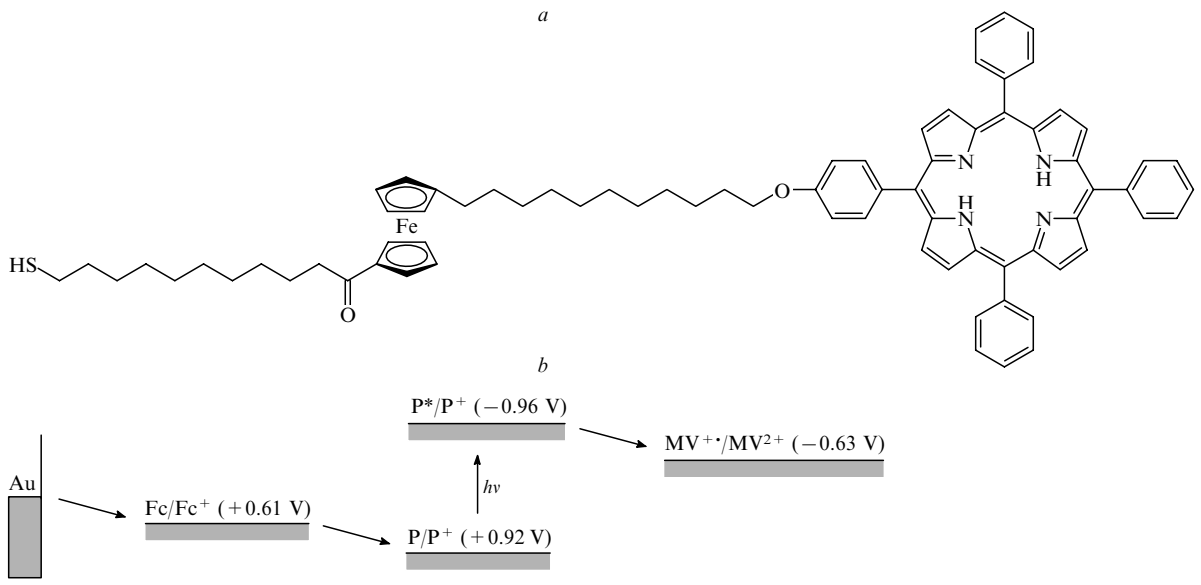


Figure 8. A scheme of a model system with two fixed redox centres, *viz*., those based on ferrocene (Fc/Fc^+) and porphyrin (P/P^+) (*a*) and the sequence of charge transfer steps to different redox centres (*b*).[116] A self-assembled layer of substituted thiols is immobilised on the surface of an illuminated gold electrode in a solution of methyl viologen (redox pair $MV^{+\bullet}/MV^{2+}$); the equilibrium potentials of the corresponding systems are shown in parentheses.

'Long-range' charge transfer is also observed for reactant species of considerable intrinsic sizes and with a pronounced degree of localisation of the transfer site (metalloproteins,[112] polynuclear complexes [71]). It should be noted that the characteristic length of the 'electronic tail' (and, correspondingly, electron overlap) depends on the electrode charge; however, the theoretical analysis of these dependences is possible so far only in terms of simplified models.[109]

The quantity z_{lim} affects not only the ovelap, which determines the prexponential factor in the equation for the rate constant of electrode reactions, but also different components of E_a: the work terms of reactants and products (if we deal with charged species, the Coulomb interactions weaken with the distance from the interface as the potential changes) and the solvent reorganisation energy. A detailed theoretical consideration of this problem is given in Refs 117, 118.

Pronounced size effects can be observed in photoelectrochemical processes involving semiconducting particles separated from the metal surface by barrier layers. The size effects are caused by a shift of absorption edge when the diameter of particles ranges from 10 to 20 nm.[119, 120] Substantial acceleration of photoelectrochemical processes occurs on passing from massive to nanosize semiconductors. This phenomenon has already found a practical application, *viz*., in photoelectrolysis of water.[121] Similar 'intrinsic' size effects of metal particles should be weaker and manifest themselves for particles with sizes below 5–7 nm. However, in principle, there exist no methodical obstacles from discovering them in the nearest future.

Prediction of the kinetics of electron transfer by taking into account all size-dependent factors becomes possible only when adequate ion–molecular models of reaction layers are built. For a number of systems, this problem can successfully be solved by invoking quantum-chemical methods [122] based on the quantum-mechanical theory of the charge-transfer elementary act.[123] Along with the classical effects of the cation size which manifest themselves in the reduction of anions on a negatively charged surface,[124] we must especially mention the inhibition of electron transfer with increase in the ligand size for a number of transition-metal complexes.[125] For non-symmetrical reactants, this dependence gives rise to various orientation effects in reaction layers.[126]

The independent (additional) possibilities of experimental simulation of the size effects of a quantum origin are provided by carrying out electron transfer processes in the STM configuration at fixed tunnelling voltages, which govern the location of energy levels of transferred electrons in the metal.[110, 127] Interesting similarities between STM and electrochemical responses can be traced for polyatomic reactants with dense outer barrier layers and for gold clusters, particularly those stabilised by alkanethiols.[128] In both cases, the current responses reveal the appearance of Coulomb blocking (up to six steps separated by potential intervals of ~ 0.3 V). The latter system, which allows one to trace the dependence of electrochemical responses on the cluster size, is considered in the literature as 'transition': for a small number of atoms in a cluster, the differences between the electrochemical charging of the gold cluster ('nanoelectrode') and an electrode process involving this cluster as a reactant in solution actually vanish.[129]

VI. Size effects in processes of new phase formation in electrochemical systems

A complex combination of size effects of different origins is realised in electrochemical processes with the formation of new phases, for instance, in electrocrystallisation processes.[25]

In the nucleation on electrode surfaces (as in the formation of a new phase in a homogeneous medium), the key role is played by supersaturation determined by the electrode potential deviation from the equilibrium value for a given redox system (overpotential η). A redox-system component formed as a result of a transfer of n electrons takes part in the nucleation process. A thermodynamic description of this phenomenon relies on the analysis of the probabilities of formation and dissolution of new-phase nuclei [5] and gives the following expression for the critical nucleus radius r_c (the minimum size, for which the probability of dissolution of a nucleus formed does not exceed the probability of its further growth):

$$r_c = \frac{\gamma A}{nF\eta} \quad \text{or} \quad r_c = \frac{2\sigma\upsilon}{nF\eta},$$

where γ is the surface tension of a two-dimensional nucleus, A is the area occupied by a mole of the substance in a monoatomic layer, F is the Faraday number, σ is the surface tension of a three-dimensional nucleus, and υ is the molar volume. When estimating the size of an extremely small critical nucleus, one cannot use the value σ characteristic of macroscopic fragments of the same solid, because, in principle, this parameter is size-dependent.

For the analysis to be correct, the EDL structure and involvement of chemisorbed solvent molecules and other solution components, as well as adatoms should also be taken into account. All these factors affect the surface energy of a nucleus and, hence, its critical size. Along with thermodynamic models, non-thermodynamic models of nucleation on the electrode surface have also been developed.[25] The latter are based on either a statistical dynamic approach or on quantum-chemical studies of different-size clusters.

The mentioned factors also play an important role in the description of steady-state and non-steady-state kinetics of nucleation and growth of new-phase particles on electrodes: in many cases, these factors can change the rate and the limiting stage of a process. Largely pertaining to potentiostatic models, the expressions for the non-steady-state current of nucleation–growth of a unit nucleus and nuclei ensembles are described in detail in numerous reviews (for example, see Refs 5, 14, 130). The time-dependent nucleus size plays a key role in deriving such expressions. The other important parameters include the number of active nucleation centres, the nucleation rate constant and a parameter characterising the kinetics of the limiting stage (the diffusion coefficient or the rate constant for electron transfer). Moreover, even the simplest approximations (for example, for the formation of spherical or semispherical nuclei on a uniform plane) allow the criteria for diagnosing the nucleation type: two-dimensional or three-dimensional growth, diffusion or kinetic control, the ratios of nucleation and growth rates, to be found. The nucleation type is elucidated from experimental current transients (for instance, power dependences at small times) by analysing the maximum current corresponding to the hindrance of growth due to the coalescence of neighbouring nuclei.

From electrochemical data, by using the corresponding algorithms, one can indirectly characterise the morphology of a system at any moment of deposition (even for a crystal size commensurable with the atomic size). However, the differences between the properties of real and model systems cause substantial deviations of the calculated values from the experimental results. For example, the calculated concentrations of active centres are often several orders of magnitude lower than those found from electron microscopy data (direct visualisation of grown crystals).

Model systems for which the active centres represent certain surface areas (for example, dislocations) and the growth rate of a new phase is limited by a process localised immediately on the surface, *viz*., the surface diffusion, are of special interest [25, 130] In this case, the key size-dependent factor is the distance between the growth steps which incorporate the adatoms slowly diffusing over the surface. However, it is difficult to fabricate such systems, especially when using real polycrystalline materials the active centres (and point defects) of which may be represented by any surface areas with small radii of curvature. The exchange of adatoms on the growth steps can be observed by means of STM.[24]

The methods of independent determination of the number and sizes of nuclei at different moments are of prime interest, especially

those that do not require the electrode to be withdrawn from solution. These requirements are fulfilled by the STM technique realised with an atomic resolution *in situ* in electrolyte solutions.[16, 17, 20, 73, 131–133] However, at present, local changes in the deposition conditions that occur near the probe, especially, for nucleation under diffusion control cannot be reliably eliminated. It was also reported that nanosize crystals are unstable in the electric field around the probe if adhesion is low (for example, this concerns the important group of model processes of metal deposition on highly oriented pyrographite). An efficient approach to the determination of the number and sizes of nuclei consists in substitution of the background solution for the deposition solution without opening the circuit.[73] The probe is brought to the surface after all the deposition stages studied are completed. This, however, dramatically reduces the time resolution.

The techniques of atomic-force microscopy in a noncontact mode progressively gain importance.[32, 134] The advantage of such methods is the possibility of studying objects of low conductivities, for example, in electroplating on wide-band semiconductors,[31, 32] in structural transformations of polymer deposits during dedoping [135] and in the course of formation of nanosize barrier oxide layers.[136] Combined photo-assisted probe techniques are being actively developed.[21, 33] It should be noted that quantitative probe-microscopic data on nanosize particles of electrodeposits (*i.e.*, where the radius of curvature of a probe is commensurable with that of the particles) can be obtained only when special convolution procedures are used, the algorithms of which are being extensively developed.[54, 137, 138]

A quantitative description of electrochemical responses in the formation of a new phase is complicated by the appearance of the so-called screening zones caused by the overlap of either the neighbouring nuclei or the corresponding diffusion layers. Certain effects of this sort can be simulated, which however always increases the number of fitting parameters, thus reducing the diagnostic possibilities of the model. Experimentally, the overlap can be avoided if the distances between the active centres are of an order of a micrometre: in this case a single nucleus can be grown on an ultramicroelectrode.[139, 140] In fact, such experiments allow one to observe the elementary events that constitute the nucleation process and then to use the obtained information for the analysis of the growth of ensembles.

Screening under diffusion control can also be used for obtaining the so-called fractal deposits (for example, see Ref. 141). Such deposits are formed in thin-layer cells, which includes the boundaries of two immiscible liquids and the solution–air interfaces. The main contribution to the growth of a new phase is made by the secondary nucleation processes which can be intensified by pulsed deposition modes (Fig. 9). Simulation of secondary nucleation which plays a significant role in many systems is a very complicated task, which defies analytical solution unless being considerably simplified. In this case, numerical techniques should be invoked.[143]

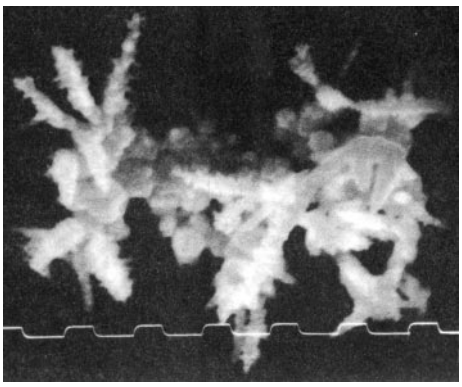


Figure 9. SEM image of platinum deposit on a carbon surface electroplated from a solution of 40 mM H_2PtCl_6 by square-wave pulses.[142] The horizontal measuring interval is 1 μm.

The technological possibilities of electrocrystallisation are extremely high and today are only partly used. The systems in which the crystals are formed on the surface of preliminarily developed adatomic submonolayers allow variation of the geometry of deposits on a nanolevel. In these layers, various two-dimensional phase transitions occur, and three-dimensional growth of nuclei is initiated by different mechanisms on domains of different structures.[144]

Tuning the fine structures by using the accompanying adsorption phenomena is also possible in the dissolution of metals: the processes of this group can be generally considered as electrocrystallisation with the formation and growth of cavity-type nuclei.

For the studies on the nanoscale level, a more precise control over the processes of new phase growth in the presence of organic additives traditionally used in industrial electroplating as the brighteners is possible by varying the ratio of the rates of nanocrystal growth in different directions.[145] Deposition of unusually long-lived metastable highly defective solids deserves mention as a promising approach.[146–148] The deposition becomes possible due to the formation of crystals on electrodes under substantially non-equilibrium conditions. A related direction is associated with the controlled variation of the stoichiometry of multicomponent phases that are deposited.[149–151]

In connection with the development of nanotechnology (see the next Section), it seems reasonable to outline the range of materials which can be deposited or formed by electrochemical mechanisms. On inert supports, one can carry out cathodic deposition of metals, alloys and certain semiconducting materials based on sulfur, selenium and tellurium and of solid complex compounds (for example, Prussian Blue and its analogues). The latter are of interest for electrochromic and sensor devices. Using anodic deposition on inert supports, one can obtain oxides and hydroxides,[152] different polymers [153, 154] and salt phases with variable electrophysical properties.[155] Anodising of metals in specially chosen media results in the formation of nanosize layers of passivating oxides many of which exhibit high photochemical activities.[156]

The formation of intercalates is an extremely important group of electrocrystallisation processes. Crystallisation of a new phase proceeds in the electrode bulk and, as a rule, is controlled by solid-state diffusion. Strains caused by intercalation can be observed by probe techniques.[157] Rapid intercalation processes are typical of a number of oxohydroxide phases and are accompanied by changes in the oxygen stoichiometry, which often proceed simultaneously with the proton transfer. High intercalation rates can be reached, for example, in materials based on oxides of ruthenium [158] and tin [159] for lattices of certain oxygen deficiencies. In such materials, as in metal hydrides, intercalation seems to be accompanied by the formation of nanosize regions with different compositions. The structure of intergrain boundaries is of principal significance for the reversibility and rate of intercalation, in particular for prevention of cracking by changing the local composition of grains.[22]

VII. Electrochemical nanotechnologies

Electrochemical fabrication of small-size articles occupies an important place in the system of chemical materials science and design of new materials having special properties. The mechanisms of formation or removal of individual small portions of solids play a decisive role in the field of electrochemical nanotechnology. These mechanisms are not quite clear which prevents the use of the most important advantage of electrochemical methods of fabricating nanoobjects, *viz.*, their controllability and the possibility of on-line quantitative monitoring. The controllability is provided by carrying out a process at a fixed potential (similar modes of deviation from equilibrium are practi-

cally unrealisable in beam and in CVD and PVD technologies). In the general case, monitoring is provided by measuring current and charge. The sensitivity to the rate of product accumulation is determined by the aforementioned limits of measuring these parameters. Additional possibilities of monitoring will arise with the use of a quartz-crystal microbalance technique, which can easily be realised in electrochemical systems, but have not yet found any practical application.

The existing nanotechnologies can be classified as local [31] and non-local.[19, 160] Most often, the latter represent different versions of lithographic techniques, *i.e.*, multistage combined technologies using photoinduced processes.

Non-local nanotechnologies based on different self-organisation processes in electrochemical systems represent an alternative to lithography. A typical example is the anodic electrosynthesis of alumina in which the ordered cylindrical pores with diameters of several tens nanometres are characterised by an extremely narrow size distribution.[145, 161] Being of interest for catalysis, this nanotube material [162] is widely used in combined technologies as a nanosize matrix. Metals [163, 164] and carbon materials [165] can be deposited into the pores of such an alumina matrix, and then alumina is removed at room temperature by dissolving it in alkali or HF. Similar processes can be realised for certain polymeric matrices (Fig. 10).

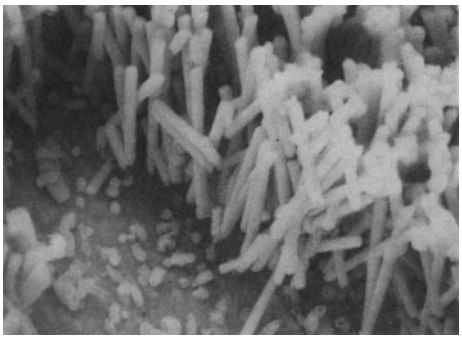


Figure 10. SEM image of an array of gold nanowires fabricated by electroplating into a polycarbonate matrix (after removal of the matrix).[166]

Electrodeposition of a metal into a porous matrix (templating) and co-deposition of a metal and a matrix (quasitemplating) form the basis of technologies for production of metallised conducting polymers.[167, 168]

Under certain conditions, the phenomenon of the formation of ordered new-phase nuclei in the absence of a matrix can also be used in nanotechnologies, for instance, in the preparation of catalytically active materials with particles of fixed sizes and also in combined low-temperature technologies for the preparation of semiconducting particles.[169–172]

Electrodeposition of lamellar bimetallic structures which is carried out either by different step-wise modes from a complex electrolyte or by consecutive deposition from different solutions constitute a separate group of processes. Continuous alternating 2-nm layers can be reproducibly obtained in systems characterised by two-dimensional growth. Layer-by-layer deposition finds wide application in the technologies of preparation of magnetic bimetallic materials.[173–176] Layer-by-layer deposition of single layers of semiconducting oxide phases [177] and of special polymeric compositions [178] is promising for the preparation of semiconducting superlattices.

Cathodic deposition of Cu/Cu_2O structures in the presence of organic complexones in a weakly alkaline medium, which is carried out in a simplest galvanostatic mode, is an example of a nanoelectrochemical technology for fabricating lamellar compositions.[179–181] Deposition of alternating layers of nanosize thicknesses is accomplished owing to a spontaneous initiation of potential oscillations caused by periodic changes in the pH and copper ion concentration in the near-electrode layer. In future, this method can be extended to other oscillating electrode processes.

The methods of dispersing metals by anodic dissolution are also worth being mentioned. Bach and coworkers [182–185] appear to be the first to apply this approach for the preparation of platinum colloids in aqueous media in the electric arc. In less severe conditions, a similar method is possible for palladium in non-aqueous solvents.[186] However, the problem of stabilisation of colloids is demanding, which requires introduction of organic additives in most cases.

We also assign the methods of immobilisation of molecular ensembles, clusters and metal particles on electrode surfaces to electrochemical nanotechnologies. The particles are bound with the surface by adsorption induced by the potential (charge) of an electrode. In a number of cases, this process occurs under electrophoretic supply and often involves surfaces preliminarily functionalised, for example, by alkanethiols. The best developed methods are those of colloid immobilisation [54, 187–189] which provide virtually monodispersed coatings. When using weak stabilisers, for example, citrates, it is possible to simultaneously provide a narrow size distribution of particles and their high adsorbabilities (Fig. 11).

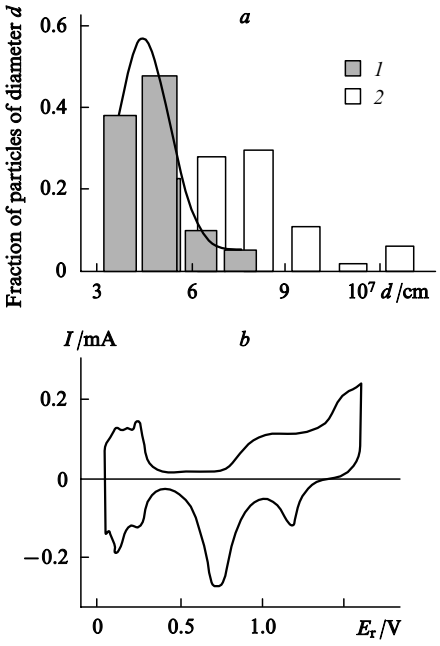


Figure 11. Size distribution of particles of immobilised platinum citrate colloid on polycrystalline gold (*a*) and potentiodynamic curve of the immobilised colloid (*b*). The distribution is plotted from STM data (*1*); for comparison, a wider distribution (*2*) corresponding to platinum electrodeposition is shown.[54]

Various local nanotechnologies can be realised in the configuration of probe microscopes [18] based on diverse processes. Thus one can locally deposit polymers and metals either by supplying reagents from the solution bulk [190] or by generating them on the probe tip.[191] It is also possible to modify a surface by transferring metal to it from the probe during short mechanical contact.[192] In this process, no electrochemical reaction occurs, and adsorption phenomena on the charged surface appear to play a significant role in the stabilisation of clusters formed. Figure 12 shows a scheme of this procedure. The methods of local etching near the tip, which are realised in STM configuration (both *in situ* [193] and *ex situ* [194]) where the role of an electrolyte is played by the moisture concentrated from air, are also gaining acceptance.

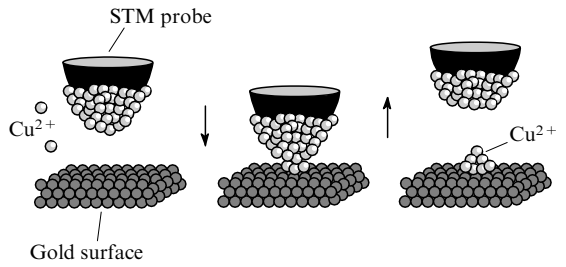


Figure 12. A procedure for local modification of a gold surface by copper clusters in an STM configuration.[20]

The adsorption and related combined nanotechnologies based on self-organisation in two-dimensional layers and spontaneous chemical deposition employ efficiently electrochemical methods to govern the process.[195]

Local modification of a surface in a scanning mode with the formation of sufficiently stable cluster ensembles is sometimes called electrochemical nanolithography.[192–193] The response time of probe microscopes leaves only few chances for nanolithography in fabricating items on the nanosize scale. However, with the progress in nanoelectronics, the scale of these electrochemical technologies will clearly increase. We can offer quite a number of examples where island, lamellar and other nanostructures formed by applying electrochemical methods are successfully used as quantum wells, superlattices, tunnelling diodes, *etc*.

Apparently, one of the main directions is associated with the achievement of quantum-size and resonance effects on the tips of STM probes modified electrochemically or by adsorption.[196, 197] In particular, this involves the quest for systems with a negative differential resistance. Figure 13 shows an example of such a response for a local quasi-one-dimensional nanostructure.

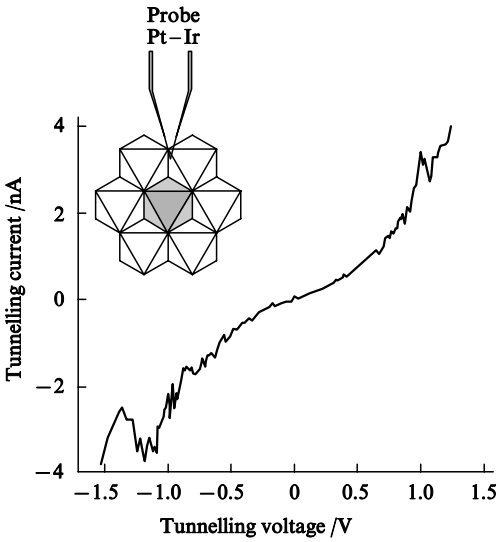


Figure 13. Tunnelling current *vs*. voltage characteristic demonstrating the negative differential resistance effect using a probe modified by heteropoly molybdate.[197]

VIII. Conclusion

The material reported in this review does not exhaust all the approaches to the research and application of size effects in electrochemistry. At present, prospects for the development of nanoelectrochemistry appear to be somewhat remarkable. This is associated with the fact that, in principle, possibilities of governing the operations on an atomic level have already been demonstrated. However, such achievements are realisable only at the lower limits of the possibilities of the available equipment.

An on-line observation of elementary steps of electrochemical charge transfer, even if for relatively slow reactions, seems to be most impressive.[24] However, this will require a substantial decrease in the operation time of probe techniques (to date, scanning of 50 images per second with an atomic resolution is apparently a record, however, not as yet for liquid phases). Conceptually, electrochemistry arrives at quite a novel stage of development when we must reconsider many common concepts and relationships. This reconsideration concerns now, particularly, the modification of the traditional Nernst equation of the equilibrium potential when applied to nanosize materials and the relationships of the classical theory of electrocrystallisation. Which of the predicted issues will remain in the status of science fiction and which will enter common research and technological practice and when this will occur, depends on many factors. However, the fast progress of nanochemistry in the recent years lends optimism.

Great expectations are associated with the integrating trends of different branches of physics and chemistry. Carrying out their experiments, modern scientists actually deal not only with elementary events that accompany transformations of single atoms and molecules, but also with transition states.[198] In the near future it may become possible to transform the experimental basis of these studies so as to adapt it to electrochemical systems.

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