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Change in the physical characteristics of the dendritic zinc deposits in the stationary and pulsating electrolysis

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ABSTRACT

The growth process of dendritic zinc deposits is investigated on rod electrode in stationary and pulsating modes of electrolysis in this study. The data on changes in physical properties (density, porosity, and specific surface area) of loose deposits in the electrolysis process are obtained. It is found that during the pauses of pulsating modes, duration of which was 15 and 30 s, there is an increase in the discharging ions concentration in the deposit depth. The change in concentration in pulsating galvanostatic mode is due to diffusion, whereas in potentiostatic mode it is due to the dissolution of dendrites in contact with the depleted solution. The decrease in the diffusion limitations leads to a decrease in the deposits elongation rate and an increase in its density. The SEM method shows that the transition from stationary to pulsating modes of electrolysis changes the loose deposit particles morphology.

1. Introduction

Zinc powders are used in the chemical, metallurgical, medical, electrical and other industries [1]. Depending on the application field, zinc particles of various sizes and shapes are necessary. In the works [2,3] it is shown that to effectively protect the steel base against corrosion, zinc-rich paints should contain spherical and lamellar zinc particles. In other cases, for example, in Zn/AgO Bipolar Batteries, high discharge characteristics can be achieved when using porous zinc anodes which are made of powders with a high specific surface [4,5].

To produce zinc powders, various physical and physico-chemical methods are used. The advantages of the electrolytic process for producing loose zinc deposits are the branched dendritic particle shape and the ability to control the deposit morphology by varying the electrolysis conditions.

In the literature, there are studies in which the effects of electrolysis conditions on the electrocrystallization dynamics and morphology of zinc dendrites in the potentiostatic [6–9] and galvanostatic [10] modes are studied. The models describing the dynamics of dendritic zinc deposits growth in constant potential [6–8] and constant current [10] conditions are developed. It is suggested [11,12] that the amount of generated hydrogen bubbles and the intensity of the hydrogen adsorption/desorption determine the morphology of the zinc particles. It is reported [4,5,9,11,13] that the electrolyte composition has an effect on the zinc current efficiency and surface area of the powder obtained after removal of loose deposit from the electrode surface.

Although much attention is paid to the processes related to obtaining the loose zinc deposits, there are no data on the use for this purpose of non-stationary electrolysis modes. However, there is a large number of papers in which the effects of pulsating [12,14–17] and reversing [18,19] electrolysis modes on the dendritic copper and silver deposits morphology [12,14–20] are studied. Murashova [21] proposed the mode of a linear increase in the current (galvanodynamic) which made it possible to obtain the copper and nickel powders [21, 22] with homogeneous particle-size distribution. Nikolić and Pavlović and others used pulsating and reversing modes to obtain 3D foam electrodes [12] and honeycomb-like copper deposits [14–16,18,19]. Due to the high rate of current (or potential) relaxation, the Faraday process in the studied conditions remained quasistationary [23].

In terms of the effect on the structure and morphology of loose metal deposits particles, using non-stationary pulsating modes (pulse and pause duration of tens of seconds) is of a big interest. In that case, the non-stationary diffusion conditions take place, and the particles morphology will depend on the transition processes: changes in the discharging ions concentration near the electrode surface and the electrode reactions rate. However, in the literature there is no data on obtaining loose metal deposits in such electrolysis modes. Therefore, one of the objectives of the present work is to study the effect of the deposition mode on the structure of zinc dendrites. Furthermore, the literature virtually presents no data on the growth of and changes in the physical characteristics of the loose deposits during electrolysis. Usually, the authors [4,5,12–16,18,19] analyze metal powders which are obtained after the removal of deposits from the electrode surface. The properties of the powders (the specific surface area, bulk density and particle size) investigated by means of SEM [4,5,12–16,18,19] and BET methods

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[4,5,13] are the mean values for the entire period of the electrolysis. To assess the electrolysis mode effect on the loose deposits morphology and predict the metal powders technological properties, major focus is on in situ evaluations of density, porosity, specific surface of deposits during electrodeposition.

The aim of this work is to study the effect of pulsating current and potential conditions on the growth dynamics, morphology, and physical properties of dendritic zinc deposits in the electrolysis process.

2. Experimental procedure

2.1. Polarization measurements and method to research loose deposits growth dynamics

Dendritic zinc deposits were obtained on the rod electrode from the zincate electrolyte containing 0.3 M ZnO and 4 M NaOH. The electrode was made of the zinc wire with a diameter of $d_0 = 2$ mm and a height of $H = 10$ mm ($S_{sm} = 0.66$ cm^2). The non-working surface of the wire was insulated. Prior to each experiment, the electrode surface was polished, degreased with a soda solution, then rinsed thoroughly with distilled water and air dried.

Research into the dynamics of dendritic zinc deposits electrocrystallization was carried out in a three-compartment standard electrochemical cell with a Solartron 1280C. The working electrode was set in the center of a cylindrical cell. The counter electrode was made of sheet zinc. An unpolarized zinc electrode was used as a reference electrode in the test solution. To determine the reference electrode reversibility zone, the zinc electrode potentials with different concentrations of zinc ions in the solution and constant alkali excess 4 M NaOH were measured (Fig. 1).

In the zincate solution, the following equilibrium reaction occurs at the zinc electrode interface [13]:

$$Zn(OH)_4^{2-} + 2e \leftrightarrow Zn + 4OH^- \quad (1)$$

The alkali excess in the test solution provides a constant activity coefficient, thus there is a linear relationship in the coordinates $E-\ln C_{Zn(OH)_4^{2-}}$:

$$E_{Zn} = -1.253 + 0.012 lnC_{\mathrm{Zn(OH)}_4^{2-}} \quad (2)$$

The line slope (Fig. 1) is 0.0121 ± 0.0017 V, which with the confidence probability of 0.95 corresponds to the Nernst equation slope at $t = 21$ °C (0.0127 V). Value −1.253 in Eq. (2) is not a standard potential, but it is close to the referential value $E^0 = -1.285$ V [24], as the activity coefficient logarithm is close to 0 [25].

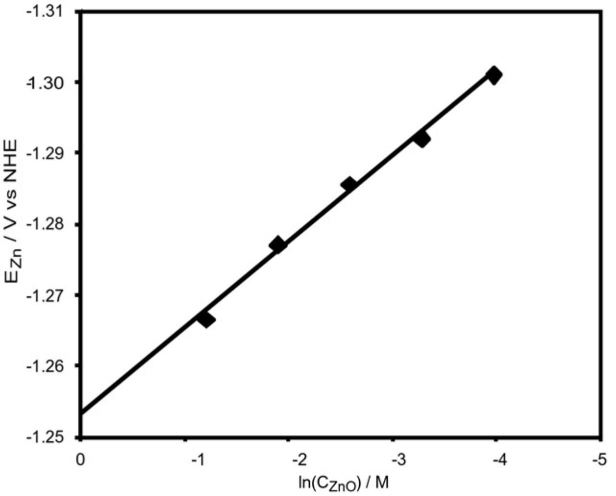

Fig. 1. Dependence of the zinc electrode potential on the zincate concentration in a solution containing 4 M NaOH.

The oxygen solubility, containing 4 M NaOH, is very low, about $2.7 \cdot 10^{-4}$ M [26]. The limiting diffusion current at this oxygen concentration equals to 0.4 A m^{-2}, which is ~0.4% of the exchange current in zincate electrolyte (91.3 A m^{-2} at zincate concentration of 0.24 M [10]). It is evident that the oxygen discharge contribution even with the absence of the external current will be very small so the empirical Eq. (2) is very close to the thermodynamic Nernst equation.

Thus, in a broad range of the sodium zincate concentration zinc electrode can be used as a reference electrode. The article further provides values of the potential relative to the zinc reference electrode in the test solution.

For polarization measurements, the electrochemical measurement unit Solartron 1280C was used. The deposit growth was recorded by Sony DSR-200SE simultaneously with polarization measurements. To measure the amount of evolved hydrogen over the electrode a funnel connected to the burette was set up [10,27], so that all the evolved gas got into the burette pre-filled with electrolyte.

2.2. Methods for determining the deposit physical characteristics and zinc current efficiency

Zinc current efficiency, density and porosity of the deposits were calculated based on the experimental data on changes in time in the diameter of the zinc electrode with the growing deposit (Fig. 2) and the volume of the evolved hydrogen.

The diameter of the working electrode with the growing deposit ($d_0 + 2y$) was measured by the video tape recording (Fig. 2B) at fixed time intervals taking into account the zoom-in of the camera. Measurements were carried out at three height points along the electrode. The average value of half of the growth in the measured diameter of the electrode with a deposit was taken as the length of the dendrites (y).

Loose deposit overall volume V_{dep} (cm^3) was determined as the difference between the volumes of the electrode with deposit and smooth electrode:

$$V_{dep}(t) = \left(\frac{\pi (d_0 + 2y(t))^2}{4} - \frac{\pi d_0^2}{4} \right) \cdot \mathrm{H(t)} \quad (3)$$

Hydrogen current efficiency during the electrolysis time t was calculated by the measured volume of the evolved hydrogen:

$$Ce_{\mathrm{H_2}}(\mathrm{t}) = \frac{2 \cdot \mathrm{V_{H_2}(t)\,F}}{\vartheta \cdot \mathrm{Q(t)}}, \quad (4)$$

where F is the Faraday's constant, A s mol^{-1}; $\mathrm{V_{H_2}(t)}$ is the amount of the evolved gas, corrected to standard conditions ($T_0 = 273$ K, $P_0 = 760$ mm Hg), dm^3; $\vartheta = 22.4$ dm^3 mol^{-1} is the molar volume of gas; $Q(t)$ is the quantity of electricity passed through the cell for time t, A s.

In the case of the galvanostatic electrolysis, the quantity of electricity is calculated by the ratio:

$$\mathrm{Q(t) = I \cdot t} \quad (5)$$

In other modes, the current varied in time. In these cases, the quantity of electricity was determined by the numerical integration of the experimental curves I–t at fixed time intervals:

$$Q(t) = \int_0^t I(t)dt \approx \sum_{i=1}^{k} \frac{I(t_i) + I(t_{i-1})}{2} \cdot \Delta \mathrm{t}, \quad (6)$$

where $I(t_i)$ is the current at the time t_i, A;

$\Delta t = t_i - t_{i-1}$ is the time interval in the integration, s;