

## EFFECT OF PARAMETERS OF PULSE POTENTIAL MODE ON CONCENTRATION CHANGES IN VOLUME OF LOOSE DEPOSIT AND ITS PROPERTIES

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Electrolytic powders are used for fabrication of electrodes of electrochemical power sources. Such powders have highly developed surface, which allows to decrease the value of overpotential on interphase boundary and to improve technological characteristics of power sources.

Crystallization of loose deposits on electrode requires currents, which exceed by several times the limiting diffusion current on the flat electrode, or potentials, corresponding to those currents. In such conditions, deposition of most of metals is accompanied by intensive reduction of gaseous hydrogen in the depth of loose layer of deposit.

Application of pulse modes of current or potential allows to change the morphology of particles of loose deposits of metal, without adding any surfactants to the solution, which include into the deposit. Pulse modes of electrolysis represent alternation of current (or potential) pulses and pauses. During the pauses, discharging ions of metal diffuse from the bulk solution inside the loose deposit, and thus lead to the increase of ions concentration near the surface of electrode and supposedly to the changes in the morphology and physical properties of loose deposits.

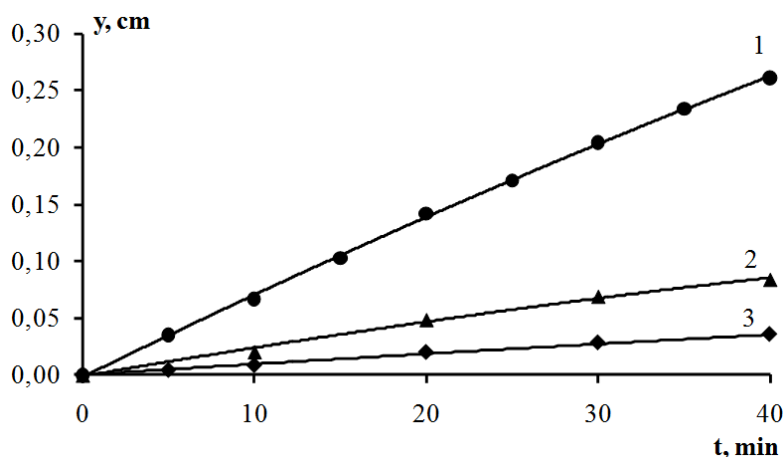
The aim of this work was to investigate the effect of concentration changes during pulse potential mode on growth dynamics, properties and morphology of loose zinc deposits.

Loose zinc deposits were obtained from zincate electrolyte, containing 0.3 mol/l of ZnO and 4 mol/l of NaOH. In order to obtain loose deposits, potential value of -0.38V relative to the zinc reference electrode was set, corresponding to the cathodic current density, which exceeded by 6 times the limiting diffusion current density on initial electrode surface. In pulse modes, we varied pulse ( $\tau_{pulse}$ ) and pause ( $\tau_{pause}$ ) durations from 1 to 30 s, while maintaining constant ratio  $\tau_{pulse}/\tau_{pause}=2$ .

To investigate the growth dynamics of loose deposits, we used an experimental set-up, which allowed us to record the growth process of deposits on a camcorder, to perform electrochemical measurements by means of electrochemical plant Solartron 1280C, and to collect gaseous hydrogen into the burette, connected to a funnel above the working electrode. Pin-type working electrode was made from the zinc wire of diameter of 2 mm and of height of 1 cm. We were measuring the potential of the working electrode relative to the unpolarized zinc electrode in the working solution. We estimated the changes in thickness of loose deposits in time, using the video record. Taking into account the volume of released gas, we calculated current efficiencies of hydrogen and metal in a certain moment of time. Changes of mass and

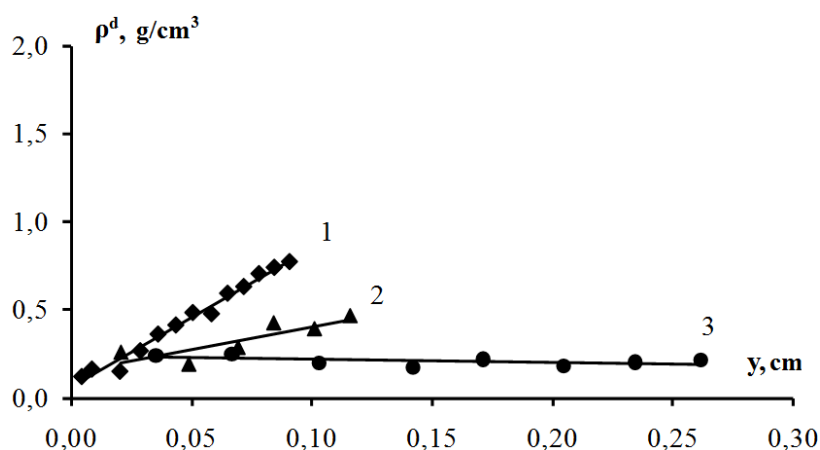
volume of loose deposits for a certain period of time allowed us to determine differential porosity in a certain moment of time.

At constant potential, a high and constant level of diffusion limitations is maintained during the whole electrolysis, and so, dendrites are lengthening with a constant growth rate (figure 1, curve 1). Growth rate of deposit decreases with a decrease of pulse duration in pulse potential mode and is less than that at constant potential (figure 1, curves 2,3).



**Figure 1.** Changes in thickness of loose layer of deposits in time.  $\tau_{\text{pulse}}/\tau_{\text{pause}}$ : 1 – potentiostatic regime; 2 – 30/30 s; 3 – 1/1 s.

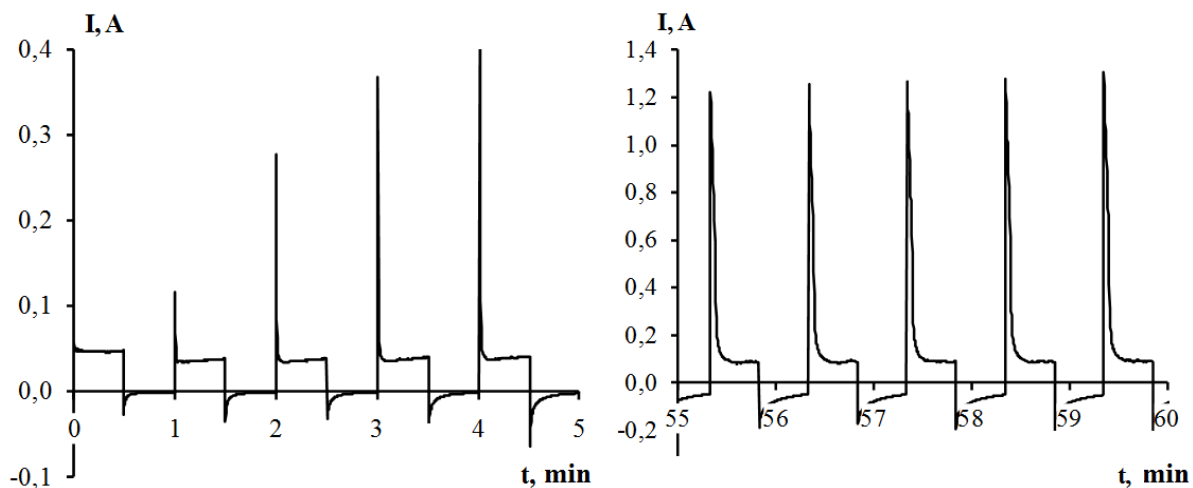
Density of zinc loose deposits, obtained at constant potential, does not change along the thickness of loose layer (figure 2, curve 3). In pulse modes, density increases along the thickness of loose layer (figure 2, curves 1,2). The shorter the duration of potential pulse, the greater the density of loose deposits.



**Figure 2.** Changes in differential density of deposits along the thickness of loose layer.  $\tau_{\text{pulse}}/\tau_{\text{pause}}$ : 1 – 1/1 s; 2 – 30/30 s; 3 – potentiostatic regime.

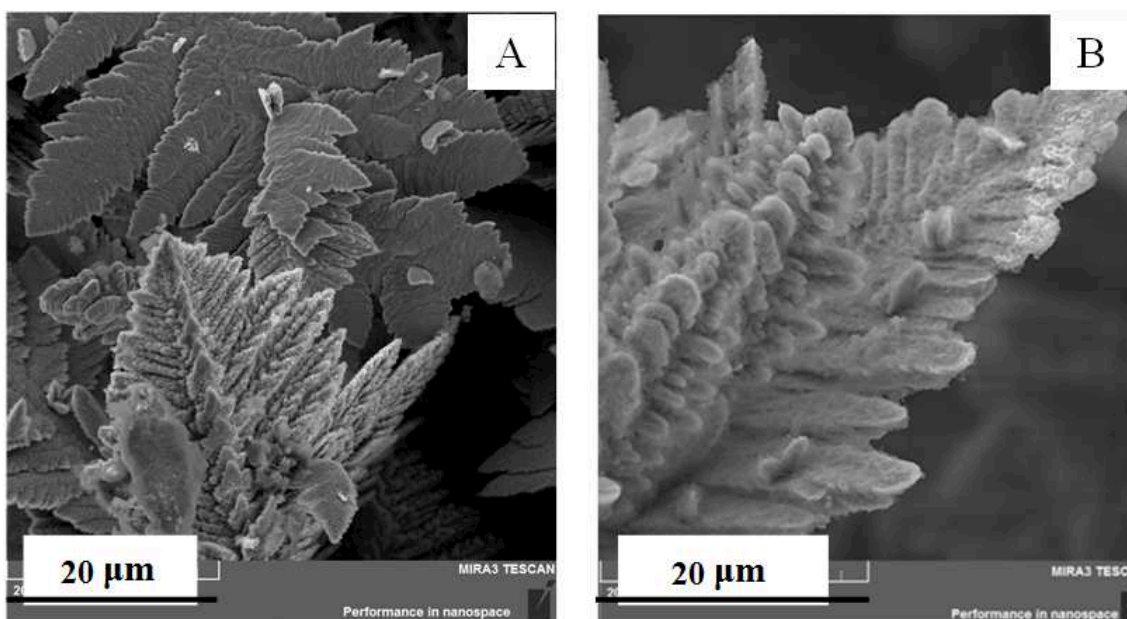
The shape of current profile maintains during a pulse and a following pause throughout the electrolysis (figure 3). At first, a peak of cathodic current appears, which is due to a decrease of concentration of discharging ions near the electrode, following by a cathodic current plateau. During the pause, the anodic process of

metal oxidation takes place on the working electrode, since the system remains under potentiostatic control and a potential of reference electrode is set on the working electrode, which value becomes more positive, relative to the potential of the electrode with deposit. This is caused by a smaller concentration of discharging ions in the near-electrode layer, compared to the bulk solution concentration, and also by the fact, that the equilibrium potential of the dendrite tips of a small curvature radius shifts to the negative values compared to the flat surface equilibrium potential [1].



**Figure 3.** Changes in current during the deposition of zinc in pulse potential regime ( $\tau_{\text{pulse}}/\tau_{\text{pause}}=30/30$  s).

The smaller the ratio of quantities of electricity, spent on the cathodic reduction during the pulse, and of that, caused by the oxidation of metal during the pause, the more dense deposits are formed on the electrode (figure 4B). At constant potential, the flat fern-like dendrites are formed (figure 4A).



**Figure 4.** Micrographs of zinc loose deposits, obtained in potentiostatic (A) and pulse potential mode at  $\tau_{\text{pulse}}/\tau_{\text{pause}}=1/1$  s (B).

In conclusion, varying the parameters of pulse electrolysis allows to obtain particles of loose deposits of metals with a morphology of different branching and different density along the thickness of loose layer.

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### **References**

1. *Diggle J.W., Despić A.R., Bockrić J.O'M.* // J. of Electrochem. Soc. 1969. V. 116. P. 1503–1514.