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Oscillations as an instrument in controllable electrodeposition of micro- and nanomaterials

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Abstract

Various examples of electrodeposition accompanied by current and/or potential oscillations are collected and discussed in respect to electrochemical phenomena inducing oscillations. Possibilities to use periodic changes of electrochemical responses to control and monitor the size, morphology, and composition of electrodeposition products are discussed. A brief comparison with other template-free electrodeposition techniques is also presented.

Keywords: Electrodeposition; Oscillations; Nucleation and Growth; Controllability; Heterostructures

Introduction

Electrodeposition presents a universal technological tool to fabricate individual and composite materials with a possibility to control and monitor the quantity of forming solids coulometrically. Demand for ‘nanomaterials’ and ‘nanostructures’ initiated a fast development of template-based electrodeposition techniques [1, 2]. This approach requires specific complex arrays to serve as templates, typically with a limited opportunity of scaling. The same problem arises for ‘nanoreactors’ [3]. However sometimes basic electrochemical knowledge can decrease the complexity. In particular, the appearance of current or potential oscillations under conventional potentiostatic or galvanostatic deposition modes in usual electrochemical cells allows one to use electrochemical responses to monitor the formation of the fragments of certain size (both in nm and μm ranges), as illustrated by the examples below.

The goal of this brief review is to collect very fragmented data scattered in the literature and to assign the examples of controllable deposition under oscillation modes to basic electrochemical phenomena. Consideration is mostly limited to deposition of more or less ordered materials and structures, or of well-shaped small fragments. To satisfy the principles of this journal, the citations of the ‘old’ articles are confined to representative examples. However the important experience can be usually found just in these ‘old’ publications and should not be missed.

Nucleation related phenomena

The appearance of the subsequent minima and maxima in nucleation-growth transients was first reported for calomel electrodeposition on mercury [4] and treated as *monolayer-by-monolayer growth*. The growth of Hg_2Cl_2 2D planes with (110) orientation was limited by slow incorporation of ions to the lattice at the edges of the planes, and allowed new (secondary) nucleation events. The overlap of current maxima could be affected by solution composition. Quantitative description of secondary nucleation reported in Ref. [4] remains valid but rarely used.

Similar oscillatory behavior is observed for formation of various deposits in which the growth of successive layers (not necessarily monolayers) occurs under kinetic control in more or less separated time domains. The most general case is metal deposition under kinetic control complicated by a certain growth-inhibiting factor. Typically this factor is *adsorption* of reaction

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by-products from solution. Some structural factors can be also operative in case of orientation-dependent growth. Inhibition results in termination of the primary nuclei growth and subsequent nucleation at newly formed surface. In respect to Ni deposition from alkaline solutions this secondary nucleation scenario was considered by Abyaneh and Fleischmann as ‘death and rebirth’ [5, 6]. Another example is Pt deposition from chloride bath, which provides the arrays of nm-size crystals, but never bright deposits. In this system, the growth of primary nuclei is inhibited by chloride ions releasing from $[\text{PtCl}_6]^{2-}$ reagent. Typically it is difficult to observe more than two distinct current maxima because secondary events are sporadic, with the growth of more than one layer simultaneously (rebirth starts before complete death). However the subsequent growth of layers consisting of single particles was observed microscopically for a limited area [7], and a good scalability was confirmed for Pt loadings from $\mu\text{g}/\text{cm}^2$ to mg/cm^2 [8]. This is surely important to fabricate well-characterized catalysts.

The most transparent manifestation of ‘death and rebirth’ is the termination of the chain growth with subsequent start of new chain growth in the course of electrodeposition of conducting polymers [9]. Sometimes oscillations of electropolymerization transients are vague enough because death and rebirth events are not synchronized at the macroscopic surface [10]. However the charge corresponding to each broad maximum can be very approximately associated with the charge spent for formation of the layer of single polymer globules, providing a tool to fabricate well-characterized electrochromic materials. Despite irreversible nature of electropolymerization processes, which formally forbids application of classical nucleation-growth approach, standard ideas of instantaneous/progressive formation of the primary and secondary nuclei can be applied at phenomenological level. The transients with several visible maxima are known for PEDOT deposition [11]. The appearance of the second maximum could be explained by the interplay of 2D and 3D primary nucleation [12, 13], but all subsequent maxima could only result from layer-by-layer growth. Simulations [14] demonstrate that the overlap of the maxima corresponding to the neighbor layers can easily screen oscillations when inhibition is not sharp enough, or rebirth of the growth is fast enough. Correspondingly, the absence of visible oscillations does not mean unambiguously the absence of layer-by-layer mechanism. Simultaneously, the transients with only two maxima do not necessarily correspond to secondary nucleation. Hypothetically [15], the second maxima can appear under condition of progressive nucleation and not too high constant growth rate.

Returning to classical result [4], we should mention indirect analogue, vertically aligned Zn hydroxide nitrate [16]. Its formation presents an example of less controllable electrochemically induced deposition (no electrocrystallization; the charge is spent for nitrate reduction accompanied by hydroxide generation). However very pronounced current oscillations allow one to monitor the growth of the separate sheets.

Diffusion and surfactant adsorption effects

Oscillations in the course of electrodeposition under highly non-equilibrium conditions are well known for dendritic ‘fractal electrodeposits’ (see [17] for recent review). This field forms an important branch of the chaotic/periodic phenomena research, and very specific branch of the kinetics of diffusion-limited electrode processes. Simultaneously it provides a basis for solution of the relevant applied problems. In respect to the latter, the efforts are mostly directed now on suppression of dendritic growth. It is important for batteries [18] and for industrial electrolysis [19] to avoid dendrites formation. More rare but also important application is dendrites deposition for catalysis mentioned in specialized review [20]. In this case the requirement is metal dispersion, not the ordering. To avoid misunderstandings, we should mention that classical dendrite formation assumes oriented growth of a single crystal. ‘Re-nucleation’ with formation of a branched nanocrystals array is also possible when migration contribution is high (no supporting electrolyte) and results in a strong local inhibition of the primary crystal growth, see examples for Cu and Ag

in Ref. [21]. This can form a link to secondary nucleation under kinetic control considered above, but up to the moment these research areas do not intersect.

The formation of well-ordered electrodeposits under diffusion limitations can result from spatio-temporal *synchronization* of various processes, e.g. inhomogeneous ions diffusion in the vicinity of growing dendrites and certain type of surface 'passivation' (inhibition of charge transfer, sometimes by surfactants). The effectiveness of this approach was exemplified experimentally by the ordered growth of Sn needles at the edges of 3D crystals with formation of a regular network (Fig. 1a) [22]. Further development of this approach [23] resulted in generalization, namely in classification of self-organized dendrite structures based on various growth dimensions (1D, 2D, and 3D). Following the same synchronization principle it is possible to combine various co-existing phenomena. An example with involvement of surface diffusion of Ag in the course of its deposition on Au can be found in Ref. [24]. Computations predict a wide variety of dendrite-based nanostructures, including ordered [25]. An interesting example of diffusion-controlled self-arranged nanostructuring was reported for template-less growth of Al wires with periodically changing diameter from ionic liquid [26] (Fig. 1b).

The most controllable combination of factors in oscillatory electrodeposition results from simultaneous action of soluble additives able to accelerate and to suppress electrode reaction. The action of at least one of these additives always assumes *adsorption*. This approach involving *surfactants* can be considered as widely understood Damascene type processes [27, 28], by analogy with a famous IBM metallization technology. Complex-forming additives are also rather typical. In the presence of oppositely acting additives polarization curves tend to negative differential resistance behavior (sometimes hidden) naturally linked to appearance of oscillations. As it is not so easy to measure steady-state polarization curve when the electrode surface undergoes evolution in the course of electrodeposition, the majority of authors consider empirically found conditions of potential or current oscillations. However these oscillating responses are informative enough, as they allow to control and monitor the thickness of layers formed during one period. One can meet 'layer-by-layer' name for electrodeposition processes of this sort. E.g., the layers of various morphologies/color [29] are formed (Fig. 1c), or the content of contaminations is changed periodically [27]. Oscillations can control crystal size/grain boundary content [30]. To induce oscillations, the surfactants adsorption can be also coupled with hydrogen adsorption [31]. Hydroxide formation can serve as one of coupled processes at certain pH [32].

Interesting configurations can be formed at liquid/liquid interface [33], namely quasi 2D Zn concentric patterns. The modes for the growth of dendrites penetrating into aqueous phase were also found, and the coupling with meniscus oscillations is noticed. Periodically twinned Cu and Co needles with high aspect ratios > 1000 were formed at water/oleic acid interface [34] (however this experiment in two-electrode configuration looks less controllable).

Oscillatory electrodeposition of heterostructures

An impressive invention of J.A. Switzer is electrochemical deposition of well-ordered $\text{Cu}_2\text{O}/\text{Cu}$ heterostructures [35] resulting from potential oscillations. This process becomes possible if the appropriate organic ligands are involved, and the potential is re-switching periodically in the vicinity of two equilibrium potentials. Light can serve as additional tool to regulate oscillations. Current state of $\text{Cu}_2\text{O}/\text{Cu}$ deposition research can be judged to certain extent from Ref. [36].

For $\text{Cu}/(\text{Cu}+\text{Sn})$, the re-switching resulting from periodically changed Ohmic drop contribution can be helpful to form bimetallic structures if potentiostatic deposition is started in the vicinity of $(\text{Cu}+\text{Sn})$ formation onset. This can be achieved using cationic surfactants [37], and electrolyte temperature can serve as additional control instrument [38]. Actually co-depositing components introduced to the bath in the form of oxoanions can serve as surfactants themselves. At potentials close to anions desorption oscillating phenomena arise, which allow to fabricate layered Ni-P, Ni-W and Co-W alloys [39].

The particular (and rare) examples presented in this subsection confirm that oscillation-based approach can be successfully applied to variation of electrodeposition composition, not only its microstructure. The search for other systems capable of application of this flexible approach is a matter for the future. The decrease of complexity as compared to alternative techniques (multistep potentiostatic modes or periodic changes of solution) is evident.

Concluding remarks

In the context of newly forming area of ‘micro(nano)galvanics’, the template-less approaches still play the important role. The most precise in respect to nm-scale spatial resolution is electrochemical atomic layer deposition (AELD) typically applied to binary semiconductors [40]. The most universal is application of complex (double- or even multi-pulse) deposition modes. Finally, local electrochemistry can be helpful, which originates from traditional electrochemical machining [41, 42]. Fig.2 compares the spatial resolution of these techniques with resolution controllably achievable with the use of oscillations of potential or current in the course of electrodeposition. Despite the boundaries of intervals marked in Fig.2 are approximate, it is easy to see that rather wide range is basically available with the use of simple potentiostatic or galvanostatic modes if oscillations appear. Additional tools to enhance oscillation behavior can be magnetic field [43] or ultrasound [44].

Oscillations can be also helpful as the monitoring tool in templated deposition, as one can conclude from illustrative examples of templating by ordered 3D ‘colloid crystals’ [45, 46]. In this case the diffusion-limited growth in the narrow template areas alternate with the growth in wider areas. Up to a dozen of clearly seen maxima and minima can be observed before the occasional inhomogeneity of the growth rate along the surface smooths out the oscillations. Relative amplitude of current oscillations decreases when an average current approaches the limiting value[47].

Electrochemical knowledge of various oscillations is very wide, deep, and quantitative. However just the oscillations related to electrodeposition were not studied actively in this uniting context (in contrast to electrocatalysis or corrosion). Probably possible applications to controllable formation of certain materials can stimulate integration of electrodeposition processes into general electrochemical oscillators research.

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Captions to Figures

Figure 1. Potential oscillations during galvanostatic deposition resulting in periodical changes of morphology: (a) Sn deposition from 2 M Sn(II) + 4.0 M NaOH on Sn [22]; (b) Al deposition on W from AlCl₃/ trimethylamine hydrochloride (58/42 mol%, 38 C) resulting in formation of wires shown at the left [26]; (c) Cu deposition on Au from 0.5 M CuSO₄ + 0.5 M H₂SO₄ + 1.5 mM *o*-phenanthroline [29]. (a) is reproduced with permission from ref. [22]. Copyright 2004 American Chemical Society. (b) is reproduced from ref. [26] with permission from Electrochemical Society. Copyright 2015. (c) is reproduced with permission from ref. [29]. Copyright 2005 American Chemical Society.

Figure 2. Schematic comparison of characteristic sizes of the structures and their fragments which can be formed by oscillation-based electrodeposition under conventional modes (purple, lower

part) and alternative more complex template-free approaches (blue, upper part). The boundaries are specifically chosen on the basis of experimental results reported in the literature. See comments in the text.